

Ester Phosphate of Discarded Palm Oil from Potato Chip Factories as Fat-Liquoring Agent

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Abstract

In Egypt most potato chip factories used palm oil for frying. The quantity of palm oil resulting from frying processes as discarded represents more than half of the total other oils used in the Egyptian food factories. Discarded palm oil resulting from frying processes was preliminary treated by purification and bleaching as well as characterized via its physico-chemical properties and fatty acids composition. Therefore, this work was devoted to explore the application of the discarded palm oil in leather industry as fat-liquoring agent.

Fat-liquors help to prevent the loosening of leather grain and ugly appearance of chrome tanned leather after drying. In addition, fat-liquoring process improves leather characters such as soft handle, full, flexibility, and pliability as well as enhancement its mechanical properties. The study involved preparation of discarded palm fat-liquor via phosphorylation process. The importance of the prepared fat-liquor is due to their environmentally friendly nature, relatively safe utilization by human being, in addition to their economical feasibility. The fat-liquored leather led to an improvement in the mechanical properties of the leather e.g. tensile strength, elongation at break and tear strength. In addition a great enhancement in the texture of the treated leather by discarded palm fat-liquor as indicated from the scanning electron microscope (SEM).

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1. Introduction

In the leather industry, hides and skins proceed via various chemical and mechanical processes to produce finished leather. Chrome tanning has been the state of the art, it accounts over 80% of the activity in the tanning process [1] and used for the production of various types of leather [2]. But chrome-tanned leather when dried out becomes bony, hard and thus will not be suitable for use in most purposes, besides its color becomes dark and gains a disagreeable appearance. This means that, as water is removed during the drying stage, cohesion of the fibers takes place resulting in hard intractable leather which is difficult to rehydrate [3]. Thus, incorporation of fatty matter into leather through fat-liquoring process will decrease the effect of air oxidation and improves leather full and soft handle, flexibility, pliability and at the same time enhance its mechanical properties [4-6]. Therefore, introducing a lubricant into the leather keeps the fibers apart during drying and reduces the frictional forces within the fiber weaves thus allowing the fibers to move laterally over each other.

The palm oil used essentially for frying can be blended with various plant oils in different proportions to obtain liquid oil [7]. Most discarded

edible oils (include palm oil & palm kernel oil) and fats are of immense importance for industrial applications as surfactant and soap manufacture [8-12]. Therefore, this work was devoted to explore the application of the discarded palm oil in leather industry as fat-liquoring agent.

The potato chip factories, in Egypt, use palm oil for frying of potato chips which are considerably popular as food in Egypt. Potato chip factories produce a large quantity of discarded palm oil. The large quantity of these oils resulting from frying processes causes pollution of environment. In nearly all countries on the earth the protection of the environment has become increasingly a very serious concern. As a result, we can utilize these quantities of wasted oils to obtain useful product.

Therefore, this work was devoted to study the phosphorylation of purified discarded palm oil as well as explore its application for further use as leather fat-liquoring. Evaluation of the resulting chrome leather fat-liquored will be taken into consideration. This will add an economical value to this waste and at the same time prevent its environmental pollution. For this purpose a commercially available discarded palm oil (by-product) was used as a starting material.

2. Materials and methods

Materials

- Palm oil samples before and after frying were collected from some Egyptian potato chip factories.
- Chemicals used for different analysis of oil were supplied by international companies (Merk, Germany and BDH, England).
- Ortho- Phosphoric acid (98.5%) was pure chemical grade.
- Local commercial full grain chrome tanned leather was used for the present investigation from Radio Tannery, Cairo, Egypt.

Note: All chemical additives doses were calculated on the basis of leather weight (w/w).

