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Manufacturing (Lithium-Sodium) Lubricant Grease Based On Syrian Base Oil And studying Its Physical, Chemical, And Rheological Properties

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Abstract: The aim of this Work is to manufacture lubricant grease from Syrian base oil (SBO). This paper discusses the preparation of Lithium-Sodium soap-based Syrian Base Oil (SBO)- using chicken fat. Lithium-Sodium soap with chicken fat were synthesized to make thickeners, then we mixed with the base oil (SBO) in various percentages (20, 25, 30) %. The physical, chemical and rheological properties have characterized. The physical-chemical tests include: dropping point, penetration number, resistance of water, corrosion of copper strip and total acid number. Then we choice the grease samples (30% thickener [70% Lithium soap, 30% Sodium soap]) that has a highest dropping point and has been studied from rheological view, by use capillary rheometer and has been determined apparent shear rate and shear stress. Then the viscous properties were studied by determining flow index (n), viscosity, and flow activation energy at constant shear stress.
Key wards: Lubricant Grease, Lithium Soap, Thickener, Dropping Point, Penetration, rheology, Shear Stress.

1. Introduction:

The word grease is derived from the Latin word (Crassus) meaning fat [1]. According to the classical (ASTM) definition: “lubricating grease is a solid to semi-fluid, Product of thickening agent in a liquid lubricant, Other ingredients imparting special properties may be included” [2]. Lubricating grease consists of three major components: Base oil (70-90)%, Thickener agents (7-30)%, and (0-10)% Additive [3]. Lubricating greases are usable and advantageous for many applications. Unlike lubricating oil, greases have little or no tendency to flow out of the friction point and we can use it to reduce the wear and friction between movable metal joints and can also be used over a wide temperature rang [4]. With respect to consistency and viscosity level greases are distinguished. Widely used abroad is the National Lubricating Grease Institute (NLGI) system of grease classification by the consistency class determined from the penetration value [5]:

NLGI class	000	00	0	1	2
Penetration at (25)°c	475-445	430-400	385- 355	340 - 310	295 - 265
NLGI class	3	4	5	6	
Penetration at (25)°c	250 - 220	205 - 175	160 - 130	115 - 85	

The rheological properties of greases are complex and dependent on both shear rate and duration of shearing [6]. Under certain loading conditions, grease would maintain its solid form and not flow or creep, even when applied to an incline or vertical surface. However, when the load reaches a certain critical point, which is beyond the grease’s “yield point,” it begins to flow like lubricating oil. Should the load be removed, the grease would then case to flow and would return to its solid state after a period of time [7].

The aims of this work is to manufacturing lubricating grease from Syrian base oil and study its chemical-physical properties then determined its rheological characteristics.

2. Materials:

Mineral oil (obtained from Banias refinery, Syria), Lithium hydroxide (obtained from Panreac, Spain), Sodium hydroxide supplied by Avon chem., UK., solvents as Hexane, Iso-propanol, and tuloin (obtained from Sigma Aldrich, Germany), chicken skin was purchased in local market.

3. Experimental

3.1. Preparing Chicken Fat:

We get chicken fat from chicken skin by grind it, then extract it in soxhlet device with in solvent (Hexane). The base-catalyzed transesterification with methanol solution of potassium hydroxide was used for complete conversion to fatty acid methyl ester (FAME) [8]. The resultant solution of (FAME) was evaporated to dryness and dissolved in methanol before injection into GC (GC 2010 Shimadzu auto injector AOC-20i).

3.2. Preparation grease:

Mixture 1: An amount of chicken fat was put in a wide -mouth glass reactor and worm it then added slowly $LiOH.H_2O$ to it. When a Saponification begun we added 5% from whole weight of basic oil which wanted to add. and uniformly mixed with a mechanical stirrer at 90 °c for half hour.

Mixture 2: In another glass we follow the same previous steps but, instead of $LiOH.H_2O$, we added NaOH.

Then we added the first mixture to another one. The temperature was then slowly raised to 120 °c after that add all the rest oil (SBO) gradualness, and maintained for 4 h with stirring. After that we raised temperature to 180 °c for 30 min with stirring. After the cooking period the mixture was allowed to cool to room temperature with continual stirring. to acquire the grease.

