Recycling and utilization of waste deep frying oil in leather industry

Habib M A*^{,1,2} & Alshammari A G¹

¹Department of Chemistry, Science College, Al Imam Mohammad Ibn Saud Islamic University (IMSIU), P.O. 90950 (11623), Riyadh, KSA ²Chemistry of Tanning Materials and Leather Technology Department, National Research Centre, P.O. 12622 Dokki, Giza, Egypt E-mail: habib 11m@yahoo.com

Received 29 January 2015; accepted 15 November 2016

The aim of this work is devoted to exploring recycling and application of the waste deep frying oil in the leather industry as a fatliquoring agent. Acid activated local bentonite clay (~ 8N acid concentration) has been investigated in order to verify its impurities absorbent capacity in the deep frying oil bleaching. The activated sample achieved the ideal bleaching capacity (88.9%) at 3% bentonite dose (based on weight of oil). The bleached oil is sulfated at optimal conditions (15% sulfuric acid based on the weight of oil, 30°C and 2 h stirring time). Sulfated oil is evaluated in order to verify their capacity to be used as a leather fatliquoring agent. The analytical data reveal that the desirable ratio of SO₃ (5.5%) that needed to running the sulfated oil in the fatliquoring process has been attained. The aqueous solution of 10 % sulfated oil (fatliquor emulsion) show a high degree of stability against metallic ions and *p*H as well as great ability to penetrate the chrome tanned leather, adding mass to the leather. The mechanical properties enhancement, what are recommended to be in the fatliquored leather has been reached. The microscopic examination of the fatliquored leather surface and fiber bundles shows that the tiny fibers are actually coated with a thin film of fat-liquor.

Keywords: Bentonite, Bleaching, Fatliquoring, Frying oil, Leather- waste

To transfer hide or skin into leather, several steps are required. In tanning step, protein chains are fixed by chrome (III) ion, as a result, tanned leather become bony, stiff, and hard in addition to its dark blue color. The hard tanned stiff leather is basically treated with a warm dilute emulsion of oil or fat in water, the process is so called fatliquoring. Fatliquoring agent is added to improve the mechanical capabilities¹. The oil imparting leather softness, durability, stretch, compressibility, flexibility, waterproofing, some protection against harmful chemicals and also adds greatly to its tensile strength². The fat is introduced into the leather in such manner that the individual fibers of tanned leather are uniformly coated. This is attained by emulsification the fatty matter in aqueous medium through the incorporation of the hydrophilic group, sulfate - OSO_3H , sulfite - SO_3H^3 (Scheme 1). Different attempts have been made to prepare leather fatliquoring agents. Guerci et al. prepare fatliquor composition based on oxysulfonated animal and vegetable origin fatty substance⁴. Fatliquor with good emulsion stability was prepared from low iodine value animal fat by oxidation of fat with the oxygen containing gas mixture and simultaneous sulfitation

using alkali and /or ammonium hydrogen sulfide⁵. Exhaustible synthetic raw materials and the ecological impact of leather chemicals create a demand for fatliquoring agents based on renewable and sustainable resources. Recycling of waste fatty material is a great benefit and some studies were devoted to this purpose. Nyamunda et al. prepare leather fatliquoring agent from waste bovine fat⁶. Discarded edible oils (include palm oil & palm kernel oil) and fats are of immense importance for industrial applications such as surface active materials and soap⁷. The economy of commercial deep fat frying has been estimated to be \$83 billion in the United States and at least twice the amount for the rest of the world⁸. Deep frying causes hydrolysis, oxidation, and polymerization of the oil. The hydrolysis increases the amount of free fatty acids, mono, and di-glycerides rather than glycerol. Dimmers and polymers are also formed by radicals9. In addition, some physical changes are occurring, such as density, viscosity, darkness and odor change. Disposal of used frying oils causes a series of environmental pollution. Utilization of these waste oils reduces contamination problems; in addition, it saves efforts exerted in