Methods

Analysis of palm Oil

a- Purification of discarded palm oil

Discarded palm oil was heated to $90 \pm 5^\circ\text{C}$ and washed with a hot brine solution [5% Na Cl, w/v]. The ratio of discarded oil and brine solution was 10: 1 (v/v). The hot mixture [discarded oil and brine solution] was stirred using a stirrer at a speed of 60 rpm for 60 min. After that, the mixture was left to rest for 8 hrs in order to separate the mixture into two phases. The bottom phase [brine solution +impurities] was separated by siphoning. Sodium sulfite anhydrous was added to catch the traces of moisture from discarded palm oil, which was then filtered through filter paper (Whatman no. 1), Girgis [13]. The color was measured using Lovibond tintometer, model E, using 5.25 inch cell, and impurities of discarded palm oil before and after purification were determined according to the methods described in the A.O.C.S., 1997 [14]; while the odor was evaluated according to the method reported by Shyam [15].

b- Bleaching of purified discarded palm oil

Purified discarded palm oil was heated to $70 \pm 5^\circ\text{C}$ and bleached with a 2% H_2O_2 solution (v/v). The sample was stirred using a stirrer at a speed of 80 rpm for 30 min while maintaining a temperature of $70 \pm 5^\circ\text{C}$. The discarded palm oil was filtered through filter paper [Whatman no. 1], Girgis [13], and the color was measured.

c- Physical and chemical characteristics

Palm oil and discarded palm oil were analyzed for its physical and chemical characteristics according to the American Oil Chemists Society Methods, (AOCS, 1998) [16]. Refractive index, acid value, peroxide value, saponification value, iodine value and unsaponifiable matters were measured. The ester value was estimated by subtracting the acid value from saponification value (SV-AV).

d- Fatty acid composition

Fried palm Fatty acid methyl esters were prepared by IUPAC standard methods, 1987 [17], and according to A.O.C.S. method [16]. Determination of fatty acid composition was performed as described by Mitruke [18] using Hewlett Packard HP 5890 series II gas chromatography, equipped with flame ionization detector (FID), operated under the following conditions:

Detector, flame ionization (FID); column, capillary, 30.0 m x 530 μm , 1.0 μm thickness, polyethylene glycol phase (INNO Wax); N_2 with flow rate, 15 ml per min with average velocity 89 cm/s (8.2 psi); H_2 flow rate, 30 ml per min; air flow rate, 300 ml per min; split ratio, 8:1, split flow, 120 ml per min; gas saver, 20 ml per min. Detector temperature, 280°C ; column temperature, 240°C ; injection temperature, 280°C . Temperature programming starting from 100°C to reach a maximum of 240°C was used for eluting the fatty acid methyl esters. The identification of peaks was made as compared with chromatograms of standard fatty acids methyl esters (Sigma, USA).

Phosphoration processes

- phosphoration of the oil (100 g) were carried out in a three necked flask fitted with a stirrer, a thermometer and also with an inlet for the addition of the reagents. Phosphoric acid (H_3PO_4 , 30% of the oil weight) was added drop wise at interval times with slow stirring while maintaining the temperature below 30°C during the addition. The overall reaction time was 3 hours.
- The phosphated oil was washed by 10% sodium chloride at ambient temperature and neutralized with $\approx 30\%$ sodium hydroxide with agitation for 30-40 min.
- The phosphated products so obtained were analyzed according to official methods [19, 20]. The product was prepared at a concentration of about 60-70% prior ($\text{pH}\approx 7$) to its uses as a fat-liquor.

FT-IR Analysis

The change in functional groups of oils were studied using FT-IR analysis, it was performed using Mattson 5000 FTIR, USA spectrophotometer with resolution 4 cm^{-1} .

Hydrophile-Lipophile Balance (HLB)

Hydrophile-lipophile balance of emulsifiers was calculated using the following equation of Griffin [21]:

$$HLB = 20 (1 - S/A)$$

Where:

S= (Saponification value of the phosphated fat-liquor).

A = (acid value of the total fatty acids of the original sample).

Fat-Liquoring Process

The leather pieces were first washed with water for about 15 minutes and water drained off. Then neutralization process was carried out using 1% sodium formate and running the drum for 15 minutes. Thereafter, 0.5 % sodium bicarbonate was added and the drum was run for further 10 min. The leather pieces gave a greenish blue color with bromo cresol green throughout the whole thickness (pH 5.0- 5.3). The neutralized leather pieces were washed with water and dyed with acid dye, 5 % for 30 minutes. Then, 6% fat-emulsion was added to the dyeing bath at room temperature. After complete addition of the fat liquor, the drum was run for 40 minutes. The leather pieces were washed with water for about 10 minutes, removed from the drum, sammed, set out and left to dry in air through hanging up at room temperature. The dried leather pieces were used for investigation.

Mechanical Measurements

Fat-liquored leather samples were cut with special steel press knives from the position parallel to the backbone and about 5 cm away from it as specified in the Egyptian Standard Methods, ES-123 [22].

