# STUDY AND EVALUATION OF AROMATIC EXTRACTS AS FLUIDS FOR CALCIUM COMPLEX LUBRICATING GREASES

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## Abstract

Utility of aromatic extracts as fluid for preparation of calcium complex greases was investigated. The physicochemical properties of three grades of these extracts were initially studied. The rheological behavior (viscosity, shear stress and shear rate) of the individual aromatic extracts, and the obtained greases from those extracts at different temperatures were also illustrated. The rheological properties of both aromatic extracts and all lubricating greases were properly fit with the mathematical model of Herschel-Bulkley. Moreover, the flow behavior of the aromatic extracts as well as the corresponding lubricating greases was non-Newtonian. The study exhibited promising results concerning the thermal, mechanical and rheological properties for the prepared greases. Hence, in this work the by-product aromatic extracts act as a good alternative fluid for calcium complex lubricating greases.

**Keywords:** Aromatic extracts, Calcium complex greases, Rheological properties, Non Newtonian, Herschel-Bulkley

## Introduction

Greases are normally given the first consideration for application in ball and roller bearings in electric motors, automotive wheel bearings, and machine tools. They are also used for the lubrication of small gear drives and for many slow-speed sliding applications [(1)]. However, chemistry of lubricating grease is quite complex, it has already been provided in the NLGI Lubricating Grease Guide [(2)]. Basically, grease contains at least two components, base fluid and thickener agent. Typical multipurpose grease contains about 60-95% base fluid, 5-25% thickener and 0-10% other ingredients providing special properties [(3)]. Such ingredients are corrosion and rust inhibitors, antioxidants, colour stabilizers, viscosity improvers and wear preventers [(4, 5)]. The base fluids can be divided into two main groups; mineral oils and synthetic oils. Mineral oils are the employed fluids in the manufacture of the great bulk of lubricating greases due to their availability and low cost [(1)]. They consist of varying proportions of paraffinic, naphthenic and aromatic hydrocarbons. Thickener agents as the second most important component of grease are used to provide a suitable consistency to the finished product. Different soap types [1,6-8] are usually used as a common thickener for grease. Generally, soap structure consists of 12-hydroxystearic acids or stearic acid esters derived from vegetable or animal oils [9], and an alkali or alkaline earth metals [10]. Soaps not only present as crystallites and dissolved molecules, but also represent as agglomerates called fibrils or fibers in a separate phase. Commercial calcium complex greases which were first described in 1940 contain acetic acid as a complementary acid [11]. Such greases have good shear stability and water resistance, low oil separation, and good load-carrying capacity. Recently, the search for alternative sources of base stocks for lubricants has gathered momentum in recent years [12,13]. Aromatic extracts which are by-products in the refining of lubricating oil basestocks and waxes will be suggested as an alternative oily component in lubricating greases. This approach would appear to be of great economic and strategic standpoints. Accordingly, the current study is concerned with the determination of the properties of subjected aromatic extracts and their feasibilities for preparation of calcium complex lubricating greases.

## Experimental

### 1- Raw materials used for preparation of the calcium complex greases

**(a) Fluid part:** Three grades of aromatic extracts; light ($AE_1$), medium ($AE_2$) and heavy ($AE_3$) distillates according to the class of lubricating base stock refinery stream were used. These extracts were supplied by Suez Petroleum Company. The physicochemical characterization of these fluids was carried out according to ASTM and IP standard test methods. The average molecular weights of AE1, AE2 and AE3 were measured by gel permeation chromatography (Water 600E) equipped with Styagel column operated at 40ºC and flow rate of 0.4ml/min. The refractive index instrument model (Water 4110) was used as a detector and toluene (HPLC grade) as a mobile phase. **(b) Fatty material:** Soybean soap stock was provided by the Cairo Oil & Soap Co. **(c) Alkali:** Calcium hydroxide solution was used as a neutralizing agent for saponification of fatty compounds. **(d) Complexing agent**: Equimolar ratio of calcium acetate and benzoic acid.