maintaining sewers and wastewater treating¹⁰. Bleaching is an essential step for recycling and enhancing the goods characters before introducing in industrial activities¹¹. Bentonite which is one of the clay mineral adsorbent consists of montmorillonite. In general, it is classified into sodium Na or calcium Ca types depending on dominant exchangeable ion¹². Sorption properties of bentonite are resulting from its high swelling capacity, surface area and cationic exchange capacity¹³. Bentonites are widely used in purification, decolorization, and stabilization of vegetable oils. It mainly used to remove undesirable colours via decreasing the levels of chlorophyll, carotene, and other colored bodies. In addition, it can be used to reduce traces of Cu⁺², Fe⁺³, phospholipids, soap and free fatty acids during bleaching¹⁴. Some properties of this clay such as surface area, porosity, and acid cities are improved commonly with mineral acid activation¹⁵. Therefore, this work aimed to investigate local bentonite clay to be used in frying oils bleaching, as well as explore the transformation of the oil into leather fatliquoring agent after sulfation. The fatliquor emulsion stability has been investigated rather than the mechanical properties of fatliquored leather after fatliquor application. Thus, the waste material will be transferred into usable goods can be subjected in the leather industry, leading to saving natural resources and reduce environmental pollution.

Experimental Section Materials

Waste deep frying oil samples used in this work were collected from local restaurants and snack shops, in Cairo zone, Egypt. The virgin oil is usually blended from palm and kernel oils in various proportions. Palm and kernel oils are the common cooking ingredient in the tropical belt of Africa and Asia because of oxidative stability and economic consideration. Bentonite clay samples were collected from a three deposit areas on Aswan, near the Nile River district, Egypt. The sample was collected from depth 5-8 m. Commercial tonsil which is an activated bentonite clay and widely used in the vegetable oil bleaching has been used as a standard to evaluate the bleaching efficiency of the local bentonite. Unfinished chrome tanned bovine hides (crust wet blue) feeds from a medium tannery was shaved to a thickness from 1.2 to 1.5 mm, cut into 50 cm \times 75 cm area. The weight of the samples was accurately recorded. Sulfuric acid (98.5%) with a pure chemical grade was used. All Chemicals used for analysis of the oil were supplied by international companies (Merck, Germany)

Purification of the waste oil

The process was carried out according to the method reported by Girigs¹⁶: The oil was heated up to $90 \pm 5^{\circ}$ C, washed with 5% Na Cl solution (10: 1 v/v). The mixture was stirred for one hour (60 rpm speed) and rested for 8 h. The lower phase (brine solution and impurities) was separated by siphoning and running off. Sodium sulfite anhydrous was added to reduce moisture and the material was then filtered through filter paper.

Pre-treatment and acid activation of bentonite

The local bentonite clay sample was crushed and dried in the open air. The dried sample was soaked in pure distilled water for several days to get rid of the impurities and heavy metals. The clear aqueous phase was then siphoned out and the process was repeated for several times. The sample was then dried in the drying oven at temperature $\pm 104^{\circ}$ C to constant weight. The dried sample was grinding using a mesh screen of size 75µm. Then, the sample was activated as 40 g of bentonite sample was mixed with 400 mL

8 N sulfuric acid in a stirring glass reaction vessel with reflux. The mixture was stirred for 3.5 h at 90°C. After that the sample was filtered and washed with distilled water, dried at 60° for 12 h and ground to desirable mm sieve^{17,18}.

Bentonite clay characterization

The physical properties of the bentonite clay samples (unactivated, activated, and commercial) were evaluated and the results have been compared with the commercial sample as a standard. HANN (H 198121) pH meter was used to measure pH value (5 g clay sample was dispersed in 50 mL distilled water). The moisture content (percentage of moisture removed when the temperature of the sample increase from ordinary temperature to 105°C) was measured through heating the sample in an electric oven at 105°C for 48 h. A definite weight of dry sample (10 g) was fired at 1000°C in the furnace and the loss on ignition (LOI) was accurately calculated. The specific surface area of the samples was conducted. BET-N2 method- volumetric analyzer (Nova-1000) used to achieve the test. The chemical composition of the un-activated, activated bentonite and commercial clay samples has been conducted by X-ray fluorescence spectroscopy, using Philips PW 2400 XRF spectrometer.

