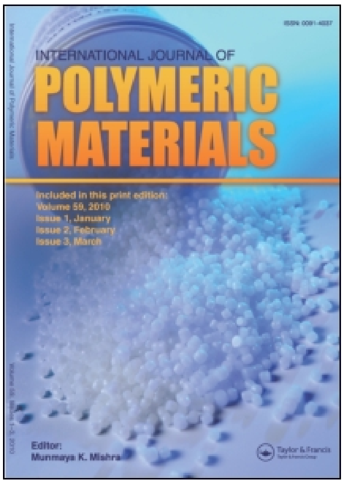

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Lubricating Oil Additives Based on Polyalkylpolyamines

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Lubricating Oil Additives Based on Polyalkylpolyamines

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This work is confined to the preparation and characterization of additives. These additives are based on the reaction of polyisobutylene with different ethanolamine and then amination with tetraethylenepentamine. The molecular weights of the prepared compounds were determined by gel permeation chromatography (GPC). The efficiency of the prepared compounds as antioxidant and detergent/dispersant additives for lube oil was studied. It was found that the efficiency increases with increasing the molecular weight and -NH- group of the prepared compounds.

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

INTRODUCTION

The study of lubrication as a science began in the 17th century with the development of bearings and axles. A lubrication system consists of moving surfaces under load with a lubricant in between. Lubrication is achieved by utilizing the physical and chemical properties of lubricating fluid [1–5]. Physical properties such as density, viscosity, heat capacity, thermal conductivity, and temperature-pressure-viscosity relationships determine the ability of the lubricant to operate under hydrodynamic lubrication [6,7].

Chemical properties such as solvency, dispersancy, detergency, antiwear, anticorrosion, frictional properties and antioxidant capacity are crucial to successful boundary lubrication. Some

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properties are controlled by the chemical composition of the base oils, and some properties are controlled by chemical additives designed for that purpose. The lubricating oil used in an internal combustion engine deteriorates in two ways: 1) It undergoes chemical and physical changes due to, primarily, oxidation, and 2) it becomes contaminated by material from the combustion chamber, its own products and airborne dust. The conditions under which oil is used in an engine are very conductive to oxidation. Oxidation products are formed whose nature depends primarily on the temperature [8,9]. In the crankcase, acidic material and complex carbonaceous products known as asphaltenes are produced which form a stable sludge that is characteristic of a low-temperature operation. The oil forms “carbon” deposits by the combination of oxidation and thermal degradation in the combustion chamber and around the piston rings. These oxidation effects aggravate the contamination of the oil beyond that resulting from fuel combustion. However, the addition of antioxidants retards the oxidation and also prevents the oil from becoming acidic. A large amount of research has been devoted to the synthesis, technology and applications of different lube oil additives [10]. In internal combustion engine service, a variety of effects tends to cause oil deterioration and the formation of harmful deposits. These deposits can interfere with oil circulation, build up behind piston rings to cause ring sticking and rapid ring wear, and affect clearances and proper functioning of critical components, such as hydraulic valve lifters. Once formed, such deposits are generally hard to remove except by mechanical cleaning. The use of detergents and dispersants in the oil can delay the formation of deposits and reduce the rate at which they deposit on metal surfaces. Detergents are generally considered to be those chemical compounds which chemically neutralize deposit precursors that form under high-temperature conditions, or as the result of burning fuels with high sulfur content or other materials that form acidic combustion products [11–13]. Dispersants, on the other hand, are chemical compounds that disperse or suspend in the oil potential sludge-forming materials, particularly those formed during low-temperature operations when condensation and partially burned fuel find their way into the oil. Detergents have some ability to disperse and suspend contaminants, while dispersants have some ability to prevent the formation of high-temperature deposits [14,15]. Incorporation of detergent and dispersant additives into a lubricant is essential to prevent harmful carbon and sludge deposits in critical areas of the engine, shutdown, 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:

- Minimizing oil thickening, thereby maintaining viscosity stability and flow properties.
- Containment of carbon sludge deposits that clog oil lines resulting in lack of oil flow and subsequent engine failure. Detergents and dispersants have a direct effect on minimizing harmful engine exhaust emissions, increasing engine life, and controlling oil consumption by maintaining clean, "in-tune" engine operation. Without these additives, deposits on the piston ring and grooves can lead to ring sticking resulting in loss of oil control [16,17]. 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. There are four different types of ashless dispersants: succinimides, succinate esters, Mannich type, and phosphorus types. Most dispersants currently in use are prepared from polisobutylenes of 1,000 to 10,000 molecular weight. Their polar functionality arises from amino and/or hydroxyl groups. Three mechanisms have been established to explain the action of the detergent additive to keep engines clean [18].

