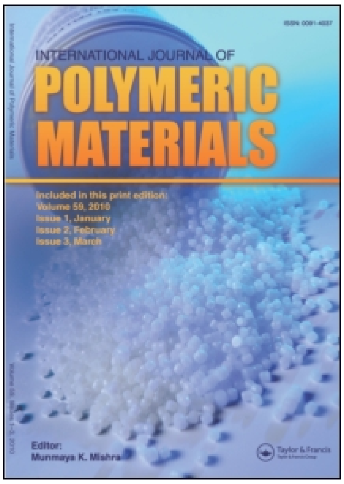

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Synthesis and Evaluation of Some Detergent/Dispersant Additives for Lube Oil

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With increasing demands being placed on lubricants for automotive engines and transmissions, it has been necessary to work to improve the function of these lubricants. Modern lubricants are formulated from a range of base fluids and chemical additives to enhance their actions or to add new properties. In this study we have confined ourselves to the study of the detergent/dispersant type of additives based on preparation of polyisobutylene succinic anhydride (PIBSA) and then the reaction of PIBSA with different polyethylene glycols and the amination of the products by different polyamines. The compositions of the prepared compounds were determined by molecular weight, I.R. and H-NMR spectroscopy. The efficiency of the prepared compounds as antioxidants and detergents/dispersants was investigated. It was found that the prepared compounds have very good dispersancy power and the efficiency increases by increasing the number of –NH groups in the prepared compounds and by increasing the molecular weight of the polyethylene glycols.

Keywords: antioxidant, detergent/dispersants, lube oil additive, lubricants

INTRODUCTION

The use of lubricants began in ancient times and has developed into a major international business of lubricating machines of increasing complexity [1]. The development of modern engine and transmission technologies would have been impossible without advanced lubricant additives chemistry and lubricant formulation.

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Modern engine oils contain a wide range of additives, which are blended with base oils to form a complete package capable of meeting demanding performance [2–4]. Lubricating oil always contains different types of additives, which differ in quantity and in quality according to the purpose of their use. Lube oil additives can be defined as materials which impart a new and desirable property not originally present in oil, or reinforces a desirable property already present to some degree in the oil [5]. Although additives of many types have been developed to meet special lubrication needs, they are used to reduce the oxidative or thermal degradation of an oil, to reduce wear, to minimize rust and corrosion, to lessen the deposition of harmful deposits on lubricated parts and to prevent destructive metal-to-metal contact [6].

Lubricating additives are classified according to function and liability into three different groups [7]:

- Designed to protect the finished lubricant in service in one way or another, by limiting chemical change or deterioration.
- Additives protecting the machine either from harmful deposits or from failure of lubricants to function properly.
- Additives which improve existing physical properties or impart new characteristics to the lube oils.

Short trips by car require many stops and do not provide for full warm-up or utilization of the engine. Engines are so lightly loaded and operated so intermittently that they rarely grow warm enough to operate efficiently. The fuel used in this type of engine is gasoline, usually considered an easily burned fuel. Gasoline is easily burned if the engine combustion chamber reaches a high enough temperature and the fuel therein is properly vaporized and mixed with adequate oxygen.

In such a combustion the gasoline is completely burned and only harmless carbon dioxide gas and steam are formed. However, if the engine does not operate long enough to heat its jacket water and crankcase to at least 50°C, some carbon dioxide and steam will blow by piston rings, condense in the cold crankcase and form liquid carbonic acid which rusts iron and steel. Thus, when the engine is cold and operated at low speeds characteristic of short trip driving, combustion is insufficient and incomplete. The formation of sludge (precursors) deposits involves three main phases. The first one is the formation of sludge in the combustion chamber by radical reaction between nitrogen oxides and fuel. The second phase consists of the precursors after many reactions with the crankcase oil [8,9]. The third phase is the agglomeration of precursors to form an oil-insoluble substance [10,11]. Thus detergent and dispersant additives for the lube oil is used.

Detergent additives act to prevent an accumulation of sludge in the crankcase [12]. Detergents are an integral part of any engine oil formulation and are typically metal salts of organic acids, containing a surface active polar group which can react with the metal surface to form a protective film that keeps the metal surfaces of an engine clean. In addition to cleaning, detergents also neutralize acidic combustion and oxidation products, thereby minimizing corrosion, rust and deposit formulation in the engine [13].

Dispersant additives act to disperse sludge formed in engines operated at relatively low temperatures [14].

The principal functions performed by detergents in engine oil formulations are acid neutralization, high temperature detergency, oxidation inhibition and rust prevention. These functions provide engine cleanliness and extended trouble-free operation. Dispersants supplement these functions and in addition provide protection against low-temperature sludge deposits [15].