### 2- Grease preparation and evaluation.

Seven types of calcium complex greases $G_1$, $G_2$, $G_3$, $G_4$, $G_5$, $G_6$ and $G_7$ were prepared according to a procedure described elsewhere[8, 11, 14]. Briefly, the procedure consists of two steps, saponification and cooling steps. The saponification step is based on mixing of soybean soapstock and 25% wt of aromatic extracts with alkaline slurry at the temperature range of 180 and190ºC. After the completion of the saponification reaction the reaction mixture is cooled while, adding the rest of the aromatic extract to attain the required grease consistency.

The consistency, dropping point tests, mechanical properties and the copper corrosion detection for the prepared greases were achieved according to the reference [(11)]. Rheological properties of both aromatic extracts and the prepared grease samples were determined at different temperatures using a programmable Brookfield rheometer model LV DV-III ULTRA (spindle SC4-18). The corresponding shear rate and shear stress were recorded every 2 minutes.

**Kinematic viscosity** was measured at 40ºC and 100ºC using capillary viscometers (ASTM D445).

## Results and discussion

The physicochemical properties of three grades of aromatic extracts [light ($AE_1$), medium ($AE_2$) and heavy ($AE_3$)] are listed in Table 1. The boiling point ranges of $AE_1$, $AE_2$ and $AE_3$ are 314-430 ºC, 334-454 ºC and 392-492 ºC, respectively. Moreover, they exhibit different values of specific gravity, sulfur percentage, pour point and viscosity. Such differences are attributed to their molecular structures and refining steps since their molecular weights are 798, 755 and 725 for $AE_3$, $AE_2$ and $AE_1$, respectively. As shown by the n-d-M results in Table 1, the average number of aromatic rings per molecule $R_A$ increases with increasing the boiling range and molecular weights of aromatic extracts. This may indicate that these grades contain mono-, di-, and polyaromatic compounds. Correlation of the average molecular weights, polydispersity and n-d-M results reveal the complex nature of the alkyl aromatic molecules. The carbon distribution and structural group analysis reveal that the three grades of aromatic extracts contain considerable portions of paraffinic side chains. The experimental data of the n-d-M method presented in Table 1, show also that the percentages of aromatic carbons are 22.9, 24.1 and 25.0 for $AE_1$, $AE_2$ and $AE_3$, respectively**.** Meanwhile, the paraffinic carbon portions (%Cp) of the molecules constitute higher percentages of 66.0 ($AE_3$), 64.2 ($AE_2$) and 61.0 ($AE_1$). The naphthenic carbon contents (%$C_N$) of the molecules are negligible.

