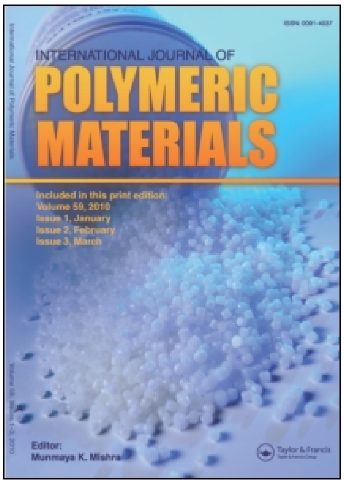

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Nehal Sabry Ahmed[a]
[a] Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

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Preparation and Evaluation of Some Lube Oil Additives Based on Polyethylene Glycol

Nehal Sabry Ahmed
Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City, Cairo, Egypt

Among the various additives employed in modern engine oils, one of the most important is the type that acts to prevent an accumulation of sludge in the crankcase and on the cylinder walls, thereby preventing sticking of piston rings and the formation of varnish-like coatings on the pistons and cylinder walls. Because of their general function of maintaining a clean engine, additives of this nature are termed detergents although it is now understood that they have little utility in cleaning a dirty engine, but by virtue of dispersing activity, prevent engine fouling. A main source of deposits is the oxidation of oil in high temperature, which can be reduced by using antioxidants. This work was limited to the preparation and characterization of different types of polyethylene glycol palmitate with different molecular weights and amination of the prepared esters with tetraethylenepentamine. The efficiency of the prepared compounds as detergents/dispersants and antioxidants was investigated and the effect of the prepared additives on other properties of lube oil was also studied. It was found that all the prepared compounds act as detergents/dispersants and antioxidant additives with no effect on the viscosity index and pour point of the lube oil.

Keywords: antioxidants, detergents/dispersants, lube oil additives

INTRODUCTION

A lubricant must provide the following basic functions: Act as a coolant by heat removal, and provide a film between moving parts to minimize friction leading to wear [1].

Incorporation of detergent and dispersant additives into a lubricant is essential to prevent harmful carbon and sludge deposits [2–6].

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Address correspondence to Nehal Sabry Ahmed, Department of Petroleum Applications, Egyptian Petroleum Research Institute, Nasr City 11727, Cairo, Egypt. E-mail: mynehal@yahoo.com

Deposits in critical areas of the engine lead to engine shut-down and repair. In addition, the basic functions of a lubricant are related to proper oil flow properties, which detergent and dispersant additives help to maintain by: (1) Minimizing oil thickening, thereby maintaining viscosity stability and flow properties and (2) Containment of carbon sludge deposits that clog oil lines resulting in lack of oil flow and subsequent engine failure. Detergents may also provide rust protection to engine parts. Dispersants began to play a major role in passenger car engine oils in the 1950s. Detergents/dispersants have a direct effect on minimizing harmful engine exhaust emissions, increasing engine life, and controlling oil consumption by maintaining clean engine operation [7–9]. Detergents are normally utilized to minimize high-temperature engine varnish and lacquer deposits whereas dispersants are used to control low-temperature engine sludge deposits [10–11]. Both are long chain hydrocarbons with polar ends. Detergents have a polar end containing a metal ion. Dispersants utilize oxygen and/or nitrogen for polarity and do not contain metal ions. In engine oils, the harmful products of combustion and other contaminants are rendered harmless by the polar ends. The hydrocarbon chain of these additives helps to solubilize or suspend the debris in the oil. Detergents and dispersants are used in a wide variety of automotive and industrial lubricants. Their major applications are in engine oils. Other applications include transmission fluids, gear lubricants, and tractor hydraulic/transmission oils. Detergents provide cleaning action in engine oils by neutralizing acids that arise from fuel combustion products. When oil is heated in the presence of air, oxidation occurs. As a result of this oxidation both the oil viscosity and the concentration of organic acids in the oil increase and varnish and lacquer deposits may form on hot metal surfaces exposed to the oil. In extreme cases, these deposits may be further oxidized to form hard, carbonaceous materials [12]. Although the complete mechanism of oil oxidation is not well defined, it is generally recognized as proceeding by free radical chain reaction [13]. Reaction chain initiators are formed first from unstable oil molecules, and these react with oxygen to form peroxy radicals, which in turn attack the unoxidized oil to form new initiators and hydroperoxides. The hydroperoxides are unstable and divide, forming new initiators to continue the reaction. Any materials that will interrupt this chain reaction will inhibit oxidation [14]. Two general types of oxidation inhibitor are used, those that react with the initiators, peroxy radicals, and hydroperoxides to form inactive compounds, and those that decompose these materials to form less reactive compounds [15]. The present work deals with the esterification reaction of palmitic acid with different types of polyethylene glycol (200, 400, 600, and 1000) to produce four types of ester (A, B, C, and D) and reaction of the prepared esters with tetraethylene pentamine. The prepared compounds are used as antioxidants and detergents/dispersants additives for lube oil.