Three mechanisms have been established to explain the action of the detergent additives to keep engines clean [16]:

- Neutralization of acidic materials.
- Peptization of solid particles in the oil.
- Solubilization of oil insoluble materials.

Additives that reduce oil oxidation are called antioxidants, which act to retard oxidation of the lubricating oil, thus preventing the formation of corrosive products. Antioxidants act in two different ways, by inhibition of peroxides or as radical scavengers, which react with peroxy radicals thus preventing further propagation of the free radical chain. Peroxide inhibitors react with hydroperoxide molecules preventing the peroxy radicals oxidation [13] resulting from high temperature. That may change the chemical structure of the base oil. These additives will be depleted depending on the length of service and the conditions imposed on them by the applications.

In the present work the preparation of polyisobutylene succinic anhydride (PIBSA), the reaction of PIBSA with polyethylene glycol (200, 400 and 600) and the amination of these products with amines having a different number of –NH groups is studied. A study of the efficiency of all prepared compounds as detergent/dispersant additives and antioxidants for lube oil-follows.

EXPERIMENTAL

Preparation of Polyisobutylene Succinic Anhydride (PIBSA) [17]

In a four-necked round bottom flask fitted with a mechanical stirrer, efficient condenser, thermometer, and nitrogen gas inlet, one mol of polyisobutylene (M.wt. = 1000) and one mol of maleic anhydride were mixed. The reaction mixture was maintained at 200°C with continous stirring for about 24 h. A slow steam of nitrogen gas was introduced to the reaction mixture (10 bubbles/min) during the entire heating period. Then, the reaction mixture was cooled to room temperature.

Reaction of PIBSA with Polyethylene Glycol (PEG)

In a three-necked flask fitted with a reflux condenser, mechanical stirrer and thermometer, there were placed one mol of PIBSA and one mol of PEG (M.wt. = 200, 400, 600) in presence of xylene as/ solvent and P-Toluene sulphonic acid (0.5% of total weight) as catalyst. The mixture was refluxed at 130°C for 3 h. Then the xylene was removed from the product by rotary extraction. This reaction was applied to three different molecular weights of PEG. Therefore, we have three different products, A, B and C.

Amination of Compound A

The PIBSA – polyethylene glycol A was reacted with polyethylene polyamine (ethylenediamine, diethylenetriamine, triethylene tetraamine and tetraethylene pentamine) to produce the additives designated as A_1, A_2, A_3 and A_4, respectively. The reaction was performed at 130°C in a round bottom flask fitted with a condenser, mechanical stirrer and a thermometer for about 2 h or until the amount of water which was calculated theoretically had been removed.

Determination of Molecular Weights

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

Determination of Nuclear Magnetic Resonance (^{1}H-NMR)

The ^{1}H-NMR spectra of the synthesized additives were measured by using Bruker 300 MHs Spectrometer W-P-300.

I.R. Spectroscopic Analysis

I.R. spectra of the synthesized compounds were determined by using a Mattson F.T.I.R. Spectrometer model. 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 were subjected to severe oxidation condition in the presence of copper and iron strips at 165.5°C for 72 hours using the Indiana test method of oxidation [18]. The oxidation stabilities of the lube oil blends were determined by taking samples at 24 hour intervals up to 72 hours. These samples were tested for:

1. Viscosity at 40°C, according to IP method.
2. Total acid number, according to IP method.

As Detergents/Dispersants

Spot method [19]. Drops were taken from the samples being oxidized at 165.5°C in the Indiana test after 24 h intervals of oxidation and up to 72 h to make sspots on special filter paper (Durieux 122) and the dispersancy of the samples were measured 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

RESULTS AND DISCUSSION

The polyisobutylene succinic anhydride was reacted with three different polyethylene glycols of molecular weight 200, 400 and 600 to produce three different products A, B and C. The determined molecular weights of the products, given in Table 1, have been found to be very near those calculated theoretically. The results show an increase in

TABLE 1 Theoretical and Determined Mean Molecular Weights of Compounds A, B and C

Prepared compounds	Theoretical	Determined
A	1298	1305
B	1498	1509
C	1698	1710

molecular weight of the prepared products with the increase in molecular weights of polyethylene glycol.

The I.R. spectram of A, B and C are not shown here but are identical and illustrate the following:

- Disappearance of two anhydride bands and appearance of carboxylic $-C=O$ at $1730\,cm^{-1}$.
- Broad band at $3100–3400\,cm^{-1}$ for $-OH$ group.
- $-C-O$ band is in the range of $1000–1250\,cm^{-1}$.

The ^{1}H-NMR spectrum not shown here for product B indicates the presence of a band centered at 1.2 ppm representing the methylene group of polyisobutylene, a band at 2.4 ppm arising from methylene bonded to the carbonyl group and hydroxyl group, a band at 3.9 ppm for the ethoxy proton and a band at 7.5 ppm for acidic proton.