**Table 1 : Physicochemical characteristics of the aromatic extracts**

| Characteristics | | Aromatic Extracts AE1 | AE2 | AE3 | ASTM |
|---|---|---|---|---|---|
| Density, g/ml at 15.6 °C | | 0.9543 | 0.9695 | 0.9697 | D.1298 |
| Sulfur, m%: X ray fluorescence | | 2.13 | 2.789 | 2.8515 | IP63/55 |
| Refractive index, $n_D^{20}$ | | 1.5408 | 1.5486 | 1.5512 | D.1218 |
| ASTM-Colour | | L5.0 | L5.0 | L5.0 | D.1500 |
| Kinematic viscosity, cSt | at 40°C | 22.077 | 51.696 | 148.543 | D.445 |
| | at 100°C | 3.380 | 5.137 | 11.404 | |
| Dynamic viscosity, cP | at 40°C | 126,9 | 213,6 | 542,4 | D.189 |
| | at 100°C | 34,2 | 88,4 | 163,7 | |
| Sp. Gr. @ 60/60 °F | | 0.940 | 0.944 | 0.963 | D.1298 |
| Pour point | | 15 | 21 | 42 | D.97 |
| Flash pt. PMC °C | | 180 | 194 | 215 | D.92 |
| TAN mg KOH/ gm | | 0.267 | 0.382 | 0.534 | D.664 |
| Molecular weight | | 725 | 755 | 798 | GPC |
| Polydispersity | | 1.265 | 1.427 | 1.648 | GPC |
| Hydrocarbon type analysis | | | | | D3238 |
| - % $C_A$ | | 22.9 | 24.1 | 25.0 | |
| - % $C_P$ | | 61.0 | 64.2 | 66.0 | |
| - % $C_N$ | | 6.70 | 7.50 | 8.60 | |
| Average no. of rings/ mol | | | | | |
| - $R_A$ | | 1.83 | 2.97 | 3.14 | |
| - $R_N$ | | 0.09 | 0.15 | 0.19 | |
| ASTM Dist. | | | | | D.1160 |
| - IBP °C | | 256 | 244 | 327 | |
| - 5.0%VOL@ °C | | 314 | 334 | 392 | |
| - 10% VOL@ °C | | 330 | 350 | 404 | |
| - 20% VOL@ °C | | 337 | 371 | 415 | |
| - 30% VOL@ °C | | 344 | 384 | 425 | |
| - 40% VOL@ °C | | 350 | 391 | 432 | |
| - 50% VOL@ °C | | 356 | 399 | 437 | |
| - 60% VOL@ °C | | 364 | 405 | 444 | |
| - 70% VOL@ °C | | 371 | 412 | 450 | |
| - 80% VOL@ °C | | 380 | 420 | 457 | |
| - 90% VOL@ °C | | 396 | 431 | 467 | |
| - 95% VOL@ °C | | 409 | 439 | 475 | |
| - FBP @ °C | | 430 | 454 | 492 | |

This difference in their constituents leads to the possibility of producing different grades of greases from aromatic extracts. However, many other factors must be taken into consideration to make sure that the aromatic extracts continue to lubricate properly over a long period. The most important of these factors are: the flow properties under shearing rates at different temperatures.

**Rheological properties of the aromatic extracts**

The rheological behaviour (viscosity, shear stress and shear rate) of $AE_1$, $AE_2$ and $AE_3$ has been determined at 40, 60, 80 and 100ºC. As can be shown in Figure 1, viscosity decreases with increasing shear rates. The decrease in viscosity is much more apparent at low shear rate, but at high shear rate, viscosity leveling off is observed. This shear-thinning behavior is commonly known as pseudo-plastic behavior [12]. It may be explained that the shear applied in aromatic extract compounds breaks down rapidly the internal structure within the bulk, and is temperature dependent. Also, the increase in temperature tends to increase molecular motion and consequently reduce attractive forces exhibited in solution. It is also observed that the flow behaviour of these aromatic extracts is non Newtonian. The rheological properties of these extracts are well fit with the mathematical model of Herschel-Bulkley [11, 15] (Table2). Results show that the corresponding shear stress of $AE_3$ is higher than both $AE_2$ and $AE_1$.