Dumbbell shaped specimens 50 mm length and 4 mm (neck width) were prepared according to ES-123 [22] for mechanical properties measurements using Rauenstein-Tensile force up to 500 Kg. The measured data are the average of four transverse and longitudinal measurements. The cross-head speed was controlled at 50 mm/min and the tests were done at room temperature (25°C).

Tensile Strength

Tensile Strength is calculated in kg/cm² from the load required to rupture the test specimen under tension (breaking load) divided by the area of the original cross section of the same specimen.

$$\text{Tensile strength (kg / cm}^2\text{)} = \frac{\text{Breaking load (kg)} \times 100}{\text{Thickness (cm)} \times \text{width (cm)}}$$

Elongation (at break)

The reading on the scale of the machine at the instant when the rupture occurred was taken to calculate the percentage of elongation.

$$\text{Percentage of elongation, \%} = \frac{\text{Increase of length (mm)} \times 100}{\text{Length of specimen, middle part (mm)}}$$

Stitch tear (single hole)

A hole (1×10 mm) was punched on the long axis of the leather specimens. The stitch tear was then calculated from the load required to tear the leather specimen from a steel rod passing through the hole of the specimen.

$$\text{Stitch tear (kg / cm)} = \frac{\text{Breaking load (kg)} \times 10}{\text{Mean thickness of leather sample (mm)}}$$

Scanning Electron Microscope

Specimens of experimental and control were prepared as circular samples (10 mm) and then 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 for the microscopic study.

3. Results and Discussion:

Purification of Discarded Oil

The effect of washing with brine solution and bleaching with H₂O₂ on the color, impurities and odor of the discarded palm oil are illustrated in Table (1).

Table (1): Effect of washing and bleaching on the color, impurities and odor of the discarded palm oil

Discarded palm oil	Lovibond color	Impurities, (%)	Odor
Before washing	36.0 Y+ 12.7 R+ 1.2 B*	1.4	Like odor to potato frying
After washing (Before bleaching)	36.0 Y+ 12.2 R+ 1.0 B*	0.8	Slight odor to potato frying
After bleaching	35.0 Y+ 6.6 R + 0.5 B*	0.7	Slight odor to potato frying

* Where: Y= Yellow, R = Red, B = Blue

Table (1) reveals that, washing with brine solution induces some improvements of the color,

odor and impurity levels. Also, it is noticed that addition of H₂O₂ improves the color due to its action as oxidizing agent which reduces the color level of

the oil pigments. These results are in good accordance with previous results reported by Woollatt [23] and Girgis [13]. The improvements may stem from the mutual solubility of the impurities isolated at the bottom [13,24].

Physical and Chemical Properties

Physical and chemical characteristics of palm oil before and after frying have been extensively investigated. The obtained results are shown in Table (2).

Table (2): Physico- chemical properties of palm oil before and after frying.

Properties	Palm oil	
	Before frying	After frying
Refractive index at 40 °C	1.4570	1.4597
Saponification value, mg KOH / g oil	199.2	199.8
Iodine value, mg I ₂ / g oil	49.10	40.5
Acid value, mg KOH / g oil	0.2	1.1
Peroxide value, m Eq/Kg	1.3	6.5
Unsaponifiable matter, (%)	0.3	0.7
Ester value (S.V- A.V), mg KOH /g oil	199.0	198.7

It was noticed from table (2) that, the saponification and ester values of both palm oil before and after frying are almost the same (199.2 , 199.0 and 199.8, 198.7 mg KOH/g oil) respectively. While iodine value before frying had a higher value (49.1 mg I₂/g oil) compared with after frying (40.5 mg I₂ / g oil) [8,13].

It is also clearly seen that, the acid, peroxide values and unsaponifiable matter of palm oil

increased after frying (1.1mg/g, 6.5 mEq/kg and 0.7%) compared with palm oil before frying (0.2 mg/g, 1.3 mEq/kg and 0.3%) respectively. These results are similar to those obtained by many investigators [13, 25, 26].

Fatty acids composition

Fatty acids composition of palm oil before and after frying is illustrated in Table (3).

Table: (3) Fatty acids composition of palm oil before and after frying.