Bleaching of the purified oil and bleaching capacity evaluation

The purified deep frying oil has been individually bleached using unactivated, activated, and standard commercial bentonite samples. The bleaching capacity was evaluated via measurement of bleached oil color, the visible spectrophotometer (WFJ525-W UV) was used to conduct the analysis. The bleaching efficiency of activated and unactivated samples has been separately evaluated to be compared with the bleaching efficiency of the commercial tonsil. The bleaching process was carried out according to the method reported by Gulsah Kirali and Oral Lacin¹⁹; the oil was kept in a round bottom three- necked flask with a stirring rod. Activated bentonite (1-4% based on the weight of oil) was added to the oil. The mixture was kept under 80° with continuous stirring for 20 min. under reducing pressure. After that, the bleached oil was separated by filtration at 50°C and kept in colored bottles. Bleaching capacity has been calculated according to the equation, BC = $[A - A / A] \times 100$, as A = and A represents absorbance of respectively²⁰. purified and bleached oils

Evaluation the effect of bleaching on the oil properties

In order to evaluate the properties enhancement of the bleached oil, they should be compared with the properties of the virgin and unbleached oils. Bleached oil (at 3% bentonite dose), unbleached oil, and virgin oil were separately subjected to chemical and physical analysis. The analytical process has been done according to the American Oil Chemists Society (AOCS, 1998). Acid value, peroxide value, saponification value; iodine value, unsaponified matters and peroxide value were measured²¹. Ester value was calculated by subtracting the acid value from saponification value.

Sulfation of oil

The oil sample was kept in a three - necked flask fitted with a stirrer, thermometer and an inlet for the addition of the chemicals. Sulfuric acid H_2SO_4 (15% based on the weight of oil) was slowly added to prevent material discharge. The overall reaction time was 2 h under low stirring while maintaining the temperature below 30°C during the addition. The sulfated oil was washed with 10% sodium chloride solution at room temperature and neutralized to *p*H 6.7-7.2 using 30% aqueous solution of sodium bicarbonate with agitation for 30 min.

Evaluation of sulfated oil

The progress of sulfation and double bond conversion were investigated through measuring organically combined SO3%, acid value²², total desulfated fatty matter²³ and iodine value²⁴.

Evaluation of fatliquor emulsion

Aqueous sulfated oil emulsion (10%) was built by slow addition of the sulfated oil to hot water (55°C) under continues stirring for 30 min. The stability towards tan liquor, hard water, and pickle liquor was measured according to the method reported by Santos and Gutterres²⁵: Three aqueous solutions were prepared with definite concentrations to represent the above three type's solution. 5% basic chromium sulfate represents the tan liquor, 5% magnesium sulfates represent the hard water and 5% sodium chloride + 1.5 % sulfuric acid represent the pickle liquor. After that, 3 mL of each solution was separately added to 20 mL of 10 % fatliquor emulsion and stability was seen for the duration of four hours. The stability towards acids was measured according to the method reported by Harris²⁶: 100 mL aqueous solution of 1% fatliquor was transferred to 250 mL extraction flask and brought to boil under a reflux condenser. The appearance of the solution was recorded as, no change, turbidity, or oil separation. In case there is no change, this was followed by the second addition of 0.1% sulfuric acid (1 mL of 10%) and the solution was boiled again for 25 min. The appearance of the solution was recorded as turbidity and separation of oil. If no change has obtained or the change was minor, re-addition of acid to provide 1% acidity and boiling for further 15min were performed again and the appearance recorded. The process was repeated with 3, 5, 7 and 9%, acidity.