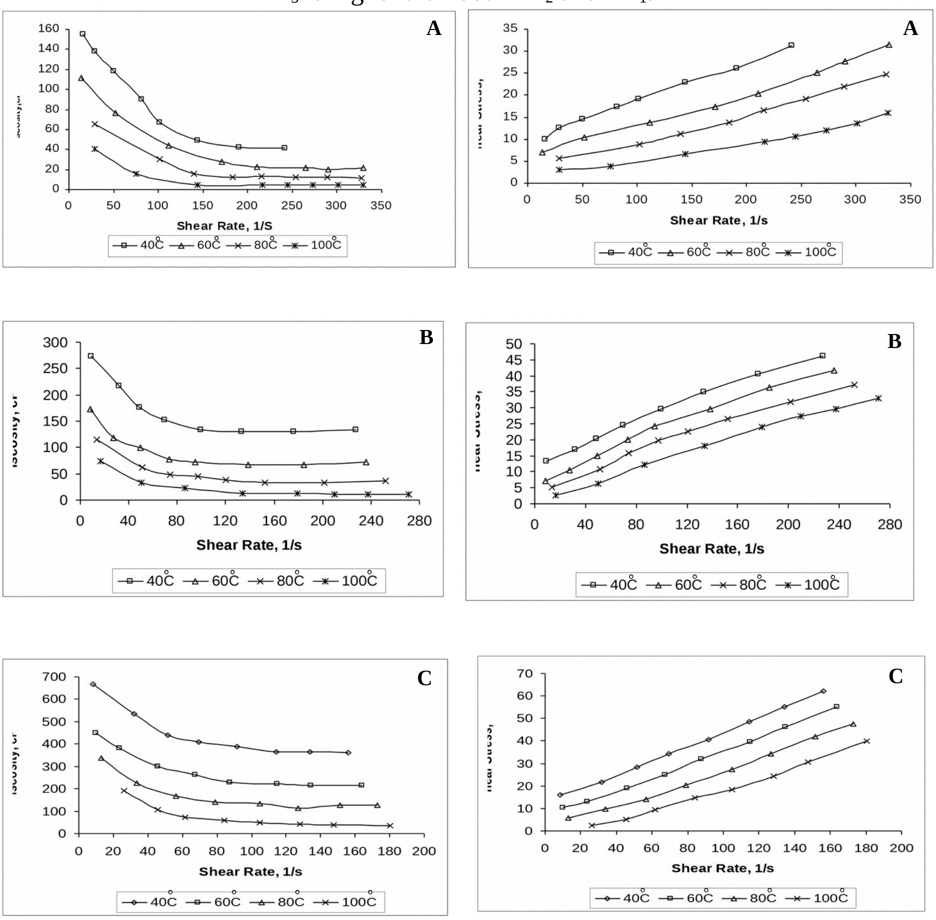


**Figure 1: Rheological behaviour for aromatic extracts at different temperatures; (A: $AE_1$; B: $AE_2$; and C: $AE_3$)**

**Table 2: Viscoelastic parameters for aromatic extracts using Herschel-Bulkley model**

| Property / Temp. | | 40ºC | 60ºC | 80ºC | 100ºC |
|---|---|---|---|---|---|
| **Consistency Index, cP** | **$AE_1$** | 19.8 | 13.33 | 5.15 | 0.40 |
| | **$AE_2$** | 136 | 75.3 | 43.0 | 1.30 |
| | **$AE_3$** | 730.4 | 210.3 | 129.8 | 11.34 |
| **Yield Stress, D/cm$^2$** | **$AE_1$** | 4.17 | 3.86 | 1.99 | 5.03 |
| | **$AE_2$** | 0.59 | 0.60 | 1.57 | 9.26 |
| | **$AE_3$** | 2.00 | 0.76 | 1.48 | 9.97 |
| **Flow Index** | **$AE_1$** | 1.01 | 1.16 | 1.05 | 1.43 |
| | **$AE_2$** | 0.92 | 0.81 | 0.84 | 1.30 |
| | **$AE_3$** | 1.02 | 0.91 | 0.82 | 1.47 |
| **Confidence of Fit, %** | **$AE_1$** | 99.9 | 100 | 100 | 99.6 |
| | **$AE_2$** | 100 | 99.9 | 99.6 | 99.3 |
| | **$AE_3$** | 100 | 100 | 99.7 | 99.8 |

