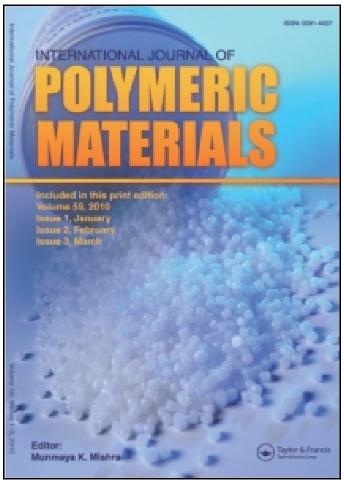

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Synthesis and Evaluation of Detergent/Dispersant Additives from Polyisobutylene Succinimides

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Lube oil additives are essential for all types of lubricating oils; they are added either to give the oils new properties as detergency and oxidation stability or to improve such properties as pour point and viscosity index. They are added at varying proportions to meet the performance requirements. The present work is concerned with studying of detergent/dispersant type additives based on synthesized polyisobutylene succinic anhydride (PIBSA) and its aminated compounds (PIBSA) with different types of polyethylene polyamine such as ethylene diamine, diethylene Triamine, Triethylene tetramine, and tetraethylene pentamine. Different types of polyisobutylene succinimides were reacted with dodecylphenol and formaldehyde to prepare different type of Mannish bases. The efficiency of the prepared compounds as antioxidants and detergents/dispersants was investigated. It was found that compound D_1 (Mannich base IV) is the best antioxidant additive for lube oil, and all the prepared compounds have excellent dispersancy power.

Keywords: antioxidants, detergents/dispersants, lube oil additives, polyisobutylene

INTRODUCTION

Lubricating oils always contain different types of additives. These additives differ in quantity and in quality according to the purpose

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for which they are needed. Lubricant additives are compounds or mixtures that upon being incorporated in base lubricating Fluids, supplement their natural characteristics and improve their field service performance in existing application. The additives must not interfere with each other. Moreover, the materials used are normally more chemically reactive than the base oil. A great deal of research is being done at present on the synthesis, technology, and applications of different lube oil additives [1–2]. Additives of many diverse 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 [3]. Oxidation stability is one of the most important properties of motor oil, playing a major role in determination of drain period in an engine, most crude oils used for the refining of lubricants contain natural oxidation inhibitors, such as polycylic aromatics and sulphur and nitrogen compounds. To a large extent, however, these compounds are removed in the refining process, which aims to achieve a high viscosity index for the lubricating oils, to compensate for the removal and to improve further the characteristics of the oil towards oxidation stability. Synthetic antioxidants are added [4–5], typical among them are hindered phenols, aromatics amines, and zinc-dialkylthiophosphates. Oil oxidation forms acidic and peroxidic compounds that attack metals, corrode bearings, and promote wear. Hydroxy acids are a major source of the oil insolubles that cause ring sticking, slugging, and impeded oil flow. These insoluble materials are formed by the hydroxyacid undergoing condensation polymerization [6]. Detergent additives act to prevent an accumulation of sludge in the crankcase [7] and on the cylinder walls. A main source of deposits is the oxidation of oil in high-temperature gasoline or diesel engines that can be reduced by using antioxidants. Dispersants, on the other hand, are additives that disperse sludge formed in engines operated at relatively low temperatures. The major use of detergent/dispersant additives is in crankcase oils for gasoline and diesel engines. Their main function is to keep particulate matter dispersed, and maintain engine cleanliness, the dirt in an engine arises mainly from the blow-by (past the piston rings), products of incomplete combustion of the fuel, and to lesser extent from oil oxidation. These phenomena lead to deposits on engine parts, for example, pistons, known as varnish, and deposits in the engine sump, known as sludge. The engine deposits depend on both fuel and lubricant degradation products. The dominant feature in any particular case will depend on the type of engine and fuel and the operating conditions. In all cases, temperature plays an important role. The formation of all types of deposits in an engine can be controlled by the use of detergent/dispersant additives. These additives can be subdivided into two classes: metallic additives include the neutral and basic sulphonates, alkyl phenates, salicylate, thiophosphonates, and phosphonates. Ashless ones are the succinimides, esteramides of high molecular weight, and the Mannish bases. Ashless lube oil detergents-dispersants are much more effective than the conventional metal salt in controlling the sludge and varnish deposits in low-temperature gasoline engine operation. An additional and important advantage of these additives is avoidance of the ash formed by the metal salt detergent on decomposition. The ashless dispersant succinimides are considered one of the most important developments in the history of lubricating oil additives [8]. Their remarkable dispersant properties under both low- and high-temperature conditions permit high-performance levels of the lubricant in passengers cars high speed diesel engines.