Leather fatliquoring process

The fatliguring process has been conducted in a pilot scale set up in the drum. Fatliquor emulsion was built as an aqueous solution of sulfated oils. The chrome tanned leather samples were individually liquored using different concentrations (4, 6, 8, 10%, and w/v)of sulfated oil as aqueous solutions (fatliquor emulsion). The fatliquoring process was performed as follows: 50 kg chrome tanned bovine leather sample that was taken from the area parallel to backbone direction was cut into $50 \times 100 \text{ cm}^2$ leather pieces. washed with sufficient amount of ordinary water, the drum has been run for 30 min. After draining the washing water. Sodium format (1.5% based on the weight of the leather) was added to neutralize the leather pieces and the drum was running for about 15 min. Sodium bicarbonate (0.75% based on the weight of the leather) was added and the drum was running for further 20 min until the leather pieces were greenish blue with Bromo cresol green through the whole thickness (pH 5.0-5.5). The leather pieces were immersed into fatliquor emulsion at a temperature (55°C). The drum was run for 40-50 min and leather pieces were then washed with water for about 10 min. The goods were left to dry in the air through hanging up at room temperature and directed to investigate.

Evaluation of fatliquored leather

Basically, the fatliquor work to add fatty matter to leather bundles, as a result, the fatliquored leather acquires softness and its mechanical properties improved. In order to examine the effect of the fatliquor concentration on the efficiency of the liquoring process, the process was carried out with different concentrations of the fatliquor emulsion. The amount of fatty matter that was added to the liquored sample after fatliquoring was measured according to stamp's method²⁷: About 5g of fat liquored leather

pieces (1cm²) was accurately weighed then extracted in a soxhlet apparatus in a mixed solvent consisting of 13 parts of methanol and 87 parts of chloroform (v/v) for about 6 h. The solvent was then evaporated and the added fatty matter was calculated as % percentage of the leather weight. Tensile strength and elongation at break % were measured using Zwick-1425. The physical properties of leather samples those were liquored with 10% liquor concentration were more heavily assessed according to the standard test methods of leather analysis. Tear strength has been assessed in accordance with the official method of leather analysis (ISO3377-1)²⁸. The flexing endurance was evaluated by a bally flexometer according to the official method of leather analysis (IUP/20)²⁹. Water vapor permeability was tested according to the official methods reported by America Standard Test Methods ASTM³⁰. In addition, the visual properties of fatliquored leather were also observed. In order to study the enhancement in the fatliquored leather fiber and to show the difference between the surface of the leather before and after fatliquoring, two different leather samples (before and after fatlquoring) have been subjected to surface study using scanning electron microscope (SEM). Circular liquored and unliquored leather samples were individually subjected to sputter coating of gold ions to prepare a conducting medium (sputter coater-Edwards-Model S-150 A, Eng.). A Jeol scanning microscope (Japan) JSM-T20 was used to achieve the goal.

Results and Discussion

Bentonite sample evaluation

The physiochemical properties of the clay should be taken into account during its selection in industrial bleaching. These properties enhanced through acidic activation, supporting its impurities absorbance capacity. Given the results in Table1, the activation process greatly changes the bulk properties of the clay prompting the decrease in the loss on ignition (LOI)

Table 1 — Physical properties of un-activated bentonite clay			
Property	Commercial sample	Un-activated bentonite sample	Activated bentonite sample
Moisture (%)	5.41	9.92	6.83
Density (g/L)	530	455	503
<i>p</i> H (10%	3.80	4.20	2.98
suspended sample) LOI (loss on ignition at 1000°C) wt. (%)	6.16	10.69	7.18
Surface area (m^2/g)	268	178	259