### Evaluation of the prepared calcium complex greases from aromatic extracts

Seven samples of calcium complex greases were prepared as described in the experimental section. Three prepared samples based on individual aromatic extracts ($G_1$, $G_2$ and $G_3$) and the other four samples based on mixed aromatic extracts ($G_4$, $G_5$, $G_6$ and $G_7$) shown in Tables (3 and 4) respectively. Results show that properties (oil separation, oxidation stability, total acid number, apparent viscosity, mechanical properties and dropping point) of the blended calcium complex grease based on mixed aromatic extracts are more efficient than those obtained by individual ones. Particularly, the $G_6$ type which contains a mixture of 40% of each $AE_2$ and $AE_3$ is the better formulated calcium complex grease. This is certainly attributed to the type of aromatic extracts ($AE_2$ and $AE_3$) which have a great compatibility with soap texture resulting in improving the grease backbone as well as the thermal and mechanical stabilities.

**Table 3: Physicochemical properties of the prepared calcium complex greases based on the individual aromatic extracts**

| Property | | Grease Type G1 | G2 | G3 | Test Method |
|---|---|---|---|---|---|
| Grease Constituents, % | $AE_1$ | 80 | -- | -- | -- |
| | $AE_2$ | -- | 80 | -- | |
| | $AE_3$ | -- | -- | 80 | |
| | Soybean soap stock | 17-18 | 17-18 | 17-18 | |
| | Calcium hydroxide | 2-3 | 2-3 | 2-3 | |
| | Equimolar ratio: Benzoic acid/ Calcium acetate | 0.1-0.15 | 0.1-0.15 | 0.1-0.15 | |
| Penetration, mm x 10 | Un-worked | 277 | 275 | 272 | ASTM D 217 |
| | Worked, 60 strokes | 283 | 278 | 274 | |
| Dropping Point, °C | | 208 | 212 | 215 | ASTM D 566 |
| Copper Corrosion, 3h/100 °C | | Ia | Ia | Ia | ASTM D 4048 |
| Oxidation Stability @ 96h, pressure drop, psi | | 3.2 | 3.3 | 3.3 | ASTM D 942 |
| Intensity of (C=O) group @ 96h | | 1.81 | 1.83 | 1.83 | ASTM D 942 |
| Intensity of (OH) group @ 96h | | 1.43 | 1.44 | 1.44 | ASTM D 942 |
| Alkalinity, wt% | | 0.40 | 0.40 | 0.41 | ASTM D 664 |
| Total acid number, mg KOH/gm@96h | | 0.852 | 0.911 | 1.185 | ASTM D 664 |
| Oil Separation, wt% | | 2.3 | 2.1 | 1.9 | ASTM D 1724 |
| Grease Code according to: | NLGI | 2 | 2 | 2 | -- |
| | Egyptian standard | LB | LB | LB | |
| Apparent Viscosity, cP @ 90 °C | | 14755 | 17155 | 22001 | ASTM D 189 |

**Table 4: Physicochemical properties of the prepared calcium complex greases based on the mixed aromatic extracts**

| Property | | Grease Type $G_4$ | $G_5$ | $G_6$ | $G_7$ | Test Method |
|---|---|---|---|---|---|---|
| Grease Constituents % | $AE_1$ | 40 | 40 | -- | 30 | -- |
| | $AE_2$ | 40 | -- | 40 | 30 | |
| | $AE_3$ | -- | 40 | 40 | 20 | |
| | Soybean soap stock | 17-18 | 17-18 | 17-18 | 17-18 | |
| | Calcium hydroxide | 2-3 | 2-3 | 2-3 | 2-3 | |
| | Equimolar ratio: Benzoic acid/ Calcium acetate | 0.1-0.15 | 0.1-0.15 | 0.1-0.15 | 0.1-0.15 | |
| Penetration mm x 10 | Un-worked | 274 | 273 | 271 | 272.5 | ASTM D 217 |
| | Worked, 60 strokes | 277 | 276 | 272 | 275 | |
| Dropping Point, ºC | | 210 | 211 | 216 | 213 | ASTM D 566 |
| Copper Corrosion, 3h/100 ºC | | Ia | Ia | Ia | Ia | ASTM D 4048 |
| Oxidation Stability @ 96h, pressure drop, psi | | 3.4 | 3.4 | 3.5 | 3.3 | ASTM D 942 |
| Intensity of (C=O) group @ 96h | | 1.81 | 1.80 | 1.81 | 1.81 | ASTM D 942 |
| Intensity of (OH) group @ 96h | | 1.42 | 1.41 | 1.40 | 1.43 | ASTM D 942 |
| Alkalinity, wt% | | 0.41 | 0.40 | 0.42 | 0.41 | ASTM D 664 |
| Total acid number, mg KOH/gm @96h | | 0.942 | 0.984 | 1.14 | 1.06 | ASTM D 664 |
| Oil Separation, wt% | | 2.2 | 2.1 | 1.8 | 2.0 | ASTM D 1724 |
| Grease Code according to: | NLGI | 2 | 2 | 2 | 2 | -- |
| | Egyptian Standard | LB | LB | LB | LB | |
| Apparent Viscosity, cP @ 90 ºC | | 16631 | 20201 | 22555 | 21201 | ASTM D 189 |