3.3. Physical And Chemical Tests:

3.3.1. Dropping Point:

Every sample of grease has been put in a cup and put it in Dropping Point instrument (Petrotest, Germany) with a thermometer, then temperature has been increased slowly until first drop fall from the cup [9].

3.3.2. Consistency (Penetration Number):

Each unworked grease's samples was put in cup of penetration instrument (GD-2801C Penetrometer, China) to measure its consistency grad, and then we worked these greases (60 double storks) in grease worker, after that we measured its consistency again [10].

3.3.3. Corrosion of Cupper Strip:

Lubricating greases shouldn't attack metals i.e. greases must protect material from corrosion. And we determined this corrosion by the copper strip test. Aggressiveness is evaluated by means of the discoloration of the copper strip. A copper strip was introduced in a beaker containing the grease tested. The beaker was then placed in an oven at 50°C for 48 h. The strip was then cleaned and compared, according to the final color, to ASTM standard strips identified by numbers and letters (1a, 1b, 2a, 2b, etc.). For example, strip no. 1a was slightly orange and strip no. 1b was dark orange. [11].

3.3.4. Total Acid Number (TAN):

The quantity of (KOH) in milligram necessary to neutralize the free acids that present in one gram of the grease [12].

3.3.5. Water Resistance:

The amount of resulting grease put in test tube, this tube contains water, after that shake it strongly for certain time, and then we compared it to know how it resistant water.

3.4. Rheological Measurement:

Rheological measurement were performed using a Capillary Rheometer (Deri F., 1989, Syria) the Temperature employed through out the experiments were standardized at (15, 25, 30)°c and a capillary dimensions L/R = 64.

We experiment this grease under pressure (596.10^3, 1054.10^3, 1406.10^3, 1650.10^3, 2275.10^3) pa.

* The Apparent Shear Rate (γ_a) is given by:

$$\gamma_a = \frac{4.Q}{\pi.R^3} \quad (1)$$

Where R: is the capillary radius, Q: is the volumetric flow rate [13].

* The Apparent Shear Stress (τ_a) is given by:

$$\tau_a = \frac{P.R}{2.L} \quad (2)$$

Where P: is pressure at capillary entrance, L: is the capillary length.

* Apparent Viscosity is given by:

$$\eta_a = \frac{\tau_a}{\gamma_a} \quad (3)$$

*Flow Activation Energy at a constant shear stress (E_η) was determined by using Arrhenius equation:

$$\eta = Ae^{\frac{E_\eta}{R.T}} \quad (4)$$

Where A: is consistency, related to structure and formulating, R: is the gas constant (8.314 J/mol.k°).

4. Result and Discussion:

4.1. Determined The Characteristics Of Fatty Acids In Chicken Fat:

4.1.1. Specification Fatty Acids in Chicken Fat:

The fat as fatty acid methyl ester (FAME) has been injected in Gas chromatography (GC) to analysis it and print the result as a chromatogram figure 1.

Depended on the percents of fatty acids in table1 we can calculate both of soap value (SV) and Iodine value (IV).

SV (mg) = 198.097 mg

IV (mg) = 80.37 gr

Also we can calculate Free Acid Number (FAN) in chicken fat relatively to Oleic acid that have molecular weight (282)gr/mol:

$$FAN\% = \frac{N \times V \times 282}{1000 \times W} \times 100 = \frac{0.1 \times 1.6 \times 282}{1000 \times 2.49} = 1.81\% \quad (5)$$

Where N: Is normality of KOH (eq/l), V: Is volume of KOH solution (ml), W: Is weight of sample (gr).