from 10.69% to 7.18%. The Surface area which is one of the most important feathers of industrial bleaching clay has increased to close to the standard commercial sample after activation. Therefore, the surface area of the activated sample $(259m^2/g)$ satisfies the surface area that is required for utilizing the clay in industrial bleaching process $(> 200m^2/g)^{31}$. In addition, the main properties of the activated sample; density, moisture, pH, and loss on ignition are compatible with the requirements needed to run the clay in the bleaching process³². Moreover, the properties of the activated sample and the standard commercial are greatly come near. The analytical data in Table 2 reveals to significant modification of the chemical composition of bentonit after activation. The higher silica content and the smaller ratio of metal oxides compared with unactivated sample attributed to the cations exchange by the protons of acid. The process results in the replacement of the metal cations (Al, Fe, and Mg) from the montmorillonite octahedral structure during the activation process, creating gaps in the octahedral structure and thus increases the ability of clay to absorb impurities³¹. Therefore, the relative amount of silica has been improved from 60.14 to 72.63% and the ratio (Si/ Al+Fe+Mg) significantly increased. The data in the table also reveal to the presence of trace amounts of exchangeable cations (K^+ , Na^+ , Ca^{+2}). These exchangeable ions have to replace by activation, but the presence of small amounts of which is due to the presence of some insoluble quartz impurities³¹. In conclusion, an obvious chemical composition similarity is almost observed in the chemical composition of the activated and standard commercial sample.

Oil purification and bleaching

The oil pretreatment mainly aimed to somewhat improve the smell and the color through getting rid of

Table 2 — Chemical composition of activated and un-activated bentonite			
Result %	Un-activated bentonite	Activated bentonite	Commercial clay sample
SiO_2	60.14	72.63	74.84
Fe_2O_3	4.11	3.18	2.71
Al_2O_3	12.98	11.27	10.24
MgO	5.45	1.96	1.45
Na ₂ O	0.20	0.21	0.19
CaO	1.83	0.59	0.51
K ₂ O	1.63	1.31	1.10
r*	2.67	4.42	5.20
*r represents the ratio $(Si^{+4}/AL^{+3}+Mg^{+2}+Fe^{+3})$			

some impurities those mainly cause odour and colour changes. Some of these impurities have been dissolved into salty washing water which has been excluded out. The frying solid impurities have been also separated through filtration, and the visual appearance of the oil has been slightly enhanced. The results for deep frying oil bleaching using different clay samples (activated, unactivated and commercial tonsil clay) is presented in Table 3.

As can be shown, the bleaching capacity of bentonite clay was improved after it was activated through using 8N sulfuric acid, even with all doses used of bentonite. However, the maximum bleaching capacity and color improvement for the frying oil were verified at 3% activated bentonite dose and the bleaching capacity has not seemed to improve with further increase in bentonite dose. The maximum bleaching efficiency of the unactivated clay at 3% bentonite dose was 76.8%. The bleaching efficiency of the activated sample was improved to reach 88.9% and comes closely to commercial samples 90.5% at the same bentonite dose. Which clearly mean that the decolourization ability of activated bentonite comes near to that of the commercial tonsil clay sample and greater than the unactived sample. The chemical properties of the different oil samples have been shown in Table 4, it was clearly observed that the bleaching

Table 3 — H	Bleaching efficiency of the different bentonite samples
	at different bentonite doses

Bentonite	Bleaching efficiency (BC %)		
dosage %	Un-activated bentonite	Activated bentonite	Commercial bentonite
0.5	71.1	81.2	81.6
1.0	73.2	83.4	84.5
1.5	74.2	85.5	86.2
2.0	74.5	86.9	86.9
2.5	75.6	87.9	88.0
3.0	76.8	88.9	90.5
3.5	76.8	88.9	91.5
4	76.8	88.9	91.5