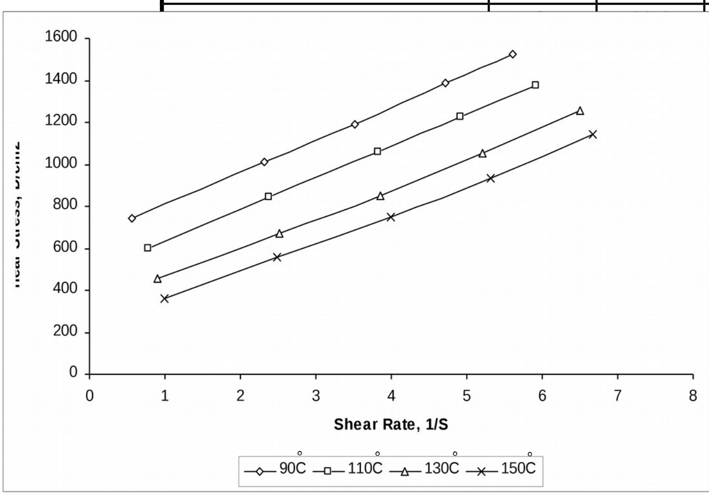
## Rheological properties of the prepared calcium complex greases

The rheological properties (viscosity, shear stress and shear rate) of the synthesized greases $G_1$, $G_2$, $G_3$, $G_4$, $G_5$, $G_6$ and $G_7$ are studied at 90, 110, 130 and 150ºC. A linear relationship between shear stress and shear rate for all samples at different temperatures is observed. Investigation of apparent viscosity-shear rate relationship at the same previous temperatures for all samples of greases displays two distinct flow regions. The first region at low shear rate from 0.5 to 2.0$s^{-1}$ reveals that the apparent viscosities decrease with increasing temperature. This indicates that the rheological flow (deformation) of the studied grease is temperature dependent. But the flow curves at high shear rates 2.5 to 7.0 $s^{-1}$ show steady portion in the second region. This implies that all grease samples exhibit independence of temperature after shear rate of 2.5$s^{-1}$. It can be also seen that the apparent viscosities of these greases decrease in the following order: $G_6 > G_3 > G_7 > G_2 > G_4 > G_1$ at all the investigated temperatures. Results of the dependence both shear stress and apparent viscosity on shear rate for ($G_6$) are shown in  shows Figure (2).

It has been found that the rheological properties of all lubricating greases correlate well with the mathematical model of Herschel-Bulkley(11, 15) (Table5). Results show that consistency index values obtained by Herschel-Bulkley decrease by increasing temperature while the reverse behavior is obtained in case of flow behaviour index. The sequence indicates that all grease samples under study exhibit non-Newtonian flows.