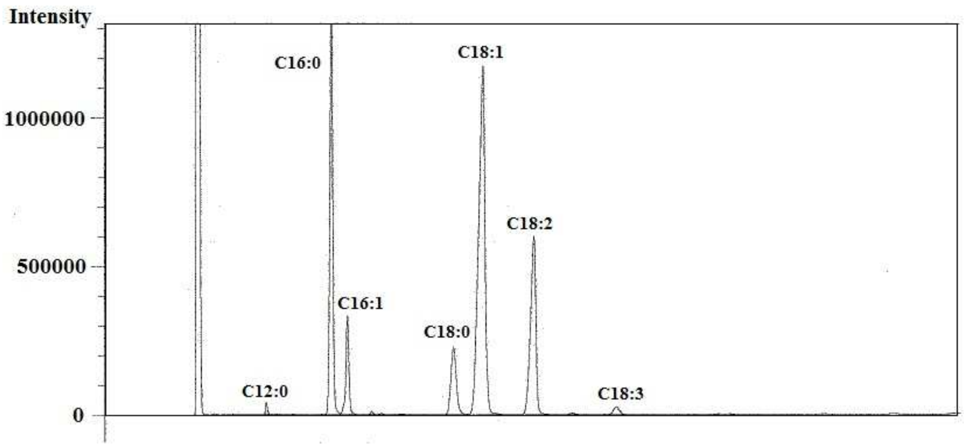

Figure 1. chromatogram of (FAME) for chicken fat

Table 1. Fatty Acid Composition

Fatty Acid	Fatty Acid's Symbol	Mean (mg/100mg)
Lauric Acid	$C_{12:0}$	0.44
Palmitic Acid	$C_{16:0}$	23.4
Palmaitoeic Acid	$C_{16:1}$	5.73
Stearic Acid	$C_{18:0}$	7.06
Oleic Acid	$C_{18:1}$	42.78
Linoleic Acid	$C_{18:2}$	18.62
Linolenic Acid	$C_{18:3}$	0.85

4.2. Determined Physical and Chemical Properties For Lubricating Grease:

4.2.1. Dropping Point:

Sample's Dropping points have been determined and printed it in table 2.

We observe from figure 2 that the maximum dropping point (145)°c is to the grease which contain (30)% thickener [(70)% Lithium soap and (30)% Sodium soap].

In general we can conclude from figure 2 that all dropping point were as high as possible when the percent of lithium soap between (70-80)% and that's because in this percent, the homogenous between both (Li, Na)soap and base oil is optimum.

4.2.2. Penetration Number (Consistency):

The penetration of the resulting mixed greases were measured at (25)°c (unworked grease samples and after worked them 60 double strokes) and table 3 shows this results.

We note from previous table the sample which has the highest Dropping point has penetration number (3) NLGI, and all remainder samples has penetration number between (1-3) NLGI (each sample according to a percent of thickeners). So we can say, these greases is best - in general - for lubricating plain and rolling bearing [2].

4.2.3. Vaporization Rate:

Resulting mixed grease samples were experimented in (25, 50, 90) °c for (22) hours, whole resulting mixed grease sample consequents are in table 4.

4.2.4. Corrosion of Cupper Strip:

The test of copper strip corrosion made it possible to evaluate the corrosively of greases with respect to copper parts or copper alloys [14, 15]. All of the greases pass this test and give the result 1b except greases (30% thickener -10%, 30% lithium soap) have result 2a.

Table 2. Dropping point for lubricating grease samples

Thickener %	20					25					30				
(Li) Soap %	90	70	50	30	10	90	70	50	30	10	90	70	50	30	10
(Na) Soap %	10	30	50	70	90	10	30	50	70	90	10	30	50	70	90
Dropping point °C	127	129	123	122	119	130	126	110	128	122	131	145	116	134	114

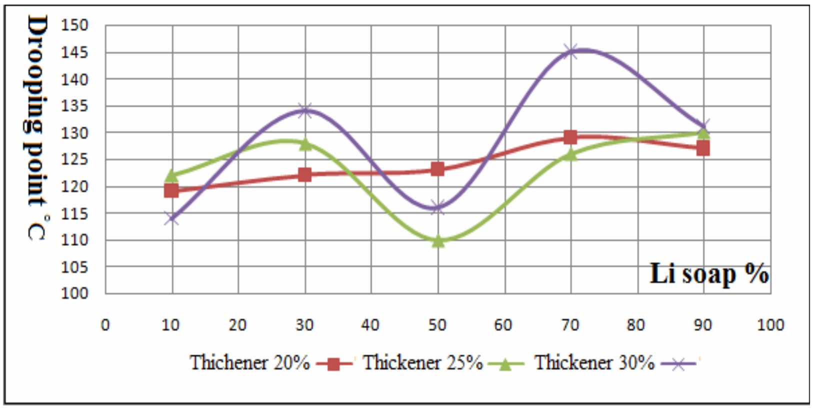

Figure 2. Dropping point for mixed lubricating grease

Table 3. Penetration number for resulting mixed greases

Thickener %	20					25					30				
(Li) Soap %	90	70	50	30	10	90	70	50	30	10	90	70	50	30	10
(Na) Soap %	10	30	50	70	90	10	30	50	70	90	10	30	50	70	90
Penetration (unworked)	250	262	269	278	289	225	233	240	246	252	230	222	227	233	238
Penetration (worked)	257	274	284	288	302	234	239	248	255	262	219	228	235	238	245