Fatty acids (%)	Palm oil	
	Before frying	After frying
Saturated fatty acids:		
Myristic (C _{14:0})	1.82	3.22
Palmitic (C _{16:0})	43.96	45.20
Stearic (C _{18:0})	4.87	7.41
Total:	50.65	59.83
Unsaturated fatty acids:		
Oleic (C _{18:1})	39.50	36.29
Linoleic (C _{18:2})	9.40	7.57
Linolenic (C _{18:3})	0.45	0.31
Total:	49.35	40.17

It can be seen from Table (3) that, the saturated fatty acids contents of palm oil before and after frying are (50.65% and 59.83%) and unsaturated fatty acids are (49.35% and 40.17%). Also, it is noticed that, the ratio of total unsaturated fatty acids

of palm oil is almost equal to the total saturated fatty acids (1:1.03), while this ratio is different after frying (1:1.49). Oleic acid constitutes more than 80.0% and 90.0% of the unsaturated fatty acids of palm oil and discarded palm oil respectively, while palmitic acids

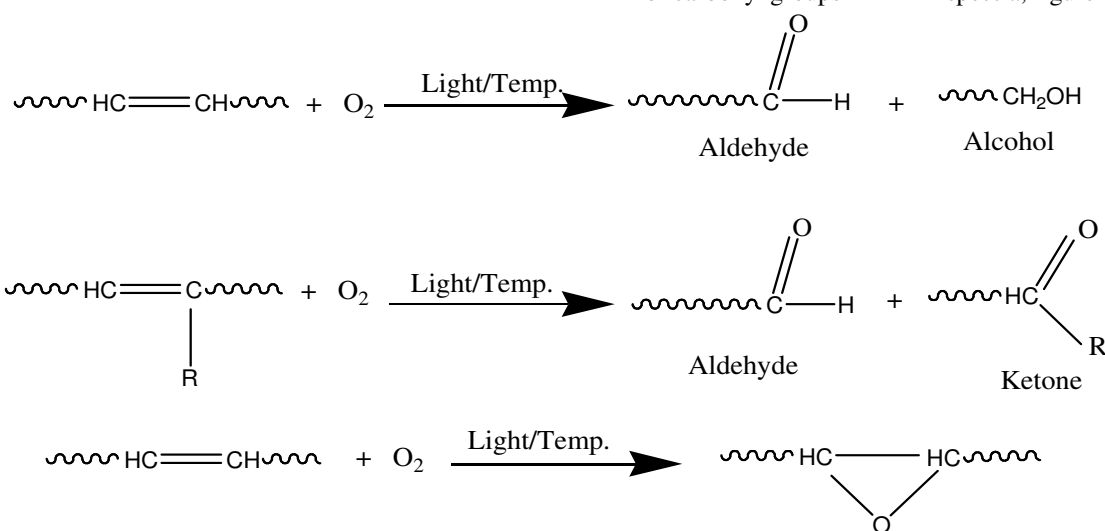
show more than 43.0% and 45.0% of the total fatty acids, respectively. On the other hand linoleic acid of palm oil has slightly higher value (9.40%) compared with discarded palm oil (7.57%).

These results are in a good accordance with those reported by Helmy & Megahed [8], Girgis [13], Tyagi & Vasishtha [26], and Megahed [27] who found that during frying, a progressive decrease in unsaturation was observed in the oil by the determination of iodine value. This decrease in