Properties of the oil	Fresh frying oil	Deep frying oil	Bleached frying oil
Acid value, mg KOH / g oil	0.4	6.9	7.1
Iodine value, mg I ₂ / g oil	52.0	44.7	43.0
Saponification value, mg	194.4	189.0	192.9
KOH / g oil			
Unsaponifiable matter, (%)	0.7	1.8	0.9
Peroxide value, m Eq/Kg	2.1	6.1	5.3
Ester value (S.V- A.V), mg KOH /g oil	194.0	182.1	185.8

process doesn't causes significant changes in acid and peroxide values of the frying oil. The saponification and ester values for the frying oil are almost the same before and after bleaching. The slight increase in acid value is due to hydrolysis of glycerides and fatty acid liberation at elevated temperature. These results are similar to those obtained by izaki³³. In addition, the unsaponified matters of the frying oil have been reduced from 1.8% to reach 0.9% after bleaching; this attributed to the reduction of impurities that was achieved through activation. However, the data in Table 4 indicates that the chemical properties of the purified oil remain inferior compared to virgin oil.

Evaluation of the sulfated oil

The degree of unsaturation, sulfur trioxide content SO_3 %, and neutral fatty matter are the most important parameters for evaluation of the sulfated product. From the data in Table 5, a remarkable decrease in iodine value of the sulfated oil indicated to the progress of double bond conversion and sulfate ion attack with the progress in sulfonation process. The significant increasing of SO₃% confirmed the addition of sulfate ion and sulfate ester formation. In supporting of that, SO₃% reached to 5.7% and the ratio that required for fatliquor production (SO₃ >5) has been reached³⁴. The increase of acid value attributed to the splitting of the triglyceride molecules rather than introduced sulfate ions. It is well known that, only about 30% of the oil have to be sulfated and two-thirds of the oil must be kept without sulfation, otherwise oil may turn completely to soaps and loses its ability to act as fatliquor. The sulfated portion acts as self-emulsifier and there no need to add an external emulsifier. In other words, the ratio of the sulfated portion to unsulfated portion has to be about $1:2^{35}$. The analytical data in Table 5 show that the ratio of neutral fat (unsulfated portion) was 72.9% and the ratio of the emulsifier portion (sulfated portion) to the emulsified portion (un-sulfated) is approximately 1: 2 since, adding external emulsifier is not required and the required ratio for self-emulsification of oil in water was attended.

Table 5 — Chemical evaluation of sulfated oil Property of sulfated oil Result Moisture % 9.5 Ash% 2.6 Acid value 10.5 Iodine value 8.1 $SO_3\%$ 5.7 Total desulfited fatty matter % 68.3 Neutral fats % 72.9

Evaluation the stability of fatliquor emulsion

The fatliquor may be added during tanning, pretanning or dying steps. So the fatliquor must possess a degree of stability during these steps, the emulsion has to be stable against the dyes and tanning materials. The oil droplets in the emulsion do not have to deposit or accumulate. On the other hand, the time required for the complete fatliquoring process is about 50-90 min depending on the type of the leather, so the solution must be stable against fat or oil accumulation during this period of time. The data in Table 6 show that the emulsion was stable up to 2.8 h (168 min.) against the pickle liquor. In addition, the emulsion exerted considerable stability towards tanning liquor and hard water reaches to 2.3 h. Basically, the fatliquor may be added at lower pH value, and the emulsion has to be stable over acid concentration until complete fatliquoring³⁶. From data in Table 7, it can be shown that the emulsion exerted good stability up to 3% sulfuric acid concentration and decomposed at 7% concentration. However, it is moderately stable at 3% sulfuric acid concentration. Consequently, it can be run during leather processing steps. This result is similar to that obtained by several studies^{25,34,37}

Evaluation of fatliquored leather

Basically, the fatliquor emulsion works to add fatty matter to the leather fibers and coating the bundles with a thin layer of fat leading to mechanical properties enhancement³⁶. The fatty matter has to penetrate leather fibers not to be accumulated on the leather surface causing fat spue or greasy stains and the fat have to access to the leather bundles. The steady improvement of the tensile strength and elongation at break % of the leather with the increase