Succinimides are effective in peptizing solids and superior to metal salt detergents in solubilizing the oil insoluble materials [8]. Also, they are basic and, therefore, neutralize acidic materials. Alkylphenol-aldehyde-amine condensation products, which are known as Mannich bases [2,8], have been used as lube oil additives of ashless phenate type [9].

Three mechanisms have been established to explain the action of the detergent additives to keep engines clean [10]. Neutralization of acidic materials, peptization of the solid particles in the oil in a finely dispersed state so that they are not deposited within the engine, and solubilizing the oil insoluble materials.

The present work deals with the condensation reaction of different amines and succinimides with formaldehyde and compounds containing a reactive hydrogen atom, for example, dodecyl phenol. Mannich bases have been prepared to be used as antioxidants and detergents/dispersants additives for lube oil.

EXPERIMENTAL

Preparation of Polyisobutylene Succinicanhydride (PIBSA) [11]

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

Reaction of PIBSA with Different Amines [11]

In a four-necked round bottom flask fitted with a mechanical stirrer and a thermometer, 0.25 mole of ethylene diamine dissolved in equal amount of toluene has been charged. An equivalent amount of polyisobutylene succinic anhydride (PIBSA) has been added to the amine over about 1 1/2 h with continuous stirring. The reaction mixture as gradually heated to about 120°C over about 2 h, under good stirring condition to get rid of the water of the reaction, and solvent. Thus, polyisobutylene succinimide of ethylene diamine (A) has been prepared. Several polyethylene amines have been used in the same technique to prepared the corresponding imides. The polyethylene amines used were, diethylenetriamine, triethylenetetramine, and tetraethylene pentamine to give the compounds B, C, and D, respectively.

Preparation of Mannich Bases

In a three-necked round-bottom flask equipped with a stirrer and a reflux condenser were placed one mole of dodecylphenol, one mole of polyisobutylene succinimide of different amine (A, B, C, and D), excess formaline solution, and 10% sodium hydroxide solution. The quantity of the latter is equivalent to 5% of the total weight of the reactants. The mixture was refluxed at 100–105°C for 2 h. The mixture was then neutralized with dil. HCl. At this point, the product was extracted with benzene and dried over anhydrous sodium sulphate. The solvent was then distilled off leaving the product as a viscous liquid. So four products of different amines are obtained which are designated A_1 (Mannich base I), B_1 (Mannich base II), C_1 (Mannich base III), and D_1 (Mannich base IV).

Determination of the Molecular Weights

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

I.R. Spectroscopic Analysis

I.R. Spectra of the synthesized compounds were determined by using F.T.I.R. spectrometer Model type Mattson. 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 [12]. 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 and (2) Total acid number, according to IP method.

As Detergents/Dispersants

Spot method [13]. Drops were taken from the samples being oxidized in the Indiana test after 24 h intervals of oxidation and up to 72 h to make spots on special filter paper (Durieux 122) and the dispersancy of the samples were measured as follows:

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

RESULTS AND DISCUSSION

The polyisobutylene succinimides of different amines [ethylene diamine (A) diethylene triamine (B), triethylene tetramine (C), and tetraethylene pentamine (D)] were prepared, the condenstaion of A, B, C, and D with dodecylphenol and formaldehyde were carried out to give A_1, B_1, C_1, and D_1 compounds to be used as lube oil additives (antioxidants and detergents/dispersants).

The I.R. Spectra of A_1, B_1, C_1, and D_1 are given in Figures 1–4.

- The N–H and O–H regions are overlapping (O–H at 3600–3200 cm^{-1} and the N–H at 3500–3300 cm^{-1})
- C–N band is in the range from 1350–1000 cm^{-1}
- C–O band is in the range from 1250–1000 cm^{-1}
- C–H of alkanes in the range from 3000–2850 cm^{-1}
- C–H of Aromatic in the range from 3000–3150 cm^{-1}
- C–H of CH_3 group appears at 1450 and 1375 cm^{-1}
- C–H of CH_2 group appears at 1465 and 1375 cm^{-1}
- C=C aromatic appears at 1475 and 1600 cm^{-1}
- P-disubstituted ring appears as one strong band from 800 to 850 cm^{-1}