EXPERIMENTAL

Esterification of Palmitic Acid

The esters of palmitic acid were prepared by reacting 1 mole of palmitic acid with 1 mole of different types of polyethylene glycol (200, 400, 600, and 1000). The reaction was carried out in a resin kettle in presence of 1% p-toluene sulfonic acid as a catalyst. The esterification reaction was carried out under a slow stream of deoxygenated nitrogen, the reactants were agitated using mechanical stirrer at 500 rpm. The reactants, which were mixed with an equal weight of xylene, were heated gradually from room temperature to 130°C using a well controlled thermostate to give products (A, B, C, and D) polyethylene glycol palmitate with different molecular weights.

Reaction of the Prepared Esters with Tetraethylene Pentamine

In a four-necked round bottom flask fitted with a mechanical stirrer and a thermometer 1 mole of tetraethylene pentamine dissolved in equal volume of toluene had been charged. An equivalent amount of ester (A) it was added to the amine over about $1\frac{1}{2}$ h with continuous stirring. The reaction mixture was gradually heated to about 120°C during about 2 h, under good stirring condition to get rid of the water of the reaction and solvent. Thus, tetraethylene pentamine of polyethylene glycol palmitate (A_1) was prepared. The same technique was used with different esters (B, C, and D) to prepare different types of amines (B_1, C_1, and D_1), respectively.

Dissolution of the Additives

The prepared compounds were dissolved in free additive base oil (SAE 30) to prepare the solutions for evaluation. In conical flask, the desired weight of the prepared compounds was added to 100 g base oil, then the mixture was allowed to stand overnight. This time was enough to cause the required swelling of the compounds. The conical flask was then immersed in an oil bath placed on a thermostated hot plate fixed over magnetic stirrer. The temperature of the oil bath was raised to 60°C and the mixture was vigorously stirred for 20 min.

Determination of the Molecular Weights

The molecular weights of the prepared compounds were determined by using Gel Permeation Chromatography (GPC), Waters 600E.

I.R. Spectroscopic Analysis

I.R. spectra of the synthesized esters were determined by using a F.T.I.R. Mattson spectrometer Infinity series Bench top 961.

Evaluation of the Prepared Compounds as Lube Oil Additives

As Antioxidants

The lube oil sample as well as its blends with 2% by weight of each of the prepared additives (A_1, B_1, C_1, and D_1) were subjected to severe oxidation condition in the presence of copper and iron strips at 165.5°C for 72 h using the Indiana test method of oxidation [16]. The oxidation stabilities of the lube oil blends were determined by taking samples at 24 h intervals up to 72 h. These samples were tested for: (1) Viscosity at 40°C, according to IP method [17] and (2) Total acid number, according to IP method [18].

Change in Total Acid Number (Δ T.A.N.). This method describes procedures for the determination of acidic or basic constituents in petroleum products and lubricants. The total acid number is determined as follows: An amount of the sample (about 0.5 g) is mixed with the titration solvent (toluene-isopropyl alcohol) and titrated potentiometrically against 0.1 N alcoholic solution of potassium hydroxide using glass and calomel electrodes.

Variation of viscosity ratio (V/Vo). The variation of viscosity ratio V/Vo has been determined using IP 48/86 [17] method where: V = Kinematic viscosity at 40°C of the sample after oxidation and Vo = Kinematic viscosity at 40°C of the sample before oxidation.

As Detergents/Dispersants

Spot method [19]. Spots have been taken from the Indiana oxidation apparatus after each 24 h oxidation interval and up to 72 h on special filter paper (Durieux 122) and dispersancy of the samples has been determined as follows:

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

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

Study the Effect of the Prepared Additives on the Other Properties of Lube Oil

As Pour Point Depressants

The selected prepared additive has been added to the lube oil in 2% concentration and the pour point has been determined before and after addition.

