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Preparation, characterization and evaluation of some metallic lube oil additives

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Abstract: *All mechanical equipment suffers from wear due to the time of use and exposure to contaminants that can damage its movable parts. One way to extend the life time of this equipment is through the use of suitable lubricating oil with different additives. Detergents, especially basic detergents, contain reserve base that will neutralize the acids to form salts. While this decreases the corrosive tendency of the acids formed at high temperatures. Dispersants also disperse sludge formed in engine operated at low temperature. In the present work, different metallic detergent/dispersant additives will be prepared via reaction of dodecyl phenol with calcium hydroxide in different ratios and different amounts of sulfur. The structures of the prepared compounds were confirmed by Fourier transform infrared spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (H^1-NMR) and molecular weight is determined. All the prepared compounds were found to be soluble in lubricating oil. The efficiency of the prepared compounds as antioxidant and detergent/dispersant additives for lubricating oil was investigated. It was found that the additives have excellent power of dispersion and detergency and the efficiency as antioxidant increases by increasing the sulfur content up to 1.5% and increases by increasing the percentage of metal in the additives.*

Key words*: Lubricating Oil Additives, Basic and Over basic Detergents/Dispersants, Calcium Phenate, Sulfonate and Salicylate, Acid neutralization, Reverse micelle.*

I. Introduction

Base stock oil properties are insufficient to meet the current demands of engine efficiency (low friction) durability, longer drain times and emissions regulations. Therefore, the lubricating oil must meet specific requirements. It must have an optimal balance of light and heavy oil components to lubricate at high temperature [1] it should not produce deposits (carbon soot and other) on moving parts. In addition, the oil should provide good protection of moving parts at high speed under deceleration of the engine [2]. Additives are therefore blended with base oils to perform two base functions. To minimize destructive processes and to confirm beneficial properties .Almost all lubricants contain additives to enhance their performance in amounts ranging between 5-25 % wt [3, 4].

Additives are synthetic chemicals used to improve different lube parameters: they can boost existing properties, eliminate adverse characteristics, or introduce new properties in the base oil [1]. Main functions of additives are: antioxidants, viscosity modifiers, pour point depressants, detergents, dispersants, antifoam agents, antiwears, friction modifiers, and antirust [5]. Various additives have been developed to control the acidity of the products of sulphurous combustion of dirty fuel and to prevent agglomeration of soot from combustion and wear particles. The agglomeration of particles can be very destructive to engines since it blocks the oil supply pipelines or even the filters. Additives which prevent the development of all these detrimental effects are known in the literature as either 'detergents' or 'dispersants'. The latter term, however, is more accurate. The primary functions of these additives are:

. to neutralize any acids formed during the burning of fuel,
. to prevent lacquer and varnish formation on the operating parts of the engine,
. to prevent the agglomeration of particles and carbon deposits which may impede the oil ways.

There are two types of detergent/dispersant additives (d/d additives): mild d/d additives and over-based or alkaline d/d additives. Mild d/d additives are often composed of simple hydrocarbons or ashless compounds (i.e., when the compound is burnt no oxides are left, since organic compounds burn to CO_2 and water). The function of these additives is to disperse soot (carbon) and wear particles. Over-based d/d additives are calcium, barium or zinc salts of sulphonic, phenol or salicylic acids. Over-based means that an excess of alkali is used in the preparation of these additives.

Detergents and dispersants constitute 2–15% of the additives [6]. These compounds keep oil-insoluble combustion byproducts in suspension and prevent the agglomeration of the oxidation products into solid particles. Commonly, these chemicals are metal-containing compounds with a large oleophilic hydrocarbon portion and a polar hydrophilic region. Polar group can link lube contaminants, while the tail section act as a solubilizer in the base oil.

The surfactants used to prepare overbased detergents have an amphiphilic structure. The polar headgroup, which typically binds to a calcium, magnesium or sodium metal cation, may be a benzene sulfonate, phenate, salicylate or phosphonate [7]. The surfactants act as a dispersed agent, while the metal carbonate acts as a neutralizing agent, and the diluent oil acts as a compatible agent. The term [8-10] “over based” demonstrates that the quantity of colloidal metal carbonate in the particle cores is greater than that is needed to neutralize the surfactant acid, otherwise it is described as “neutral” or “low basicity”, indicating that the over based detergents have a greater acid neutralizing capacity than their neutral salts. In the present work, different metallic detergent/dispersant additives will be prepared via reaction of dodecyl phenol with calcium hydroxide in different ratios. The structures of the prepared compounds were proved using Fourier transform infrared spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (H^1-NMR) and molecular weight is determined. The efficiency of the prepared compounds as antioxidant & detergent/dispersant additives for lubricating oil was investigated.