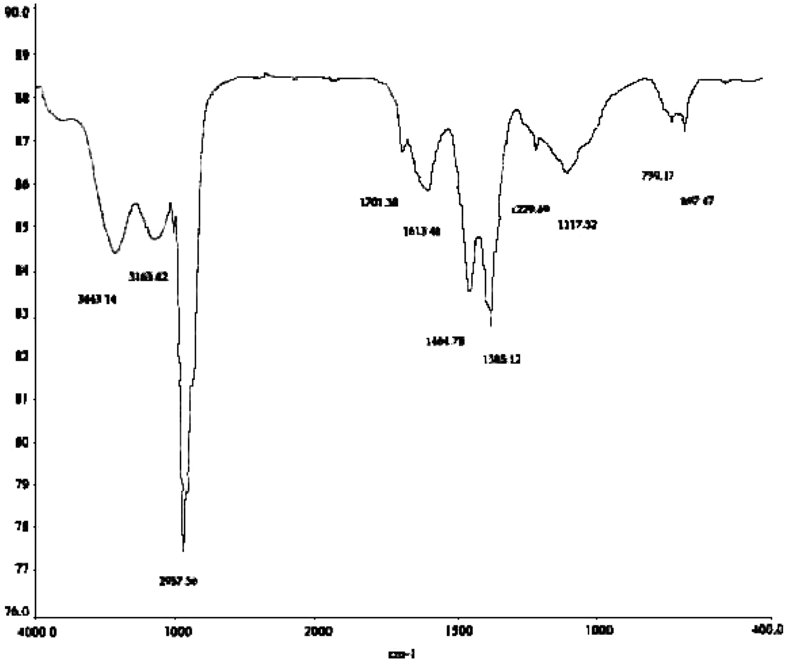

FIGURE 1 IR spectrum of A_1.

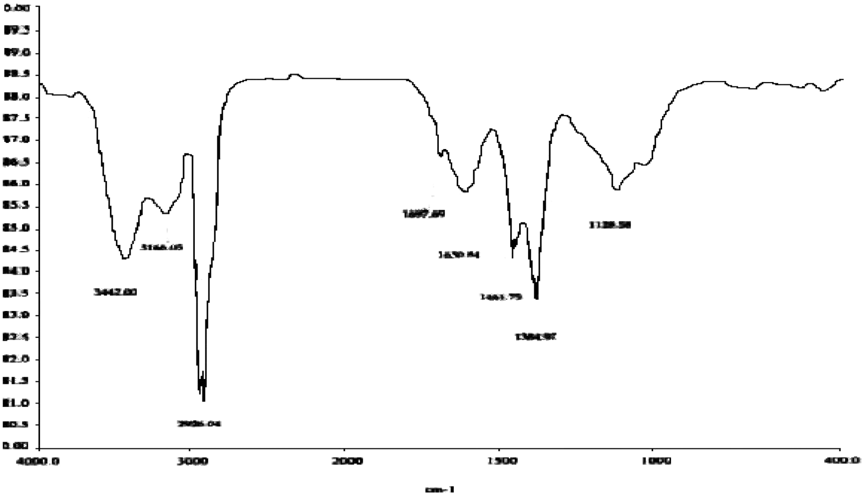

FIGURE 2 IR spectrum of B_1.

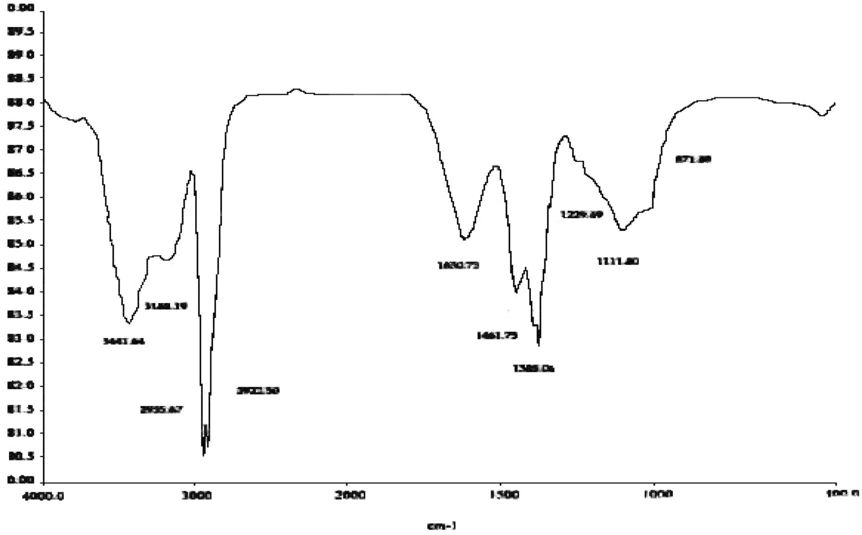

FIGURE 3 IR spectrum of C_1.