As Viscosity Index Improvers

The standard method IP 266/68 [21] has been followed. The viscosity index is an emperical number indicating the effect of change of temperature on the viscosity of an oil. A high viscosity index signifies relatively small change of viscosity with temperature.

RESULTS AND DISCUSSION

Polyethylene glycol palmitate with different molecular weights was prepared (A, B, C, and D). The amination reaction of the prepared esters (polyethylene glycol palmitate) with polyethylene polyamine (tetraethylene pentamine) was carried out to give (A_1, B_1, C_1, and D_1) to be used as lube oil additives (detergents/dispersants and antioxidants). The I.R. spectrum of the prepared esters is given in Figure 1, which illustrates, the following:

$-C{=}O$ band of ester appears at 1740–1720 cm^{-1}
$-OH$ band of glycol appears at 3000–3500 cm^{-1}
$-CH_2$ group appears at 1465–1375 cm^{-1}
$^{-}CH_3$ group appears at 1450–1375 cm^{-1}
$^{-}C{-}O$ band is in the range from 1250–1050 cm^{-1}

The measured molecular weights and corresponding theoretical values of the prepared esters (A, B, C, and D) are listed in Table 1. It is obvious from the data given in this table that the experimental and theoretical values are in good accord. This indicates that the reactions were completed successfully and confirms the formation of the desired

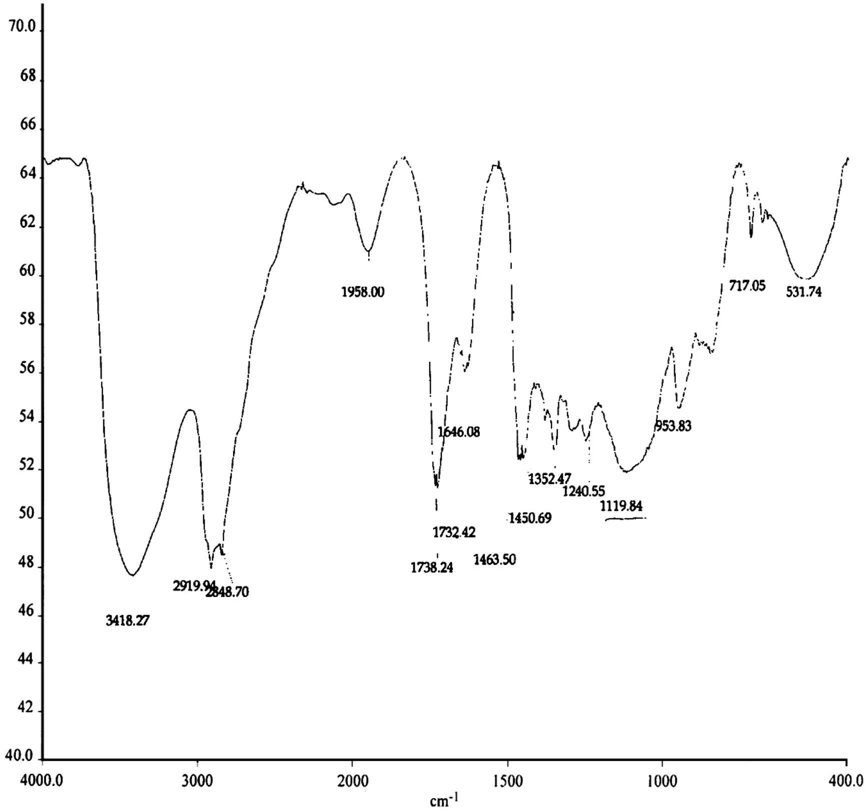

FIGURE 1 I.R. spectrum of the prepared ester.

compounds. This conclusion is based on the coincidence of the values of the theoretical and experimental molecular weights.

The amination of the prepared esters was carried out by the reaction of esters (A, B, C, and D) with tetraethylene pentamine to produce

TABLE 1 Theoretical and Experimental Molecular Weights of the Prepared Esters

Prepared esters	Theoretical M.wt.	Experimental M.wt.
A	438.43	440
B	638.43	643
C	838.43	845
D	1238.43	1240

different types of amines (A_1, B_1, C_1, and D_1). Tetraethylene pentamine is a highly preferred class of amine reactants because it contains five reactive amine hydrogen atom (NH group) [22].