II. Experimental

2.1. Sulfurization and neutralization of dodecyl phenol:

0.1 mole of dodecyl phenol and 0.05 mole of calcium hydroxide with variable amounts of sulfur (0, 0.025, 0.05, 0.1, 0.15, and 0.2) mole were mixed in three necks round bottom flask equipped with a mechanical stirrer, reflux condenser and thermometer. The reaction mixture was maintained at temperature 130°C. Then the temperature was raised gradually to 160°C for 2 hours. And it was raised gradually to 190°C for 2 hours. (33% of the reactant volume) of white oil are added. Then we obtained the products (A, B, C, D, E and F).

2.2. Basing and overbasing process:

Sulfurized calcium salt of dodecyl phenol (E) was mixed with 30 gm. of toluene and 9.8 gm. of methanol then the excess of calcium hydroxide was added by a percent of 1mole of calcium phenate to 1 mole of calcium hydroxide (basic salt (E_2)) and 1 mole of calcium phenate to 2.5 mole of calcium hydroxide (over basic salt (E_3)). The mixture was stirred in a three neck flask, CO_2 was inserted with a rate of 50 ml/min. for half an hour. Then 10 gm. of white oil was added as a diluent. Solvent was removed using rotary evaporator at 90°C. Therefore we have two different products, the designation of the prepared compounds are shown in Table (1).

Table (1): The designation of prepared compounds.

Abbreviation	Prepared Compounds
A	Neutral non sulfurized calcium dodecyl phenate (%S=0)
B	Neutral sulfurized calcium dodecyl phenate (%S=0.25)
C	Neutral sulfurized calcium dodecyl phenate (%S=0.5)
D	Neutral sulfurized calcium dodecyl phenate (%S=1)
E	Neutral sulfurized calcium dodecyl phenate (%S=1.5)
F	Neutral sulfurized calcium dodecyl phenate (%S=2)
E_2	Basic sulfurized calcium dodecyl phenate (%S=1.5)
E_3	Over basic sulfurized calcium dodecyl phenate (%S=1.5)

2.3. Characterization of the prepared compounds:

2.3.1. Infrared Spectroscopic Analysis:

The prepared compounds were characterized by using F.T.I.R. Spectrometer Model Type Mattson-Infinity Series Bench top, which made in USA.

2.3.2. Determination of Molecular Weights:

The molecular weights of different prepared compounds were determined by physical method known as “cryscopic method”, it is based on the principle that the freezing point of pure solvent such as benzene changes on contamination with any foreign material for example: crude oil sample.

The average molecular weight is measured according to the following equation:

$$M.wt = \frac{const.\ K}{\Delta T} * \frac{wt.\ of\ crude\ oil\ (g.)}{wt.\ of\ solvent\ (g.)} * 1000$$

Where: ΔT is the decrease in the freezing point.

K is a constant depending on the type of solvent.

e.g K for benzene = 5.12

2.3.3. Proton Magnetic Resonance Analysis:

The prepared compounds were characterized by ^{1}H-N.M.R. spectroscopy. Using ^{1}H-N.M.R. type [300 M.Hs. spectrophotometer W-P-300, Bruker].

2.4. Evaluation of the Prepared Compounds as Lube Oil additives:

2.4.1. As Antioxidants.

The lube oil samples as well as its blends with 2% by weight of each of the prepared additives were subjected to sever oxidation condition in the presence of copper and iron strips at 165.5°C for 72 hrs using the Indiana test method of oxidation [11]. The oxidation stability of the lube oil blends were determined by taking samples at 24 hrs, intervals to 72 hrs. These samples were tested for:

1- Variation of viscosity ratio V/V_o.

The variation of viscosity ratio (V/Vo) has been determined using IP 48/86 method, where:

V = Kinematic viscosity at 40 °C of sample after oxidation.

Vo = Kinematic viscosity at 40 °C of sample before oxidation.

2- Change in total acid number (ΔT.A.N.).

The change has been calculated according to IP 177/83 method, where.

ΔT.A.N. = (total acid number of sample after oxidation – total acid number of sample before oxidation).

3- Optical density using infrared techniques.

The infrared spectra of oxidized oils have been determined in the range of the carbonyl group absorbance (1500-1900 Cm^{-1}). The spectra have been superimposed upon that of unoxidized oil. The absorbance (A) has been calculated according to

$A = \log I / I_o$

Where: I is % transmittance of the oil after oxidation and I_o is the transmittance of the oil before oxidation.