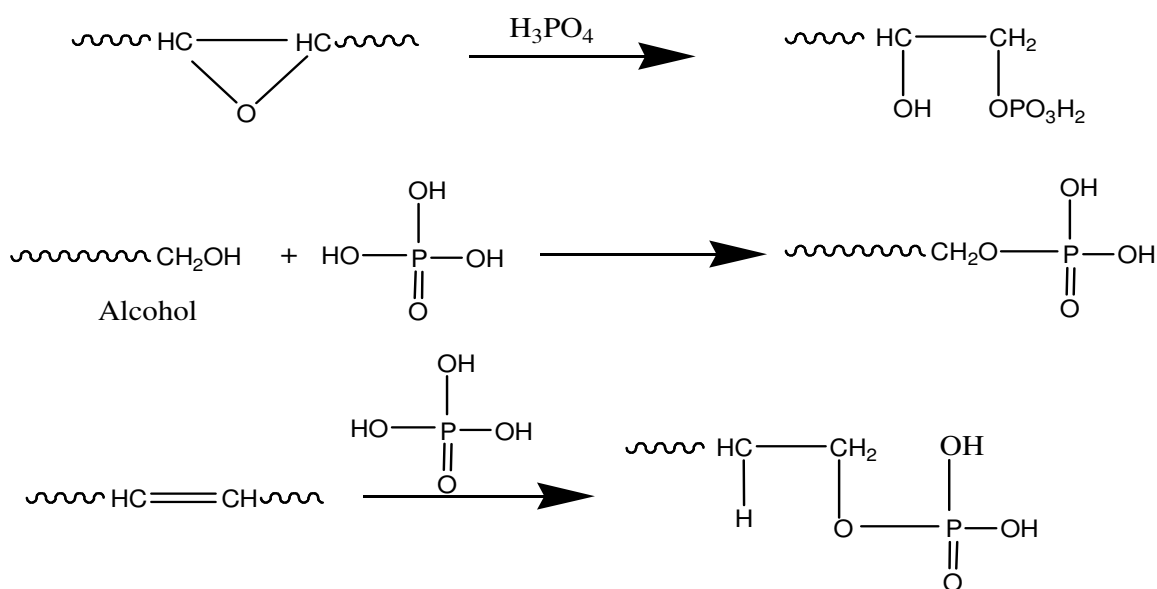
unsaturation could be due to the destruction of double bonds by oxidation, Tables (2,3).

Phosphoration Reaction

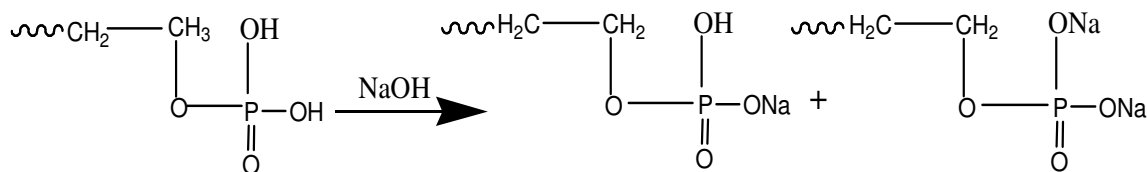
The discarded palm oil is oxidized by air under high temperature resulting in the scission of double bonds leading to increase the reactive centers of the fried oil which easily reacts with H_3PO_4 , as illustrated in schemes (1-3). This is confirmed by decreasing the percent of unsaturation fatty acids and iodine value as shown in tables (2,3) and appearance of carbonyl groups in FT-IR spectra, figure (1).



Scheme (1): Oxidation reactions and possible products



Scheme (2): Phosphoration reactions and ester-phosphate products



Scheme (3): Neutralization of Phosphated products

It can be seen from schemes that, the hydrophilicity of the Phosphated product increased due to the formation of polar groups (hydroxyl and ester phosphate groups) as confirmed by FT-IR, Figure (1).

FT-IR Analysis

Figure 1 illustrates the spectrum of palm oil, discarded palm oil and phosphate palm oil samples with the FT-IR/ Absorbance in the range of 4000 to 500 cm^{-1} . The spectrum of palm oil before frying shows characteristics absorption band associated with common oil. The stretching and bending absorption peaks at 3004 and 723 cm^{-1} are given by olefinic (cis = CH). The strong absorption peaks at around at 2900 to 2850 cm^{-1} are assigned to CH_3 and CH_2 asymmetric stretching vibration. Also, the spectra show stretching

absorption bands at 1652 cm^{-1} and 1467 cm^{-1} which correspond to non-conjugated (cis C= C) bond and C-H scissoring respectively, Guillen and Che Man [28, 29]. The spectra of discarded palm oil show stretching absorption bands at 1745 cm^{-1} , 1172 cm^{-1} and 3527 cm^{-1} corresponding to C=O, C-O and OH groups respectively. The appearance of bands at 2720 cm^{-1} indicates the presence of C-H aldehydic group.

While the spectrum of phosphate discarded palm oil shows characteristic absorption peaks at 1090 cm^{-1} corresponding to sym. dihydrogen phosphate and at 1035 cm^{-1} corresponding to asym. groups. It can also be seen from Figure (1) that, a strong broad band appeared at 865 cm^{-1} and (3527 & 3475) cm^{-1} which corresponds to the mono hydrogen phosphate and hydroxyl groups respectively.