Solubility of the Prepared Compounds in SAE 30 Base Oil

The solubility of the prepared compounds in the base oil was investigated according to the method described in Experimental. The solubility test was carried out to determine which of the prepared compounds would be tested as detergents/dispersants and antioxidants.

Evaluation of the Prepared Compounds as Lube Oil Additives

As Detergents/Dispersants

The action of the prepared compounds (A_1, B_1, C_1, and D_1) as detergents/dispersants for lube oil depends mainly on their structure. These additives consist of three components, each of which possess a special function. These parts are as follows:

1. Polar component that contains the ethylene oxide group. This group is effective in adsorbing the polar solid particles of the oxidation products.
2. Hydrocarbon tail, that helps in dissolving the additive molecules in the lube oil and sustains the oxidation products dispersed in the oil.
3. Basic-NH groups that neutralize some of the acidic oxidation products.

The doped oil samples were subjected to severe oxidation conditions using the Indiana test method at 165.5°C with continuous stirring at constant rate. Samples were taken at intervals of 24 h and up to 72 h of oxidation and tested for their dispersancy. The efficiency was taken as the ratio of the diameter of the black spot (contains the oxidation products) to the total diameter of the spot arises as a result of spreading the oil on the chromatographic sheet.

When the efficiency of the dispersant additive increases the diameter of the black spot increases. This is due to the enhanced capability of the doped oil to carry the oxidation products to a longer distance from the center of the spot. The measured values of dispersancy are given in Table 2.

The data listed in Table 2 show the poor dispersancy of lube oil without additives, and the prepared compounds have excellent dispersancy power (81–96%). The increase in dispersancy values with

TABLE 2 Dispersancy of Lube Oil Sample and its Blends Containing Additives A_1, B_1, C_1, and D_1 after Different Oxidation Periods

	Dispersancy		
Sample	24 h	48 h	72 h
Blank oil	35	33	32
Lube oil + A_1	81	83	85
Lube oil + B_1	83	86	87
Lube oil + C_1	90	92	95
Lube oil + D_1	92	93	96

Additive concentration is 2% by weight.

increasing oxidation time is explained by a formation of more oxidation products that could be dispersed with oil doped with the prepared compounds. This finding revealed that the prepared compounds act as excellent dispersants over all the test time and have excellent dispersancy power for the sludge and solid particles formed during lube oil oxidation [23]. It is clear that the addition of these additives disperse solid particles into the oil and thus prevent their agglomeration and preciptation on metallic parts of engines causing their damage and neutralize some of the acidic product of oxidation (acids, alcohols, and hydroxyacids). This may be explained by the presence of NH group and ethylene oxide groups in these additives (A_1, B_1, C_1, and D_1), which formed hydrogen bonds with polar groups of oxidation products [22,24]. The number of ethylene oxide groups increases by increasing the molecular weight of polyethylene glycol used in the reaction.

As Antioxidants

The prepared compounds (A_1, B_1, C_1, and D_1) were added to a sample of "SAE 30" lubricating oil free of any additives, and the blends obtained were subjected to severe oxidation conditions using the Indiana test methods at 165.5°C with continuous and constants rate of stirring [16]. Samples were taken at intervals of 24 h and up to 72 h of oxidation and tested for their oxidation stability (viscosity ratio V/Vo and total acid number [Δ.T.A.N]. Results are given in Figures 2 and 3.

All the prepared additives (A_1, B_1, C_1, and D_1) impart better oxidation resistance properties to the lube oil compared with the undoped oil. This is due to the presence of amine group in their structures, which acts as chain breaking inhibitor (antioxidant) by donation of a labile hydrogen from −NH group to stabilize the chain radical of