2.4.2. As Detergents / Dispersants.

1. Spot method

Drops were taken from the samples being oxidized in the Indiana test after 24 hrs. intervals of oxidation and up to 72 hrs. to make spots on special filter paper (Durieux 122) and the dispersancy of the samples were measure as follows [11, 12] :

$$\% \text{ Dispersancy} = \frac{\text{Diameter of the black spot}}{\text{Diameter of the total spot}} \times 100$$

The efficiency of dispersants has been classified as follows:

- Up to 30% : no dispersancy.
- 30-50 % : medium dispersancy.
- 50-60 % : good dispersancy.
- 60-70 % : very good dispersancy.
- Above 70% : excellent dispersancy.

2. Determination of potential detergent / dispersant efficiency (PDDE):

Two factors are necessary to determine PDDE.

a) Detergent index :-

This method based on centrifugation. A suspension was prepared from the base oil containing 1.5% additive and 2% carbon black. This suspension was shared by ultrasonic equipment. Afterwards, the blend was diluted with kerosene and the mixture was centrifuged for 30 min. The blend was examined in photometrical equipment at 530 nm. Detergent index (DI) determined on the basis of the intensity of transmitted light:

$$DI = (I_1 / I_0) \times 100$$

Where: I_1 is the intensity of the light after transmission through the blend containing carbon black; I_0 is the intensity of the light transmitted through the blend free of carbon black.

b) Washing efficiency :-

The washing efficiency (WE) was measured by Zaslavskii's modified method based on thin layer chromatography. The efficiency was evaluated within 0 –125mm. The results of numerous potential experiments attested that these two methods were suitable to estimate the potential of detergent/dispersant efficiency (PDDE) in oil solutions:

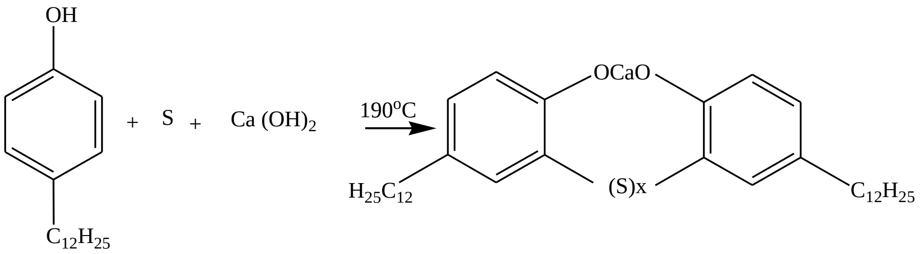
$$PDDE = \frac{DI + WE}{225} \times 100,$$

Where DI is the detergent index (%), WE is the washing efficiency (mm), 225 is the maximum value of DI +WE (DI max = 100, WE max = 125) [13].

III. Results and Discussion

3.1. Sulfurization & neutralization of dodecyl phenol:

Dodecyl phenol reacts with calcium hydroxide and different ratio of sulfur to give neutral sulfurized calcium salt of dodecyl phenol (A, B, C, D, E and F). Sulfurization and neutralization of dodecyl phenol illustrated in scheme (1) as follows:



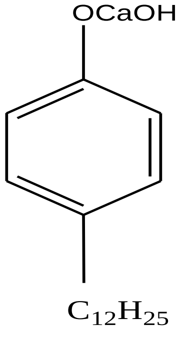
Where X is a variable (0, 0.025, 0.05, 0.1, 0.15, and 0.2) mole

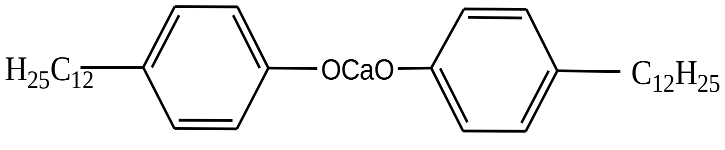
Scheme (1): Reaction of formation of neutral sulfurized calcium phenate.

Table (2): The physico-chemical characteristics of the prepared compounds.

Characteristics	A	B	C	D	E	F
Mean M.wt	420	433.68	494.62	911	638.89	710
Theoretical M.wt	562	592	632	672	712	744
T.B.N	35.5	37.7	40.75	47	55	57.6
Calcium wt%	2.98	3.12	3.14	5.22	4.05	2.96
Sulfur wt%	0	1.685	2.728	4.122	5.586	6.203
Carbon wt%	77.069	76.8	77.44	73.96	75.23	74.34
Hydrogen wt%	8	8.02	7.9	7.98	6.73	7
Oxygen wt%	14.931	11.095	8.792	8.718	8.404	9.497

From the results of molecular weight, it is clear that the experimental results differ from the theoretical results, which may be due to formation of compounds as bi-products other than the expected compounds. The general formulas of these compounds are:





And the general formulas of the prepared additives are shown in Table (3)

Table (3): The general formula of the additives prepared

Sample	experimental formula
A	$C_{26.96}H_{33.6}O_{3.9}Ca_{0.31}$
B	$C_{27.76}H_{34.78}S_{0.23}O_{10}Ca_{0.34}$
C	$C_{31.9}H_{39.07}S_{0.42}O_{2.7}Ca_{0.39}$
D	$C_{58.79}H_{72.69}S_{1.17}O_{4.96}Ca_{1.19}$

E	$C_{40}H_{43}S_{1.113}O_{3.74}Ca_{0.7}$
F	$C_{43.98}H_{49.7}S_{1.37}O_{4.189}Ca_{0.52}$

The infrared spectrum of product (C) is shown in Fig (1), which illustrate the following:

1) Disappearance of OH group band (at 3300 Cm^{-1}) in the prepared compound (C).
2) Appearance of C-S peak at 700 Cm^{-1} in the prepared compound (C).
3) Appearance of S-S peak at 550 Cm^{-1} in the prepared compound (C).

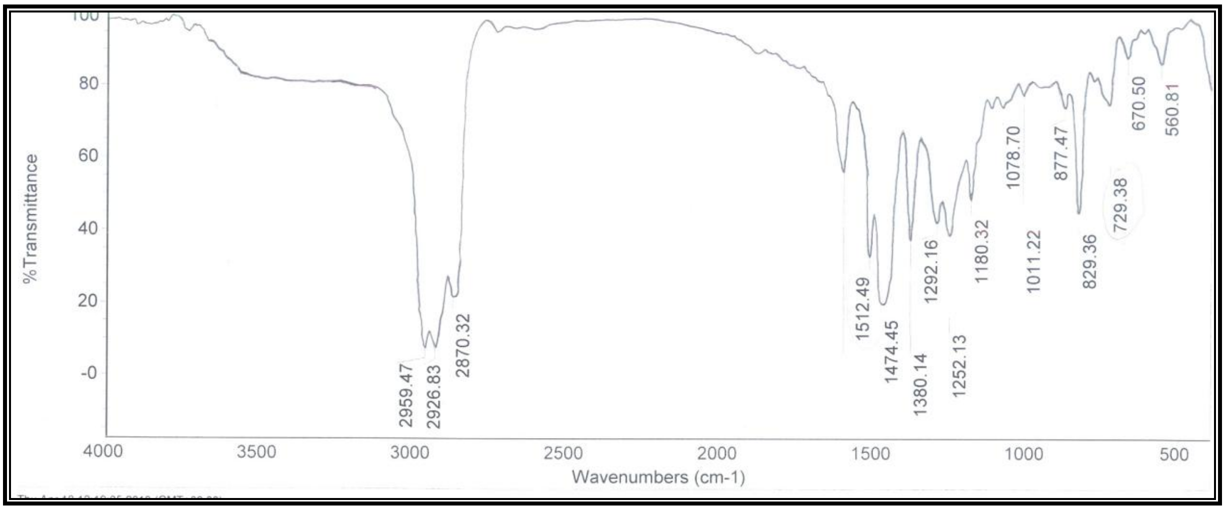


Figure (1): Infrared spectrum of compound (C)

The H^{1}NMR spectra of compounds (E, E_2 and E_3) are shown in Figs. (2-4), which illustrate the following:

1. A peak appears at 8-9 nm in case of compound (E), which indicates the presence of phenolic OH. This peak disappears in case of compound (E_2) and (E_3), this may be due to the presence of percentage of unreacted dodecyl phenol in the preparation of the neutral compound.
2. A peak appears at 0-2 nm in case of three compounds (E, E_2 and E_3) which indicates the presence of alkyl hydrogen.
3. A peak appears at 6-8 nm in case of three compounds (E, E_2 and E_3) which indicates the presence of benzene ring.
4. A peak appears at 3-4 nm in case of three compounds (E, E_2 and E_3) which indicates the presence of Ar-CH group.