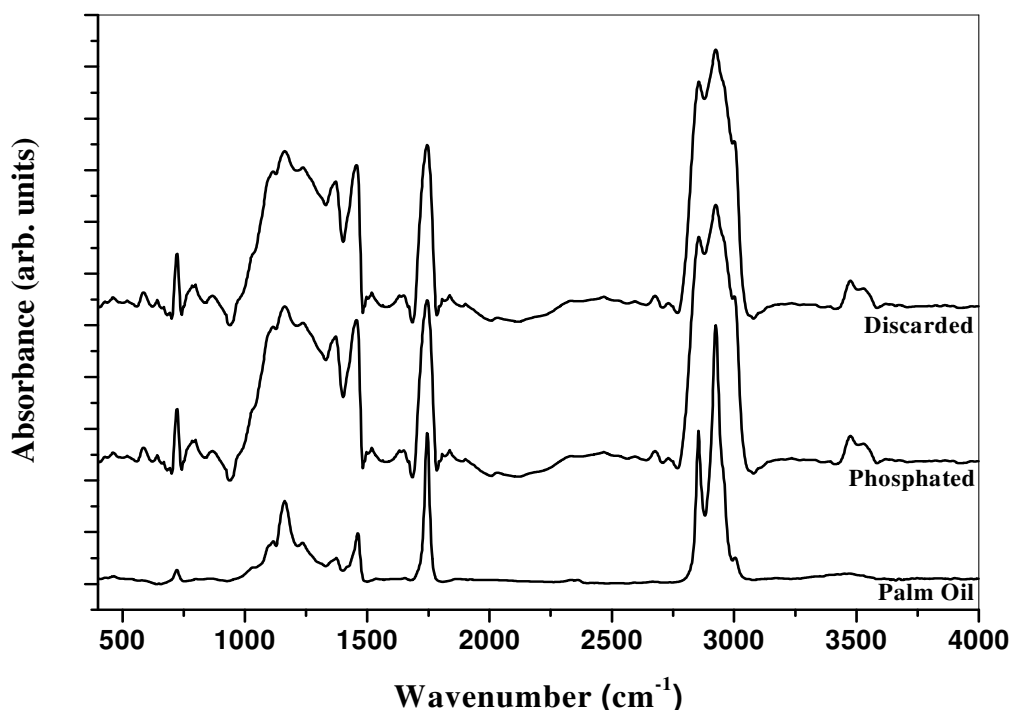


Figure (1): FT-IR Spectra of Palm oil, discarded palm oil and phosphated discarded palm oil.

HLB of the Prepared Fat-liquor

The HLB is an expression of the relative simultaneous attraction of surfactant for water and/or for oil (or for the two phases). The HLB of surfactant (Phosphoated oil) determines the emulsion types that tend to be formed, Griffin [21].