Table 4. Rate of greases Vaporization

Temperature (°C)	Vaporization rate (%)
25	0
50	< 0.55
90	1 - 1.5

4.2.5. Water Resistant:

We observed that the resulting greases are swelling that's because this grease absorbed small amount of water so we can say, this grease doesn't fit to use in wet places because of it can remind its mechanical properties, foul its structure and it possible to drift from lubricant fraction.

4.2.6. Total Acid Number (TAN):

When we do this test, we discern that all resulting greases have weak acid feature, and we registered this results in table 5.

Table 5. Values of Total Acid Number for Resulting Greases

Thickener %	20					25					30				
(Li) Soap %	90	70	50	30	10	90	70	50	30	10	90	70	50	30	10
(Na) Soap %	10	30	50	70	90	10	30	50	70	90	10	30	50	70	90
TAN (%)	0.32	0.31	0.20	0.25	0.25	0.26	0.31	0.29	0.20	0.22	0.21	0.25	0.21	0.28	0.19

4.3. Rheological properties:

4.3.1. Flow curves:

The flow curves, i.e. plots of shear stress versus shear rate for the lubricating greases have been measured over a temperature (15, 25, 30)°c and L/R = 64.

A typical result for the plots is shown in figure 3. It can be seen that the linearity of these line is good and they obey the power low at a certain range of shear rate.

$$\tau = k.\gamma^{n} \qquad (6)$$

Where k is consistency index and n is the non-newtonian index. n values were calculated from the slope of the fitted lines in figure 3 [13].

$$n = \frac{d\log\tau}{d\log\gamma} \qquad (7)$$

We can see that all the value of n were less than 1 ($n<1$), Indirectly suggested that lubricating greases were pseudo plastic [16].

4.3.2. Viscosity curves:

Fig. 4 shows plots of the viscosity versus shear rate at (15, 25, 30)°c and L/R=64. It could be noted from figure.4 that the apparent viscosity decreases with increasing shear stress, this behavior was attributed to alignment or arrangement of chain segments of the grease thickeners in the direction of applied shear stress [17].

4.3.3. Flow Activation Energy:

The effects of temperatures on flow behavior can be understood through the viscosity curves for the samples at different temperatures. Fig.5 shows the viscosity curves of the lubricating grease at three temperatures (15, 25, 30)°c.

Fig. 5 explains the relationship between apparent viscosity (η) and apparent shear rate (1/T) at a constant shear stress (τ). Flow activation energy can be calculated from the slope of lines in figure. 5 [18].

$$E_{\tau} = R\left[\frac{d\ln\eta}{d\frac{1}{T}}\right]_{\tau} \qquad (8)$$

The flow activation energy represents the effect of the temperature on the flow behavior of material. More (E) resulting more sensitivity of the materials viscosity to the temperatures. This behavior probably attributed that when the temperature is increased so the tendency of chains network to move is also increase, subsequently decreasing in resistance between grease layers and this refer to reduction in grease viscosity.