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

Products from the oxidation of lubricating oils include carboxylic acids, ketones, and alcohols, which then condense to form polymeric materials. These oxidation products lead to the formation of varnish and sludge and to an increase in viscosity. Oxidation inhibitors reduce the quantity of oxygen reacting with oil by forming inactive soluble compounds and by passivating metal-bearing surfaces to retard the oxidation rate. Several effective oxidation inhibitors have been developed [18,19] and are used in almost all of the conventional motor oils today. These inhibitors, while exhibiting good antioxidant properties, are burdened by economic and oil-contamination problems. A need therefore exists for an improved antioxidant that is stable at evaluated temperatures, that can be employed in reduced concentrations, and that is economical and easy to produce. In the present work we deal with the preparation of polyisobutylene succinic anhydride (PIBSA) and the reaction of PIBSA with different ethanolamines and then amination of these products with tertraethylenepentamine. The efficiency of the prepared compounds as antioxidant and detergent/dispersant additives for lube oil will be investigated.

EXPERIMENTAL

Preparation of Polyisobutylene Succinic Anhydride (PIBSA) (20)

In a four-necked round-bottom flask fitted with a mechanical stirrer, efficient condenser, thermometer, and nitrogen gas inlet, one mole of polyisobutylene (Mwt = 1,000) and one mole of succinic 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 Ethanolamines

In a three-necked flask fitted with a reflux condenser, mechanical stirrer and thermometer, one mole of PIBSA and one mole of monoethanolamine were added together with xylene as solvent and p-toluene sulphonic acid (1% of total weight) as a catalyst. The mixture was refluxed at 130°C for 3 h. Then xylene was extracted from the product by rotary evaporator to give product (A). This reaction was applied to the preparation of compound (B) from two moles of PIBSA and one mole of diethanolamine and for the preparation of compound (C) from three moles of PIBSA and one mole of triethanolamine.

Amination of the Prepared Compounds (A, B and C)

The PIBSA-monoethanolamine (A) was reacted with tetraethylene pentamine. 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, in a nitrogen atmosphere in the presence of 1% p-toluene sulphonic acid as a catalyst and toluene as a solvent. The reflux of the reaction mixture was continued until the theoretical amount of water was collected azeotropically by a Dean and Stark trap. At the end of the reaction the solvent was distilled under reduced pressure to give compound (A_1). This reaction was applied to prepare compound (B_1) from the reaction of B (PIBSA-diethanolamine) with tetraethylenepentamine and to prepare compound (C_1) from the reaction of C (PIBSA-triethanolamine) with tetraethylene pentamine.

Determination of Molecular Weights

The molecular weights of the prepared compounds were determined by using gel permeation chromatography (GPC), Waters 600.

IR Spectroscopic Analysis

IR spectra of the synthesized compounds were determined by using FTIR 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 were subjected to severe oxidation conditions in the presence of copper and iron strips at 165.5°C for 72 h using the Indiana test method of oxidation (21). The oxidation stabilities of the lube oil blends were determined by taking samples at 24-hour intervals up to 72 h. 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 (22)

Drops were taken from the samples being oxidized in the Indiana test after 24-hour 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:

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

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 amines (monoethanolamine, diethanolamine, and triethanolamine) so we have 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 IR spectra of products A, B and C are identical so that the spectrum of (A) illustrates the following:

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

So from the IR spectra and determination of molecular weight, the formation of compounds A, B and C was successful.

Amination of the prepared compounds A, B and C with tetraethylene pentamine gave products A_1, B_1 and C_1 to be used as lube oil additives. The molecular weights of A_1, B_1 and C_1 are given in Table 2, which indicates that the theoretical and measured values are in accordance with each other, provided that the reactions were completed. The IR spectrum of A_1 illustrates the presence of $-C{=}O$ of amide at $1640\,cm^{-1}$, which proves the formation of amide compounds.

Evaluation of the 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 a lube oil sample without additives. The evaluation can be divided into two main divisions as follows.

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

Prepared compound	Theoretical	Determined
A	1159	1150
B	2301	3286
C	3443	3418

TABLE 2 Theoretical and Determined Mean Molecular Weights of the Prepared Compounds A_1, B_1 and C_1

Prepared compound	Theoretical	Determined
A_1	1330	1350
B_1	2643	2693
C_1	3956	4023

As Antioxidants

The prepared compounds A_1, B_1 and C_1 were added to the sample of SAE-30 in concentrations ranging from 0.25% to 3.00% and the blends obtained were subjected to severe oxidation conditions using the Indiana test method at 165.5°C with continuous 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 increases in viscosity ratio V/V_o and total acid number, ΔTAN, of the doped lubricating oil samples with respect to the undoped sample. The variations ratio V/V_o with oxidation time for all doped oil samples are illustrated in Figures 1–3. The following findings can be drawn from these figures.