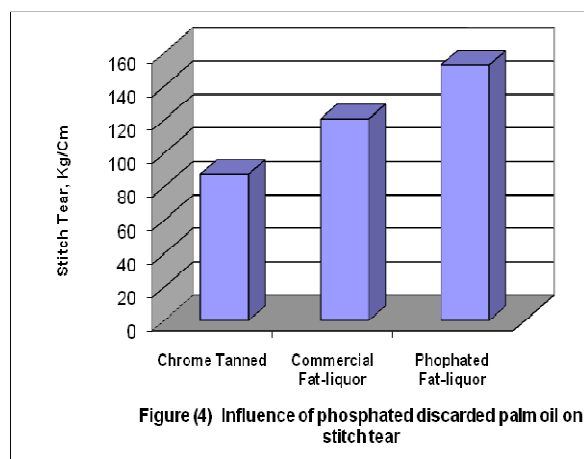
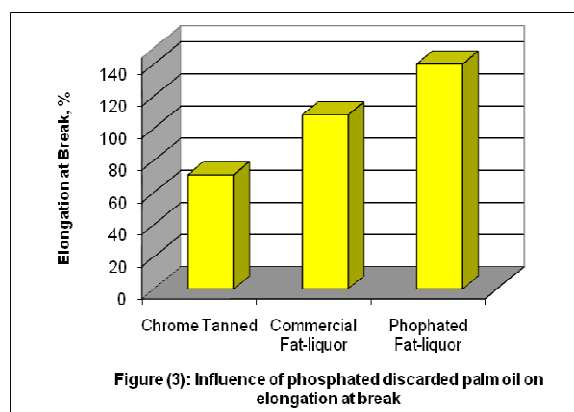
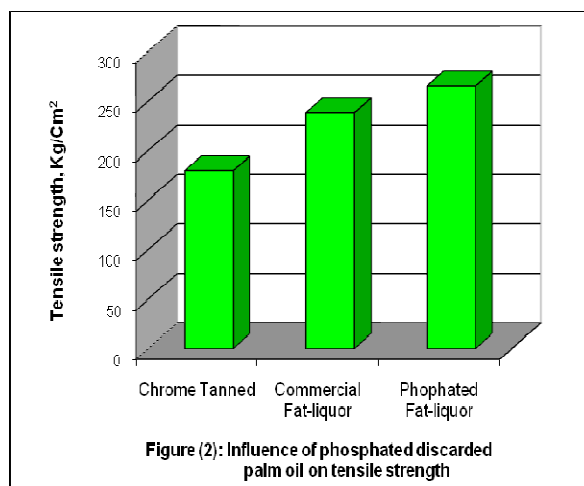
As previously mentioned, fat-liquoring is one of an important step in leather manufacturing, as it is intended to lubricate the leather fibers resulting in softness, pliability, flexibility, full and stretchy depending upon its final utility. Fat liquor helps to prevent both loosening of the leather grain and ugly appearance after drying and at the same time, improving the mechanical properties of leather. Thus, the fat separated from the emulsion is deposited inside the leather and fixed to the leather fibers. Therefore, the stability of fat-liquor in its water emulsion is an important factor in fat-liquoring of leather. i.e., if the fat-liquor is unstable, it cannot give a proper fat-liquoring effect. So that, for the application of the prepared Phosphated fat-liquor in leather treatment, it's necessary to evaluate the stabilization of the fat-liquor emulsion by Hydrophile-Lipophile Balance (HLB).

Therefore, the prepared Phosphated fat-liquor has HLB value of 11.06 i.e., it forms a "O/W" emulsion type, and simply dispersible in water. This means that a fineness of emulsion is formed since Phosphated ester or acids as well as the non-Phosphated portion of the ester present in the fat-liquor are emulsifiable. So that the prepared fat-liquor can form a stable emulsion and transfers from the aqueous bath to the leather and penetrates in it. The fat molecules and the fiber undergo physical bonding. However, the physically bonded fat molecules might undergo some chemical reactions with its surroundings [30].

Mechanical Properties of Fat-liquored Leather

The fat-liquoring process was carried out on neutralized leather using about 5% per 100 g leather. The mechanical tests include the measurement of the tensile strength, elongation at break and stitch tear. The mechanical properties have been given the greatest consideration on the evaluation of fat liquored leather, because, it gives an indication of fiber lubricity. The mechanical properties were evaluated according to Egyptian standard specification of leather [31].

It is found from figures (3,4) that, elongation at break and stitch tear are higher than that one of famous fat-liquor TRUPONOL® PEW2, (Phosphoric esters of synthetic fattening substance, pH ≈7) used in Egyptian tanneries, but tensile strength figure (2) is relatively high.



The improvement in the mechanical properties of the treated leather is due to good lubrication of the fibers as shown in SEMicrograph. The phosphated portion of oil (hydrophilic fatty matter) during liquoring of chrome tanned leather is chemically bound to the leather fibers, i.e. interacts with active centers in the collagen molecules of

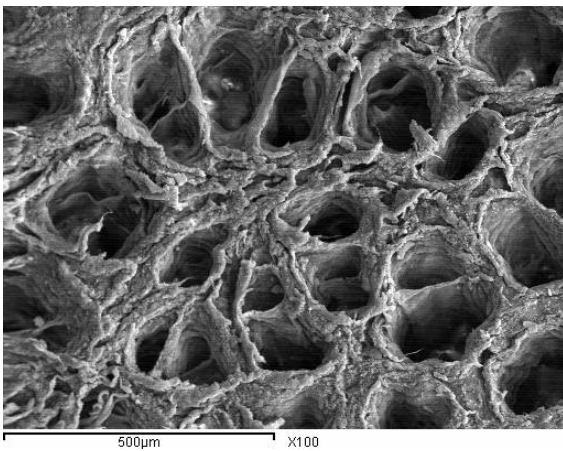
leather fibers, while the emulsified portion (hydrophobic portions) is mainly located between the fiber bundles. Because the prepared fat-liquor contains hydrophilic and at the same time hydrophobic portions can penetrate into the leather fibers with the prepared fat-liquor because of its good penetration power and the stability of its emulsion (HLB concept).