The determined mean molecular weights of all products given in Table 1 have been found to be very near to that calculated theoretically.

EVALUATION OF PREPARED COMPOUNDS AS LUBE OIL ADDITIVES

Prepared compounds have been added to undoped lube oil samples “SAE-30” and the oxidation stability as well as detergency/dispersancy of all samples under evaluation has been determined and compared with lube oil sample without additives. The evaluation can be divided into two main divisions.

As Antioxidants

The prepared additives A_1, B_1, C_1, and D_1 were added to a sample of “SAE-30” lubricating oil free from any additives, and the blends obtained were subjected to severe oxidation condition at 165.5°C with continuous and constant rate of stirring. Samples were taken at intervals of 24 h and up to 72 h of oxidation and tested for their oxidation stability expressed as increase in viscosity ratio (V/V_o), total acid number (T.A.N.), compared with lube oil sample free from additives. Results are given in Figures 5 and 6.

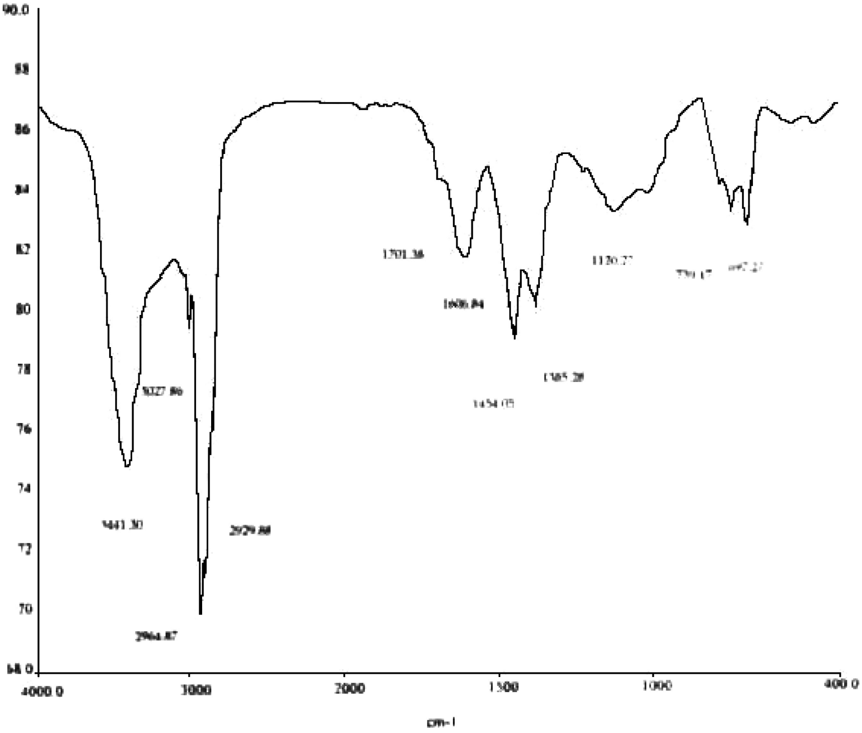

FIGURE 4 IR spectrum of D_1.

All the prepared compounds impart better oxidation resistance properties to the lube oil compared with the undoped oil. This may be attributed to the presence of phenolic and amino groups in their structures. The efficiency of phenolic compounds as antioxidants is attributed to the fact that they are chain-breaking inhibitors. The phenolic and aromatic amines inhibitors function by donation of a labile hydrogen from such groups as OH or NH to stabilize the chain

TABLE 1 Theoretical and Determined Mean Molecular Weights of the Prepared Compounds A_1, B_1, C_1, and D_1

Prepared compounds	Theoretical	Determined
A_1	1414	1416
B_1	1457	1460
C_1	1500	1505
D_1	1543	1545