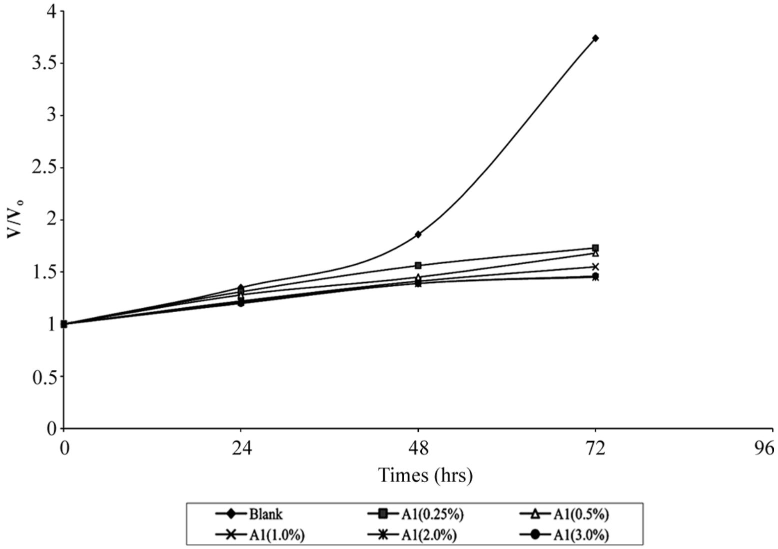

FIGURE 1 Variation of V/V_o with oxidation time of lube oil without and with additive A_1 at different concentrations.

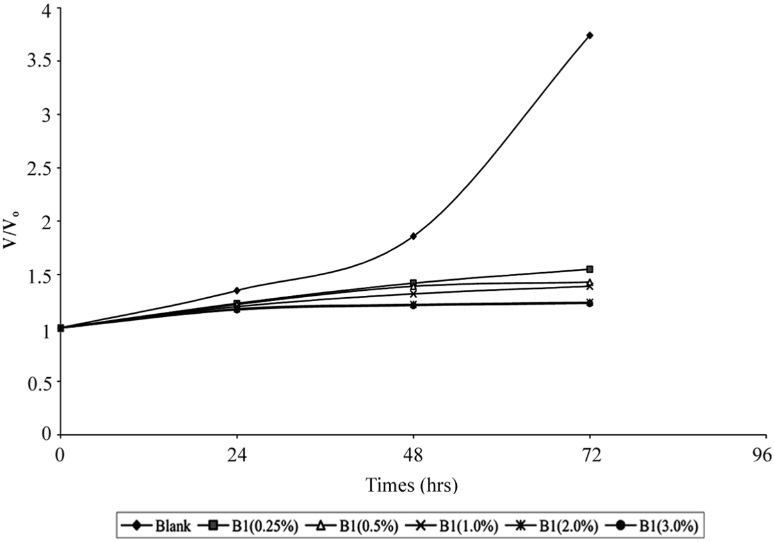

FIGURE 2 Variation of V/V$_o$ with oxidation time of lube oil without and with additive B_1 at different concentrations.

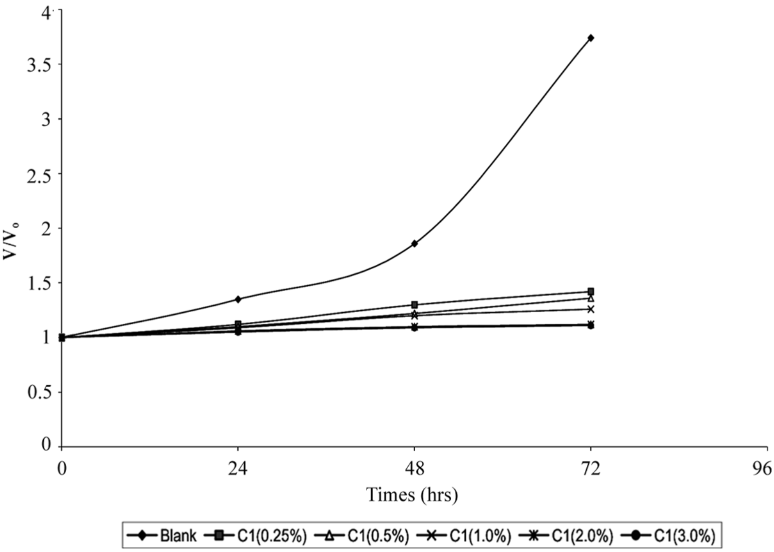

FIGURE 3 Variation of V/V$_o$ with oxidation time of lube oil without and with additive C_1 at different concentrations.