Table 6 — Stability of fatliquor towards tan liquor, hard water and pickle liquor			
Solution	Stability		
5.0 % basic chromium sulfate(tan liquor)	Up to 2.3h		
5.0 % magnesium sulfate(hard water)	Up to 2.2h		
5.0 % sodium chloride + 1.5% sulfuric acid(pickle liquor)	Up to 2.8 h		

Table 7 — Stability of fatliquor towards acid concentration		
Sulfuric acid conc. %	Stability	
0.1	stable	
3.0	stable	
5.0	partially stable	
7.0	decomposed	
9.0	decomposed	

in the fatliquor concentration (Fig. 1 and Fig. 2) is visible evidence of the fatliquoring success. It proves the direct effect of the fatliquor on the leather properties. Therefore, the mechanical properties of the leather are only improved when the fat droplets able to penetrate the leather adding mass and coating the leather bundles; as a result, the leather acquires desirable mechanical properties^{6,25,37}. The data in Fig. 1 and Fig. 2 revealed that the fatliquor of sulfated oil and commercial fatliquor have nearly the same effect in the mechanical properties enhancement. Figure 3 illustrates the relation between added fatty matter and the fatliquor concentration. The data





Fig. 3 — Effect of fatliquor concentration in the fatty matter added to fatliquored leather

shows that the added fatty mater increase as fatliquor concentration increase and maximum fatty mater can be added to the leather (8.6) was achieved through treatment with 10% fatliquor concentration. In addition, the fatliquor was able to add quantities of fat approaches to those were added by the commercial fatliquor at the same liquor concentration. In addition, some other mechanical properties of fatliquored leather at 10% fatliquor concentration were illustrated in Table 8. The data in the table showed that the mechanical properties of fatliquored samples are in the recommended values of Egyptian standard specification of chrome tanned leather with a thickness between 1.2-1.5 mm³⁸. The flexing endurance test shows no damage up to 100000 cycles. Moreover, Water vapour permeability and tear strength of the samples those were liquored with prepared and commercial fatliquors are nearly the same. The scanning electron microscope (SEM) of the leather samples before and after fatliquoring (Fig. 4a-b) showed that the leather gained a smooth surface without greasy stains and the leather bundles have been coated with a thin layer of fatty material.



Fig. 4 — SEM (X 1000) of wet blue crust leather fiber before and after fatliquoring

Table 8 — Physical test of the unfinished wet blue leather after liquoring with 10 % fatliquor concentration			
Leather test	Water vapour permeability (mg/cm ² h)	Flexing Endurance	Tear strength (N)
Result	3.71	No Spoilage @	96.00
	3.08*	100 000cycle	102.00*
		No spoilage @ 100000cycle*	
*samples liquored with commercial fatliquor			

Conclusion

Local bentonite clay has been used to add value to the deep frying oil; the clay was used as a bleaching agent and impurities absorbent after activation with 8N sulfuric acid. The bleaching efficiency of the clay is found to be almost similar to tonsil commercial clay. Fatliquoring agent with a considerable quality was prepared from the bleached oil via sulfation process. The fatliquored wet blue crust leather shows mechanical properties enhancement in the recommended values. The research adds a value to side product waste and transfers it into a usable product.

References

- 1 Kaussen M, J Am Leather Chem Assoc, 93 (1998) 16.
- 2 Covengton A D, Leather Technol Chem, 85 (2001) 24.
- 3 Wang X C, Feng J Y, An H R & Sun M, J Soc Leather Technol Chem, 88 (2004) 228.
- 4 Guerci A, Dipinto D & Caselette H G, *Hoechst* Aktiengesellschaft, Germany, U S patent 5529704, Jun 1996.
- 5 Monheim H H, Richrath L & Duessledorf R B, *Henkel Kommanditgesellschaft auf aktien*, *Dusseldorf*, Germany, U S patent 4903362, Feb. 1999.
- 6 Nyamunda B C, Moyo M & Chigondo, Ind J of Chem Techol, 20 (2013) 116.
- 7 Tan B K & Flingoh C H, Olein and stearin from Malaysian palm oil: Chemical and physical characteristics (PORIM Technology), 1981, ISSN No. 4, 0127.
- 8 Helmy H E & Megahed M G, J Food Dairy Sci, 1 (2010).
- 9 Pedreschi F, Moyano P, Kaack K & Granby K, Food Res Intl, 38 (2005) 1.
- 10 Encinar J M, Gonalez J F & Rodriguez- Reinares A, Fuel Pro Technol, 88 (2007).
- 11 Choe E & Min D B, J Food Sci, 72 (2007) 77.
- 12 Hassan M S & Abdel Khalek N A, Appl Clay Sci, 13 (1998) 99.