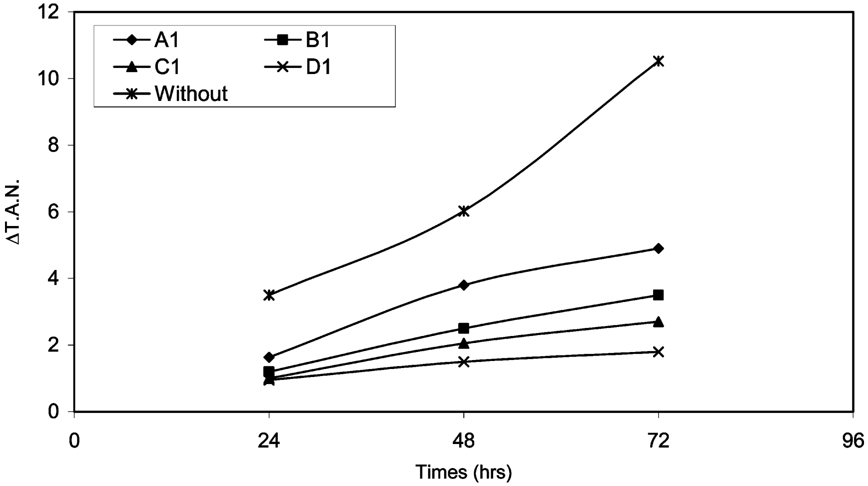

FIGURE 5 Variation of ΔT.A.N. with oxidation time of lube oil without and with additives A_1, B_1, C_1, and D_1.

radicals, that is, these inhibitors destroy the peroxide radicals, and thus the oxidation chain is broken. The presence of the amino group in the structure of the prepared compounds neutralizes, some of the acidic products of the lube oil oxidation. It was found that compound

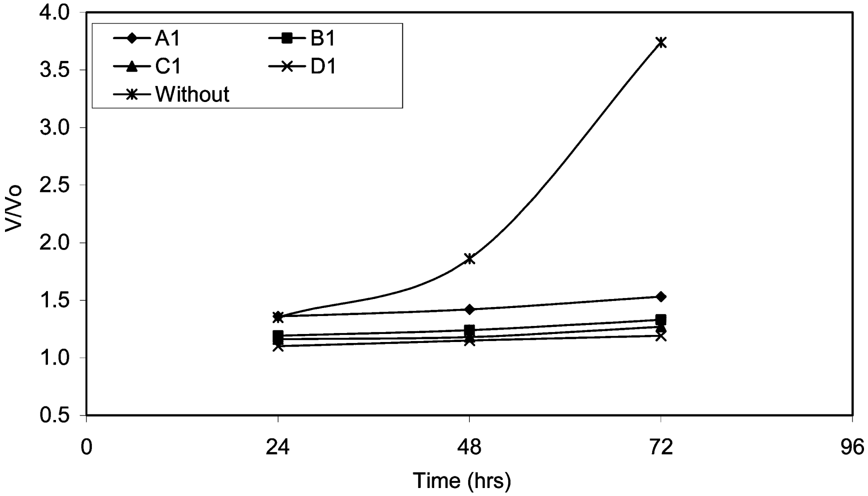

FIGURE 6 Variation of V/Vo with oxidation time of lube oil without and with additives A_1, B_1, C_1, and D_1.

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

	Dispercancy Time hours		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 2% additive A_1	70	73	76
Lube oil + 2% additive B_1	73	77	80
Lube oil + 2% additive C_1	76	80	84
Lube oil + 2% additive D_1	80	83	90

D_1 is the best lube oil antioxidant, followed by C_1, B_1, and then compound A_1. The efficiency of compound D_1 compared with the others is because it contains more NH groups in its structure [14].

As Detergents/Dispersants

The prepared compounds A_1, B_1, C_1, and D_1 have been added to lube oil samples in concentration of 2 wt%, using the spot test method. Results given in Table 2 show clearly that the prepared compounds have very good to excellent dispersancy power (70–90%) for the sludge and solid particles formed during lube oil oxidation, compared with the lube oil only.

Compounds A_1–D_1 at the beginning of oxidation (after 24 h) show somewhat moderate dispersancy power for lube oils as indicated by the data given in Table 2. After 48 h their efficiencies as dispersant become clear. The data also show that compound D_1 gives excellent dispersancy power during the lube oxidations. It is clear that the addition of these compounds not only disperses solid particles in the oil and thus prevents their agglomeration and precipitation on metallic parts of engines that can cause damage, but also neutralizes some of the acidic products of oxidation due to their basic nature. Increasing the N−H groups in the structure of the prepared compounds promotes their capacity in dispersing sludge and solid particles in lube oils. This may be explained by the fact that the NH groups from hydrogen bonds with polar groups of oxidation products such as alcohols, aldehydes, ketones, acids, and so on [15–16].

CONCLUSIONS

1. Four Mannich bases were prepared by using dodecyl phenol, formaldehyde, and different amines of polyisobulylene succinimide and the structure confirmed by using I.R. spectroscopy and determination of molecular weight.

2. The efficiency of the prepared compounds as antioxidants and detergents/dispersants was investigated.
3. The prepared compounds impart better oxidation resistance properties to the lube oil compared with undoped oil.
4. The prepared compounds have excellent dispersing power for sludge and solid particles.

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