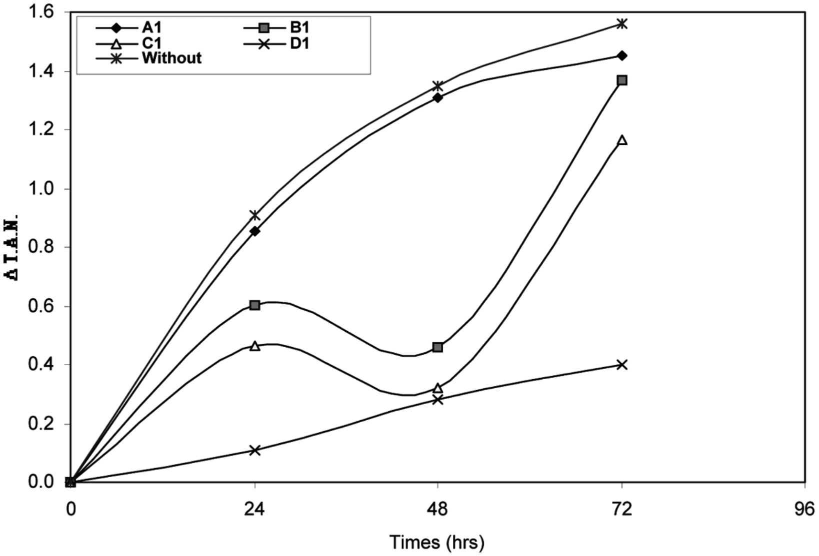

FIGURE 2 Variation of Δ T.A.N with oxidation time of lube oil without and with additives A_1, B_1, C_1, and D_1.

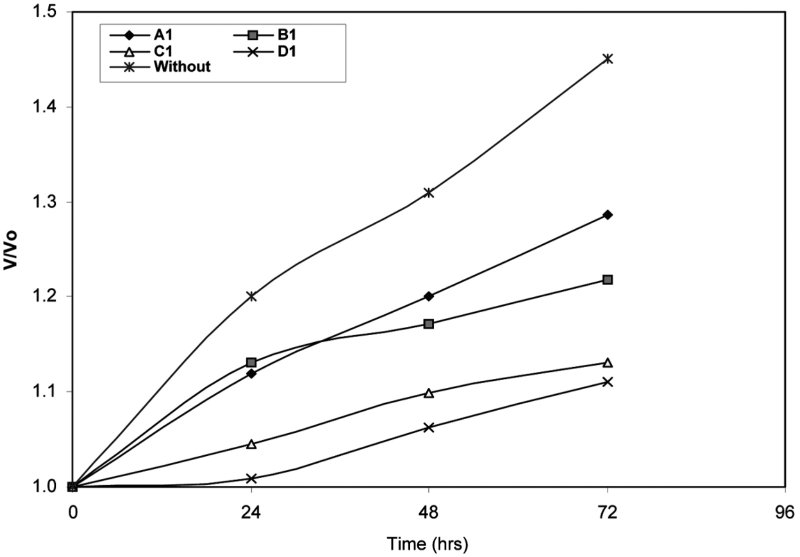

FIGURE 3 Variation of V/Vo with oxidation time of lube oil without and with additives A_1, B_1, C_1, and D_1.

oxidation reaction, that is, the NH group in the prepared compounds neutralize some of the acidic products of lube oil oxidation [25].

Effect of the Prepared Additives on Other Properties of Lube Oil

As the prepared additives have been found to give good results as detergents/dispersants and inhibit oil oxidation, their effect on other properties of lube oil has been studied. Thus, a sample (D_1) has been blended with lube oil (2 wt%). Its effect as viscosity index improver and pour point depressant for the lube oil sample was studied.

Effect on viscosity index. Viscosity index is an emperical number indicating the effect of change of temperature on the Kinematic viscosity of an oil. The viscosity index of lube oil sample without additive have been found to be 93, and with the prepared additive it is 94, which is nearly the same.

Effect on pour point depression. The pour point of the lube oil sample without additive is $-4°C$ and with the prepared additive is $-4°C$. From the study, one may conclude that the prepared additives have no effect on viscosity index and pour point of the lube oil.

CONCLUSIONS

All findings and discussions outlined heretofore reach the following conclusions:

1. Four types of polyethylene palmitate with different molecular weights were prepared and the structure confirmed by using I.R. spectroscopy and determination of molecular weight.
2. Amination of the prepared esters by reaction with tetraethylene pentamine.
3. All the prepared compounds are soluble in the lube oil.
4. The prepared compounds have been evaluated as lube oil additives (detergents/dispersants and antioxidants). It was found that the prepared compounds are good detergents/dispersants additives for the lube oil and impart better oxidation resistance properties to the lube oil compared with undoped oil.
5. The effect of prepared additives on properties of lube oil such as viscosity index and pour point was studied. It was found that the prepared additives have no effect on the viscosity index and pour point of lube oil.

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