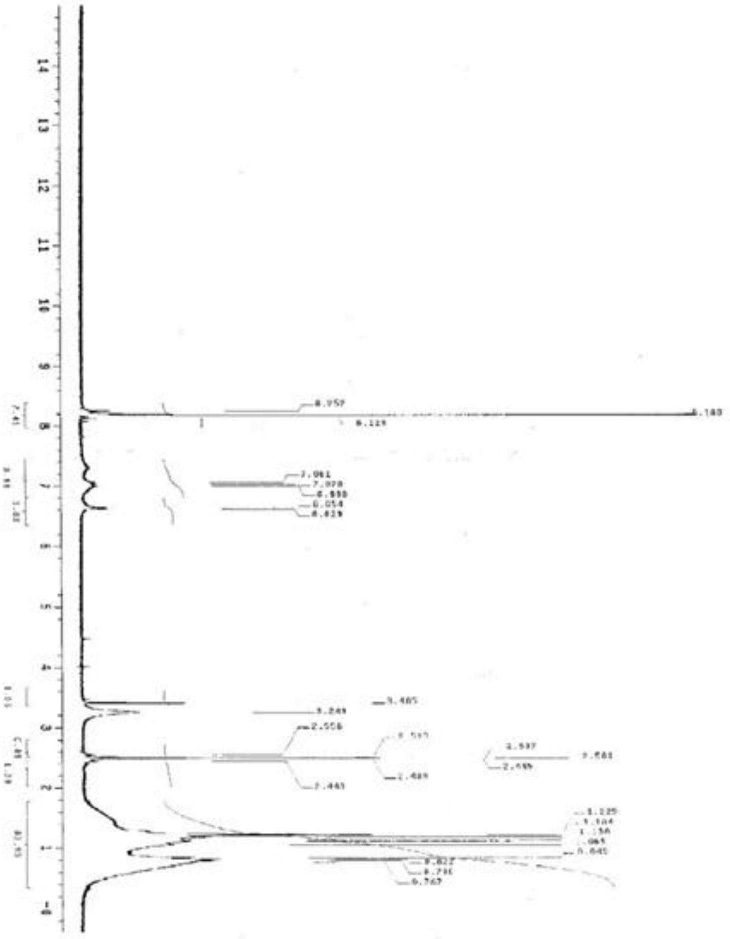


Figure (2): The HINMR spectrum of compound (E)

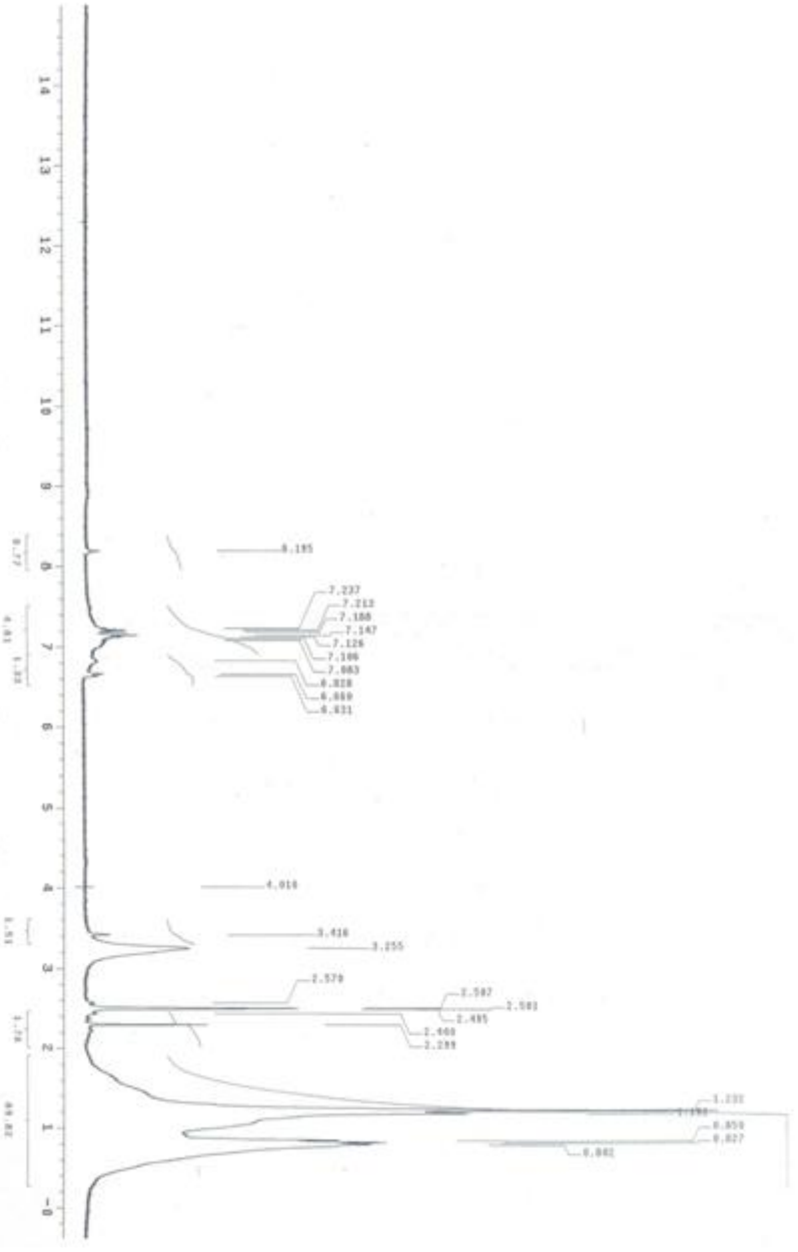


Figure (3): The HINMR spectrum of compound (E₂)