So, the determination of molecular weight, I.R. and ^{1}H-NMR spectroscopy, the reaction of polyisobutylene succinic anhydride with polyethylene glycol was carried out successfully. Amination of the prepared compound A with ethylene diamine, diethylene triamine, triethylene tetramine and tetraethylene pentamine gave products A_1, A_2, A_3 and A_4, respectively, to be used as lube oil additives.

The molecular weights of A_1–A_4 are given Table 2 which indicates that the theoretical and the measured values are in accord with each other, which prove that the reactions were completed. The I.R. spectra

TABLE 2 Theoretical and Determined Mean Molecular Weights of Compounds A_1–A_4

Prepared compound	Theoretical	Determined
A_1	1340	1346
A_2	1383	1391
A_3	1426	1430
A_4	1469	1475

illustrates the presence of broad band at 3200–3600 cm^{-1} for −NH and −OH, and the presence of −C=O amideat 1649 cm^{-1}, which prove the formation of A_1–A_4.

The ^{1}H-NMR spectrum of product A_2 indicates the presence of a band centered at 1.2 ppm representing the methylene group of polyisobutylene, the band at 2.8 ppm arising from methylene bonded to carbonyl groups and hydroxyl group, a band at 3.9 ppm for ethoxy proton and a band at 7 ppm for −NH of amide.

The compounds B and C were aminated with tetraethylene pentamine to give B_1 and C_1 to be used as lube oil additives.

Evaluation of the Prepared Compounds as Lube Oil Additives

The prepared compounds A_1, A_2, A_3 and A_4 were added to the undoped lube oil samples, SAE – 30, and the oxidation stability as well as detergency/dispersancy of all samples under evaluation were determined and compared with lube oil sample without additives. The evaluation can be divided into two main categories as follows:

As Detergents/Dispersants

The doped oil samples were subject to severe oxidation conditions using the Indiana test method, as described above, in which the efficiency of the dispersant additive increases the diameter of the black spot. 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 spots. The measured values of dispersancy are given in Table 3.

The results in Table 3 show clearly that the prepared compounds have very good to excellent dispersancy (70–81%) for the sludge and solid particles formed during lube oil oxidation, compared with the lube oil only.

TABLE 3 Dispersancy of Lube Oil Sample and its Blends Containing Additives A_1–A_4 after Different Oxidation Periods

	Dispersancy time (hours)		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 2% additive A_1	69	72	75
Lube oil + 2% additive A_2	73	75	76
Lube oil + 2% additive A_3	76	77	79
Lube oil + 2% additive A_4	78	79	81

TABLE 4 Dispersancy of Lube Oil Samples and its Blends Containing Additives A_4, B_1 and C_1 after Different Oxidation Periods

	Dispersancy time (hours)		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 2% additive A_4	78	79	81
Lube oil + 2% additive B_1	79	81	83
Lube oil + 2% additive C_1	80	83	84

This is due to the fact that the polar parts in the prepared additives are effective in adsorbing solid particles of the oxidation products. It is generally agreed that the additive is adsorbed on the surface of the carbon particles and thus prevent their agglomeration due to electrostatic phenomena [20,21] between polar group in additive molecule and the carbon particles. Thus it maintains the carbon particles in the oil in a finely dispersed state so they are not deposited within the engine but may be easily removed with the oil when it is drained. It was also found that the efficiency of the prepared additives as lube oil dispersants increases by increasing the number of –NH groups in the structure of the prepared additives. This may be explained by the fact that –NH groups from hydrogen bonds with polar groups of the oxidation products, so compound A_4 gives excellent dispersancy power during the lube oxidations. This occurs when A_4 is produced from A with tetraethylene pentamine, so the prepared compounds B and C

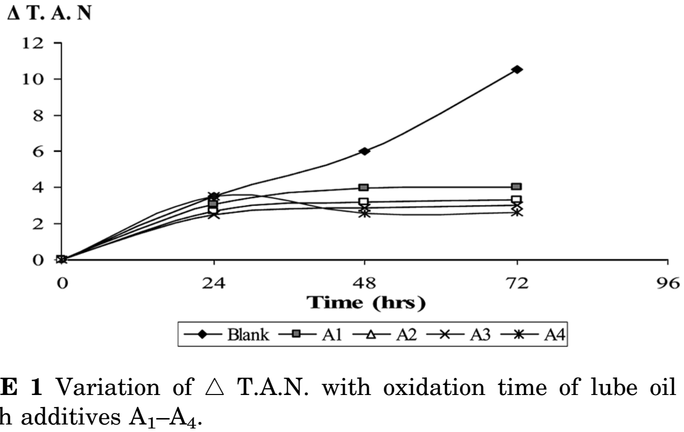

FIGURE 1 Variation of △ T.A.N. with oxidation time of lube oil without and with additives A_1–A_4.