- The change of viscosity ratio V/V_o increases with increasing oxidation time.
- At any oxidation time the viscosity ratio V/V_o decreases with increasing concentration of the prepared compounds. The undoped oil always attained at higher values of V/V_o than those obtained from the oil samples blended with the prepared additives. The change in V/V_o decreases with increasing N-H groups in the molecule of the prepared compounds. Thus using the compound C_1, which was prepared from triethanolamine, gave better results than compounds A_1 and B_1, which were prepared from monoethanolamine and diethanolamine, respectively. In all cases, the results indicate that there is quite a wide difference between the lube samples mixed with prepared products and that of the neat lube oil. The efficiency of the prepared compounds as antioxidants is considered to be higher for the additive that yields lower ΔTAN with oxidation time for all doped oil samples as seen in Figures 4–6.

These figures show that there is a minimum value for ΔTAN for the additives containing more N-H groups. The efficiency of the prepared compound C_1 as an antioxidant is better than A_1 and B_1. This is due to the increased number of N-H groups in each molecule which, in turn,

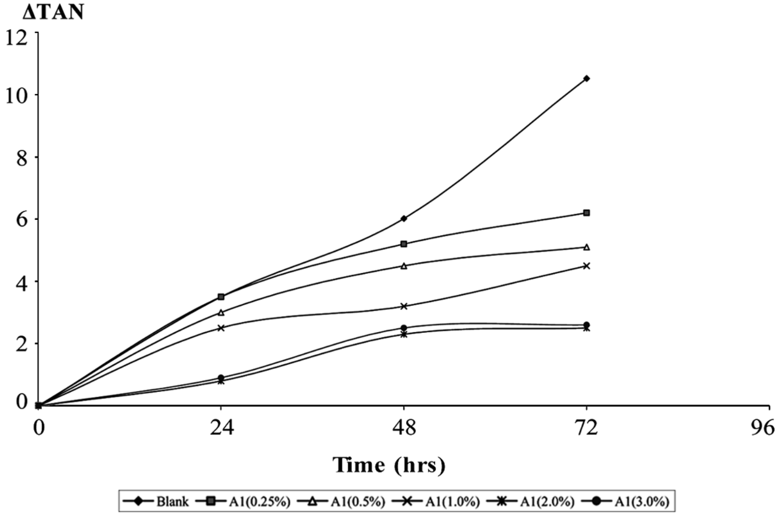

FIGURE 4 Variation of ΔTAN with oxidation time of lube oil without and with additive A_1 at different concentrations.

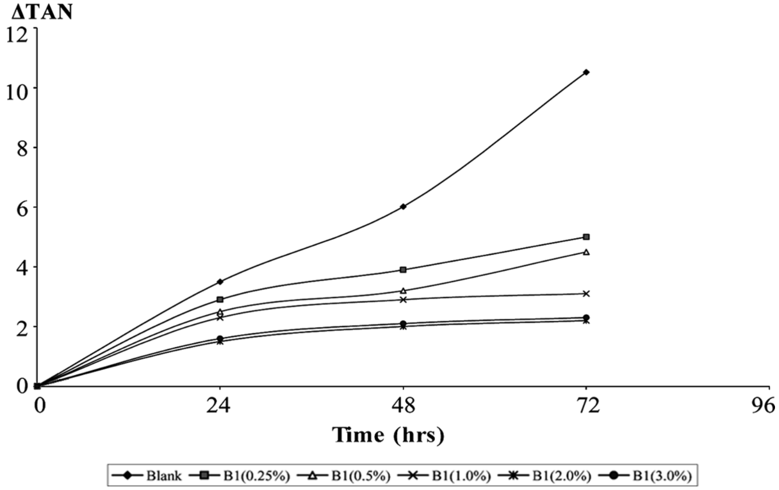

FIGURE 5 Variation of ΔTAN with oxidation time of lube oil without and with additive B_1 at different concentrations.

increases basic character of the compound C_1, and hence acts as a better neutralizing agent for the acidic oxidation products [23]. The measured values of V/V_o and ΔTAN for the doped oil samples with