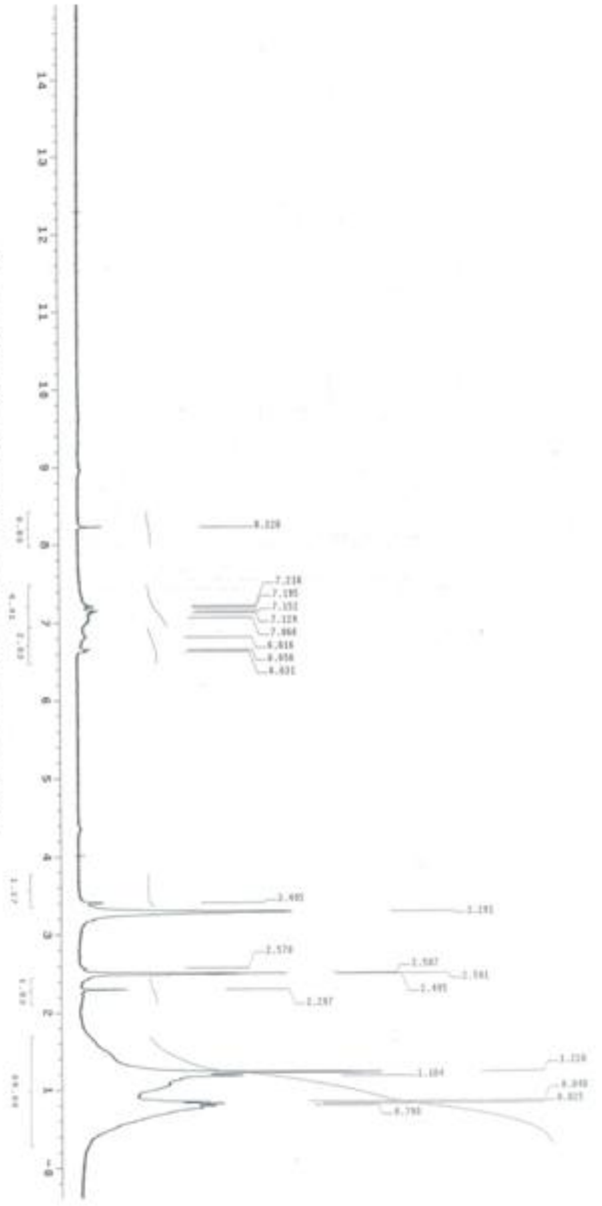


Figure (4): The H1NMR spectrum of compound (E_3)

3.2. Evaluation of the Prepared Compounds as lubricating oil additives:

3.2.1. As Antioxidants.

All the prepared compounds were added to a sample of lube oil "SAE-30" free from any additives, in 2% concentration, and the blends obtained were subjected to serve oxidation condition as described previously and the oxidation stability expressed as increase in viscosity ratio (V/Vo) and total acid number (T.A.N.), and optical density (Log I/Io) that compared with lube oil sample free from additives, the results are shown in Figs. (5-7).

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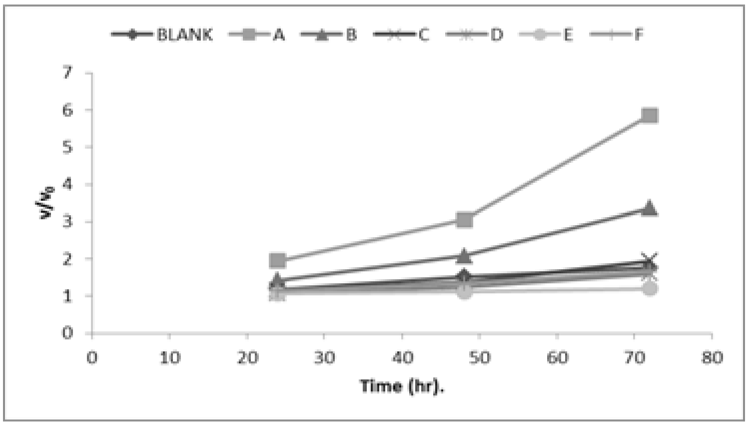

Figure (5): Variation of V/Vo with oxidation time of lube oil without and with additives (A, B, C, D, E and F).