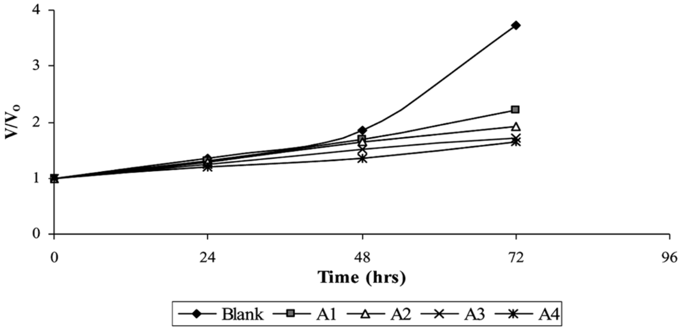

FIGURE 2 Variation V/V$_o$ with oxidation time of lube oil without and with additives A_1, A_2, A_3 and A_4.

were aminated by using tetraethylene pentamine to give products B_1 and C_1 and the dispersancy of the samples of oil with these additives, given in Table 4 indicates that B_1 and C_1 give better dispersants than A_1. This may be due to the increased number of ethylene oxide units of the polyethylene glycols used in the reaction.

As Antioxidants

The different prepared compounds A_1, A_2, A_3 and A_4 have been added to lube oil samples in 2 wt.% concentration and the blends obtained were subjected to severe oxidation condition at 165.5°C as described in the experimental section. The oxidative stability is expressed as an increase in viscosity ratio (V/V$_o$), and in the total acid

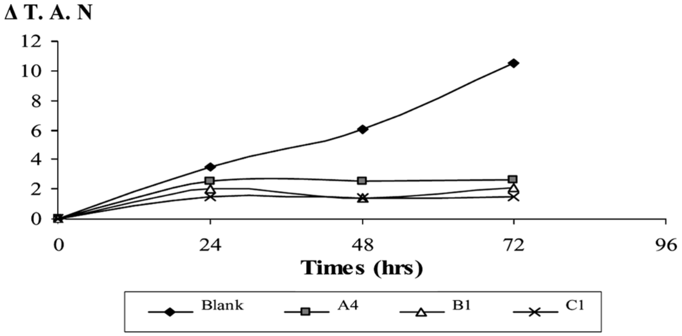

FIGURE 3 Variation of △ T.A.N. with oxidation time of lube oil without and with additives A_4, B_1, and C_1.

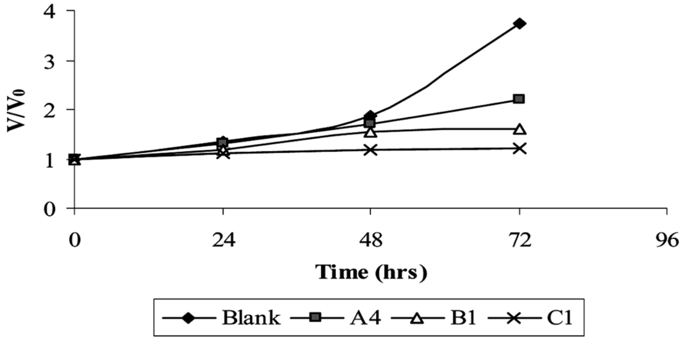

FIGURE 4 Variation V/V_o with oxidation time of lube oil without and with additives A_4, B_1, C_1.

number (T.A.N.), compared with lube oil sample free from additives. Results are given in Figures 1 and 2, which indicate the following:

All the prepared additives, A_1, A_2, A_3 and A_4, impart better oxidation resistance properties to the lube oil than the undoped oil. This is due to the presence of amine groups in their structure, which act as chain breaking inhibitors (antioxidants) by donation of labile hydrogens from –NH groups to stabilize the chain radical of oxidation reactions, i.e., the –NH groups in the prepared compounds neutralize some of the acidic products of lube oil oxidation [22]. It was found that the efficiency of compound A_4 is the best as lube oil antioxidant, followed by A_2, A_3 and compound A_1 comes last. This is due to A_4 containing more –NH groups in its structure. By comparing compounds A_4, B_1 and C_1 in Figures 3 and 4 it was found that C_1 is more efficient than B_1 and A_4 due to the increased molecular weight of polyethylene glycol.

CONCLUSIONS

The conclusions to be derived from the results of this study are:

1. All the prepared compounds are soluble in lube oil.
2. All the prepared compounds have very good to excellent dispersancy relative to the lube oil only.
3. The efficiency of the prepared additives as lube oil dispersants increases by increasing the number of –NH groups in the structure of the prepared additives and by increasing the molecular weight of polyethylene glycol used in the reaction.
4. All the prepared additives impart better oxidation resistance properties to lube oil relative to the undoped oil.

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