**Table 5: Viscoelastic parameters for prepared greases based on aromatic extracts at different temperatures using Herschel-Bulkley Model**

| Property \ Temp. | | 90ºC | 110ºC | 130ºC | 150ºC |
|---|---|---|---|---|---|
| **Consistency Index, cP** | **$G_1$** | 15798 | 11278 | 7865 | 3780 |
| | **$G_2$** | 19247 | 15357 | 9452 | 4351 |
| | **$G_3$** | 24371 | 18425 | 11298 | 6873 |
| | **$G_4$** | 17494 | 13854 | 7582 | 4128 |
| | **$G_5$** | 22683 | 14982 | 9674 | 6247 |
| | **$G_6$** | 24185 | 18795 | 11583 | 7186 |
| | **$G_7$** | 23726 | 15547 | 10864 | 6457 |
| **Yield Stress, D/cm²** | **$G_1$** | 84.5 | 54.2 | 39.7 | 26.4 |
| | **$G_2$** | 88.7 | 57.5 | 43.1 | 31.2 |
| | **$G_3$** | 92.6 | 61.8 | 46.5 | 37.8 |
| | **$G_4$** | 86.1 | 55.8 | 41.6 | 27.8 |
| | **$G_5$** | 87.2 | 56.6 | 44.2 | 29.6 |
| | **$G_6$** | 91.3 | 60.4 | 45.7 | 35.7 |
| | **$G_7$** | 90.7 | 58.8 | 44.9 | 36.2 |
| **Flow Index** | **$G_1$** | 0.47 | 0.61 | 0.77 | 0.91 |
| | **$G_2$** | 0.43 | 0.57 | 0.68 | 0.84 |
| | **$G_3$** | 0.38 | 0.51 | 0.64 | 0.72 |
| | **$G_4$** | 0.45 | 0.59 | 0.66 | 0.86 |
| | **$G_5$** | 0.42 | 0.56 | 0.65 | 0.83 |
| | **$G_6$** | 0.41 | 0.55 | 0.64 | 0.79 |
| | **$G_7$** | 0.44 | 0.57 | 0.67 | 0.81 |
| [illegible] | [illegible] | [illegible] | 100 | 100 | 100 |
| | [illegible] | [illegible] | 99.9 | 100 | 99.9 |
| | [illegible] | [illegible] | 99.7 | 99.8 | 99.8 |
| | [illegible] | [illegible] | 99.9 | 100 | 100 |
| | [illegible] | [illegible] | 99.9 | 100 | 100 |
| | [illegible] | [illegible] | 99.8 | 99.8 | 99.9 |
| | [illegible] | [illegible] | 99.9 | 99.9 | 100 |



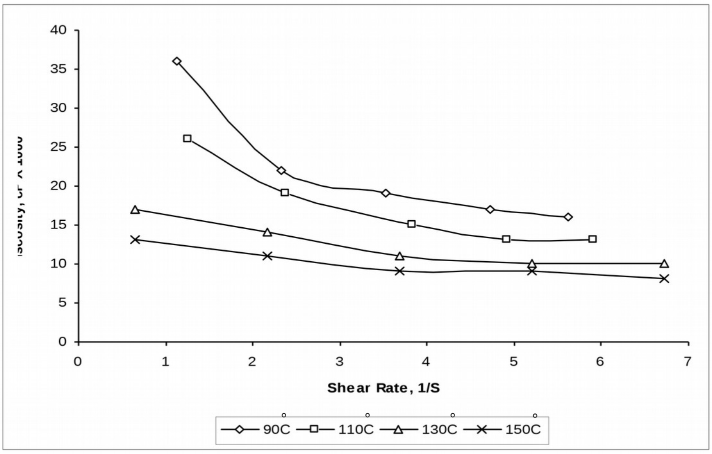



**Figure (2): Variation of shear stress and viscosity with shear rate for the calcium complex lubricating grease, $G_6$, at different temperatures**

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