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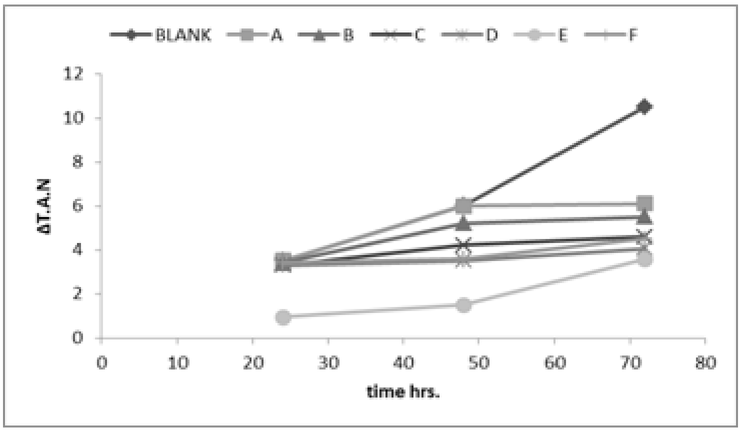

Figure (6): Variation of ΔT.A.N. with oxidation time of lube oil without and with additives (A, B, C, D, E and F).

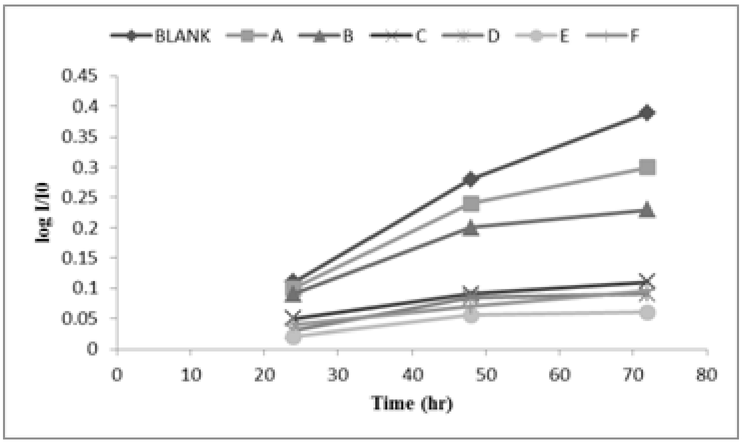

Figure (7): Variation of Log I/Io with oxidation time of lube oil without and with additives (A, B, C, D, E and F).

Inspection of the results obtained in Figs. (5-7) indicate that:

The oxidation stability of the additives prepared increases with the increase of their sulfur content up to 1.5% sulfur & then decreases again. It is clear from Figs. (5-7) that additive (E) which has been prepared using a molar ratio of sulfur to phenol 1.5: 1 is the best one in this respect. Introducing sulfur in the structure of the phenates leads to increasing in their antioxidant properties and this may be attributed to the fact that they inhibit oxidation by reduction of peroxides beside the inhibition through chain breaking resulting from the reaction. The reaction of sulphurized phenates prevent oxidation through two mechanisms: chain breaking and peroxide decomposition, while non sulphurized metal phenate act only as chain breaking agents.

Effect of using different ratios of calcium hydroxide.

The previous results show that compound (E) gives better results so we prepared the basic and over basic (E_2, E_3) of the same compound. The T.B.N. of the prepared compounds are shown in Table (4)

Table (4): T.B.N. of the prepared compounds

Compound	T.B.N.
E	55
E2	102.2
E3	277.9

The results of additives with different calcium hydroxide ratios are given in Figs. (8-10), it was found that the additives prepared with higher calcium hydroxide ratio (overbasic (E_3)) are more efficient as antioxidant than other prepared additives this may be due to the presence of alkaline calcium carbonate which can neutralize acidic compounds formed during oxidation of lube oil. Increasing the proportions of metal in the phenate, increase their antioxidant properties and this may be attributed to the fact that excess base in the additives can neutralize the excess of acids formed during oxidation of lubricating oil.

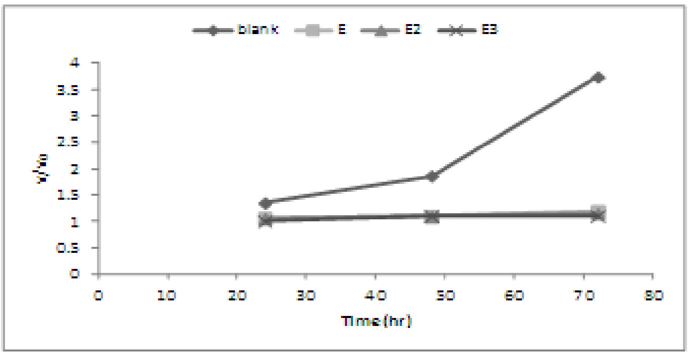

Figure (8): Variation of V/Vo with oxidation time of lube oil with additives of sulfur ratio = 1.5% with different basicity (E=neutral, E_2=basic and E_3=overbasic).