- 13 Siguin D, Ferreira S, Froufe L & Garcia F, *J Mater Sci*, 29 (1994) 4379.
- 14 Rossi M, Gianazza M, Alamprese C & Stanga F, J Am Oil Chem SOC, 78 (2001)1051.
- 15 Gates W P, Anderson J S, Raven M D & Churchman G, *J Appl Clay Sci*, 20 (2002) 189.
- 16 Girgis A Y & Grasas y, Aceites, 55 (2004) 264.
- 17 Folietto E L, Volzone C & Ppoto L M, Braz J Chem Eng, 20 (2003) 139.
- 18 Folietto E L, Collazzo G C, Volzone C & Porto L M, Braz J Chem Eng, 28 (2011) 169.
- 19 Kirali G & Lacin O, J Food Eng, 75 (2006) 137.
- 20 Falaras P, Kovais I, Lezou F & Seiragakis G, *Clay Mineral*, 34 (1999) 221.
- 21 Firestone D, Official Methods and Recommended Practices of the American Oil Chemists Society, Fifth Edition includes all changes 1993-1997, Edition Analytical methods (Champaigen-Illionois) 1998.
- 22 ASTM D500 95 Standard Test Methods of Chemical Analysis of Sulfonated and Sulfated Oils, 31, 2003.
- 23 ASTM D 5353 95 Standard Test Methods of Chemical Analysis of Sulfonated and Sulfated Oils, 31, 2009.
- 24 Cunnif, "*Official Methods of Analysis*" 16th Ed., chapter 41 (AOAC International) 1995.
- 25 Santos M & Gutterres M, J Clean Prod, 15 (2007) 12.
- 26 Harris J, Bulletin, 140 (1946) 17.
- 27 Stamp D H, J Am Leather Chem Ass, 7 (1974) 290.
- 28 International Union of Leather Technologist and Chemists Societies (2001) IUPAC/6: "Measurements of tensile strength and percentage elongation ". Society of Leather Technology and Chemists.
- 29 International Union of Leather Technologist and Chemist societies (2001) IUP/20: "Measurements of flex resistance by flexometer method", Society of Leather Technologist and chemists.
- 30 ASTM D5052 00 (2010), Standard Test Method for Permeability of Leather to Water Vapour.
- 31 Didi M A, Makhoukhi B, Azzouz A, Villemin D, *Appl Clay Sci*, 42 (2009) 336.
- 32 Wu Z S , Li C , Sun X F , Xu X L, Dai B , Li J E & Zhao H S, *J Chem Eng*, 14 (2006) 253.
- 33 Izaki Y, Yoshikawa S & Ochiyama N, Lipids, 19 (1984) 324.
- 34 Mohamed O A, Habib M A & El sayed N H, Egypt J Chem, 52 (2009) 507.
- 35 Stather F, Herffeld H & Hartung W, Gesamt Abhandl, 9 (1953) 3.
- 36 Chen Z G & Wang Q E, Leather Sci Eng, 11 (2001) 18.
- 37 Habib M A & Alshammaria A G, J Soc Leather Technol Chem, 98 (2014) 199.
- 38 ES 122, Egyptian Standard Methods (1966).