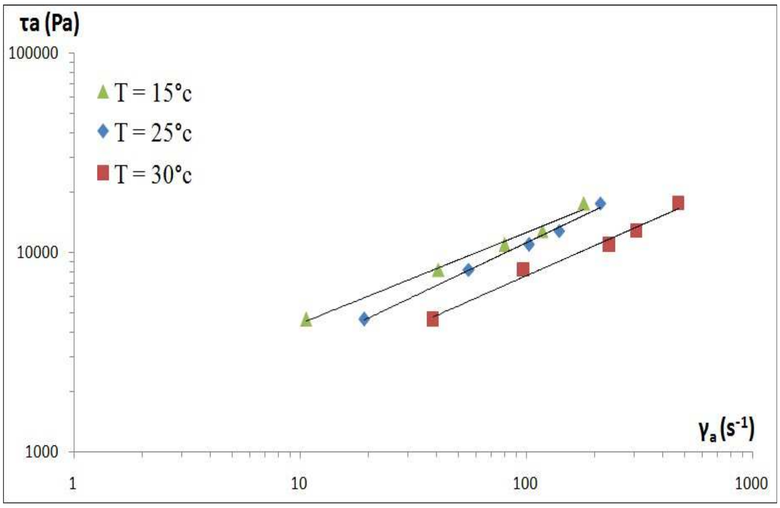

Figure 3. Flow curves of lubricating grease

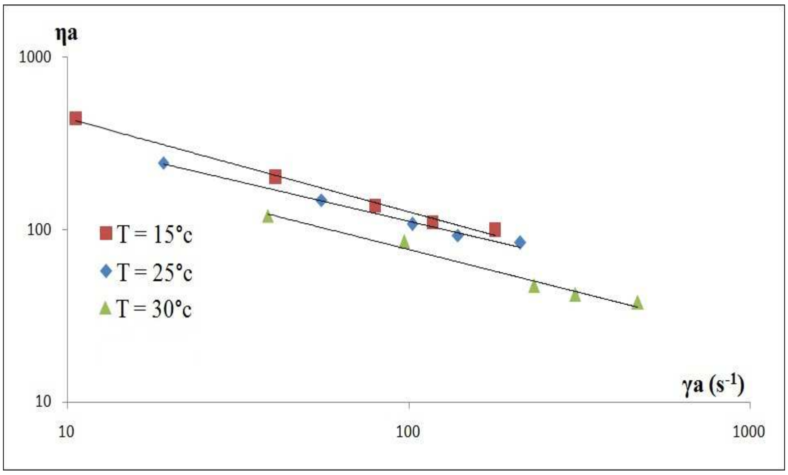

Figure 4. Viscosity curves of lubricant greases

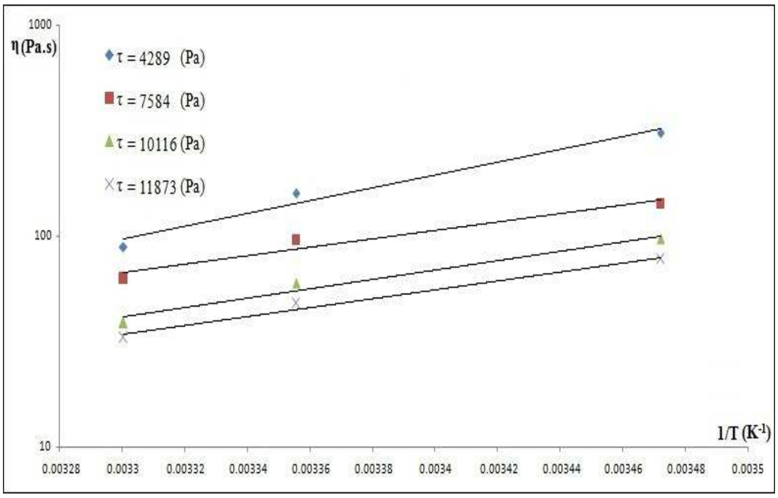

Figure 5. apparent viscosity versus 1/T

Table 6. Values Of n (Non-Newtonian Index)

Temperature (°c)	15	25	30
n	0.456	0.539	0.503

5. Conclusions:

1- Lubricating grease has been manufactured from Syrian base oil.

2- The greases which we made include mixed soap as thickener agent (Lithium and sodium soap) by different percentage.

3- The physical-Chemical characters for resulting greases have been studied, and we found that the highest dropping point we obtained is (145)°c for grease which include (30)% thickener agent [70% Lithium soap, 30% Sodium soap]. The resulting greases have relatively low acid number, middle resistant against water, and penetration number between (2) and (3) NLGI.

4- Prepared greases are useful in general for lubricating plain and rolling bearing.

5- The greases that we made are pseudo plastics in behavior.

6- The apparent viscosity of the grease that we test it, decrease with increasing apparent shear rate and shear stress and this result is characterize pseudo plastic materials.

7- The flow activation energy represented the effect of the temperature on the flow behavior of material and we observed that the viscosity decrease with increasing temperature.

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