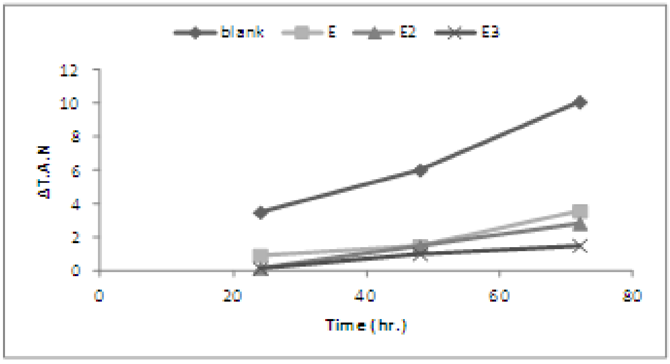

Figure (9): Variation of T.A.N. with oxidation time of lube oil with additives of sulfur ratio = 1.5% with different basicity (E=neutral, E2=basic and E3=overbasic

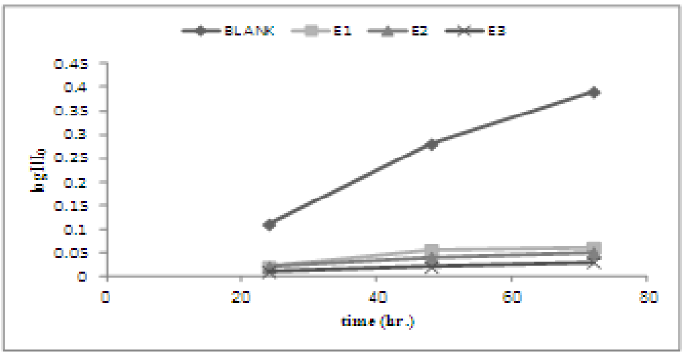

Figure (10): Variation of Log I/Io with oxidation time of lube oil with additives of sulfur ratio = 1.5% with different basicity (E=neutral, E_2=basic and E_3=overbasic).

3.2.2. As Detergents/Dispersants.

All the prepared compounds have been added to the oil samples in concentration of 2% wt, using spot test method results given in Table (8) show clearly that the prepared compounds have very good and excellent dispersion power (61-97%) for sludge and solid particles formed during lube oil oxidation compared with lube oil free from additives [14]. It is clear that the oxidation of these compounds disperses solid particles in the oil thus prevent their agglomeration and participation on metallic parts of engines.

Table (5): Percentage of dispersion (spot test method) of the lube oil sample and it is blends with additives after different oxidation time (hrs.).

sample	**Percentage of dispersion, time hrs.**		
	24 hrs.	48 hrs.	72 hrs.
blank	35	33	32
A	80	83	85.06
B	70	91.35	90.24
C	90.38	94	93.88
D	80.77	84.31	95.56
E	90.2	95	97.06
F	88.46	88.89	90.74
E_2	91.49	89.36	86.67
E_3	89.58	89.8	88.24

The results of numerous experiments attested that these two methods were suitable to estimate the potential detergent/dispersant efficiency (PDDE %) in oil solutions:

$$\mathrm{PDDE} = \frac{\mathrm{DI} + \mathrm{WE}}{225} \times 100,$$

Where DI is the detergent index (%), WE is the washing efficiency (mm), 225 is the maximum value of DI +WE (DI max = 100, WE max = 125)

The results are shown in Table (6).

Table (6) Percentage of potential detergent/dispersant efficiency (PDDE) of the prepared compounds

Sample	**PDDE %**
A	53.78
B	80.64
C	81.8
D	85.56
E	87.94
F	77.8
E_2	88
E_3	91.11

It seems that all results give very good and excellent behavior according to potential detergent / dispersant efficiency.

IV. Conclusion

The conclusions could be derived from the results of this study that:

- Preparation of neutral calcium phenates and their corresponding basic and superbasic additives.
- All the prepared compounds are good soluble in lubricating oil (SAE 30).
- The structures of the prepared compounds were confirmed by (F.T.I.R), (G.P.C) and (^{1}H-N.M.R).
- The efficiency of the prepared compounds as lube oil additives (antioxidants and detergents/dispersants) was studied. It was found that all the prepared additives have excellent power of dispersion and detergency.
- It was found that the efficiency of the prepared compounds as antioxidants increases with increasing its basicity

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