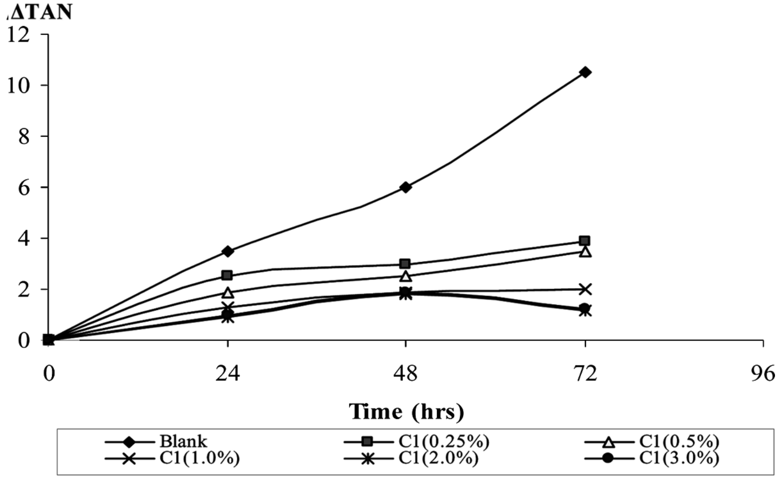

FIGURE 6 Variation of ΔTAN with oxidation time of lube oil without and with additive C_1 at different concentrations.

concentrations ranging between 0.2×10^3 ppm and 3×10^3 ppm are plotted in Figures 1–6. These plots reveal that the maximum activity is attained when the concentration of the additive is 3×10^3 ppm. Further increase in additive concentration leads to a slight reduction in the activity of this additive. In this respect, it seems that when the concentration increases, the solubility of the prepared compound decreases. Accordingly, the dispersion of the additive in the lube oil decreases with increases in concentration.

As Detergents/Dispersants

The oil samples mixed with prepared products have been subjected to severe oxidation conditions using Indiana test method for intervals of 24 h of oxidation. After each interval, spots have been taken and allowed to disperse on special filter papers for 48 h and the results were compared with those of undoped lube oil samples. The results given in Tables 3–5 indicate the following:

- In all cases the results indicate that there is a wide difference between the lube oil samples mixed with prepared products and those without additives.
- The efficiency of the prepared additives as lube oil dispersants increases by increasing the concentration of additive used.
- Increasing the number of -NH groups in the structure of prepared additives increases their capacity in dispersing sludge and solid particles present in the lube oil samples. This may be explained by the fact that -NH groups form hydrogen bonds with oxidation products. It is generally agreed that the additive is adsorbed on the surface of the carbon particles and thus prevents their agglomeration due to electrostatic phenomena (24) between polar group in additive molecular molecules and

TABLE 3 Dispersancy of Lube Oil and its Blends Containing Additive A_1 in Different Concentrations after Different Oxidation Periods

	Dispersancy time (hours)		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 0.25%	62	63	65
Lube oil + 0.5%	63	65	67
Lube oil + 1.0%	65	68	70
Lube oil + 2.0%	70	73	75
Lube oil + 3.0%	71	73	75

TABLE 4 Dispersancy of Lube Oil and its Blends Containing Additive B_1 in Different Concentrations after Different Oxidation Periods

	Dispersancy time (hours)		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 0.25%	65	70	75
Lube oil + 0.5%	69	72	77
Lube oil + 1.0%	75	79	82
Lube oil + 2.0%	80	82	85
Lube oil + 3.0%	81	83	86

TABLE 5 Dispersancy of Lube Oil and its Blends Containing Additive C_1 in Different Concentrations after Different Oxidation Periods

	Dispersancy time (hours)		
Sample	24	48	72
Lube oil only	35	33	32
Lube oil + 0.25%	69	73	79
Lube oil + 0.5%	74	79	85
Lube oil + 1.0%	83	85	87
Lube oil + 2.0%	85	90	95
Lube oil + 3.0%	86	91	96

the carbon particles. Thus, it maintains the carbon particles in the oil in a finely dispersed state so they are not deposited inside the engine, but are easily removed with the oil when it is drained.

- It was found that the additive C_1 is a more efficient dispersant than B_1 and A_1. This may be due to the additive C_1 containing more NH groups in its structure than B_1 and A_1.

CONCLUSIONS

The following conclusions could be derived from the results of this study.

1. The prepared additives impart better oxidation resistance properties to lube oil.
2. The efficiency of the prepared compound C_1 as antioxidant is better than A_1 and B_1.

3. The efficiency of the prepared additive as lube oil antioxidant and dispersants increases by increasing the concentration of additive used.
4. Increasing the number of -NH groups in the structure of prepared additives increases their efficiency as dispersants for sludge and solid particles.

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