In general, the physical properties which are recorded above demonstrates to a far extent the suitability of the prepared phosphated local fried palm oil for fat-liquoring of chrome tanned leather, where by values which lie more or less within the

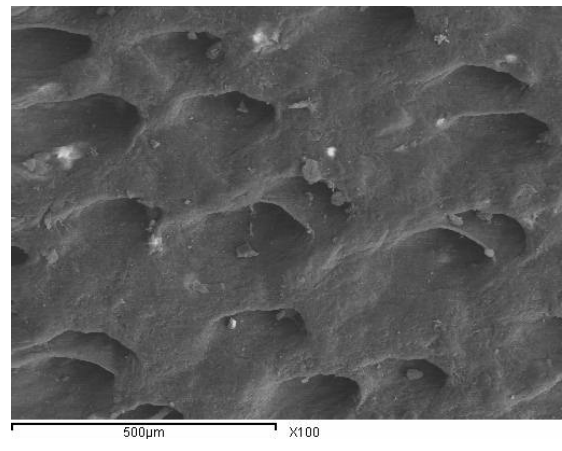
limits of the Egyptian standard specifications, are attained.

Scanning Electron Microscopy (SEM)

SEM looks deeply into hide fiber structure and shows the effect of fat liquor on fiber and grain surface. SEM of the grain surface (x 100) of the fat liquored leather exhibits a soft grain without any fatty-spew; Figure (5-a & b). Also, the cross-section (x 500) of leather fiber before and after fat liquoring showed a significant lubrication of fiber bundles; Figure (6-a & b).

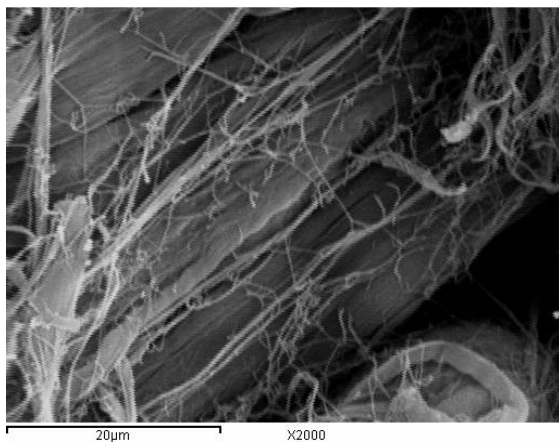


a) Chrome tanned leather

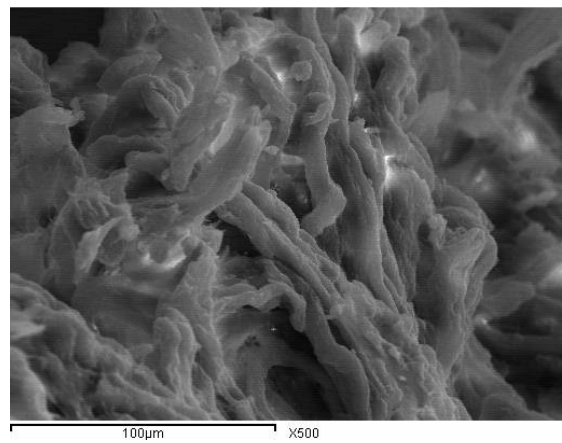


b) Fat-liquored leather.

Figure 5: SE-Micrograph for fiber bundles (X500).



a) Chrome tanned leather.



b) Fat-liquored leather.

Figure 6: SE-Micrograph for grain surface (X100).

Conclusion

In conclusion, it can be stated that this study on fat-liquoring of chrome tanned leather proved that:

- 1- The utilization of phosphated discarded palm oil (by product) as fat-liquoring agent.
- 2- An Improvement the texture and strength properties of leather fat-liquored using Phosphated discarded palm oil.
- 3- Substituting successfully part of the imported leather fat-liquoring agents.

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