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# Synthesis and utilization of non-metallic detergent/dispersant and antioxidant additives for lubricating engine oil



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## ABSTRACT

In the present work, different ashless detergent/dispersant additives based on propylene oxide (PO) were prepared via reaction of propylene oxide with different tertiary amines and the products which obtained were reacted with different organic acids. The structures of the prepared compounds were confirmed using fourier transform infrared spectroscopy (FT-IR), proton nuclear magnetic resonance (<sup>1</sup>H NMR) and gel permeation chromatography (GPC) for determination of molecular weight. All the prepared compounds were found to be soluble in lubricating oil. The efficiency of the prepared compounds as antioxidants and detergent/dispersant additives for lubricating oil was investigated. It was found that the additives have excellent power of dispersion, detergency and the most efficient additives as antioxidant those prepared by using n,n-dimethyloctadecylamine and di-n-butyl dithio phosphoric acid.

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## 1. Introduction

The development of lubricants has become an integral part of the development of machinery and its corresponding technologies. It is irrevocably and interdisciplinarily linked to numerous fields of expertise and without this interdisciplinary aspect, lubricant developments and applications would fail to achieve success [1].

Additives are synthetic chemicals used to improve different lubricant parameters, they can boost existing properties, eliminate adverse characteristics, or introduce new properties in the base oil. They can be added to base oils at percentage levels up to 5–30% of total weight [2]. At low temperature, the lubricant is expected to flow sufficiently in order that moving parts are not starved of oil. At high temperature, they are expected to keep the moving parts separated to minimize wear. The formation and accumulation of carbon deposits in the intake valves and ports of the fuel system during the operating of an internal combustion engine, is a common problem, which result in a decrement of the operational efficiency of the engine, due to these deposits restricting the flow of air–fuel entering the combustion chamber. The reduction of deposit levels has been the result of uses the detergent / dispersant additives [3].

Detergents and dispersants, often called DD or HD (heavy-duty) additives have been indispensable for the development of modern

engine oils for gasoline and diesel combustion motors. Detergents are the metal salts of organic acids [4,5]. The acids normally used to synthesize these compounds include arylsulfonic acids such as alkylbenzenesulfonic acids and alkylnaphthalenesulfonic acids; alkylphenols; carboxylic acids such as naphthenic acids, and petroleum oxides; and alkenylphosphonic and alkenylthiophosphonic acids.

Dispersant molecules are added to disperse the largely carbonaceous particulate by-products of the combustion process and engine oil degradation. This solid material leads to the formation of “sludge” in petrol engines (“soot” in diesel engines) which comprises both organic and inorganic components, accumulation of which can cause engine damage through wear and oil filter [6]. There are four different types of ashless dispersants: (1) succinimide, (2) succinate esters, (3) mannich types and (4) phosphorus types [7].

The lubricating oils consist of hydrocarbons with (C<sub>20</sub>–C<sub>70</sub>) carbon atoms. At higher temperature these hydrocarbons are oxidized to form acids, alcohols, aldehydes, ketones, esters and peroxides. All these compounds form the solid asphaltic materials. For this reason, the addition of antioxidants is necessary to all lubricating oils to minimize the formation of such compounds [8,9]. As the role of antioxidants is to protect the type of base oil by either scavenging (alkyl and peroxy) radicals, or decomposing hydroperoxides into stable products [10,11]. The present work aims to preparation of different ashless detergent/dispersant additives based on propylene oxide and evaluation of the prepared compounds as antioxidant and detergent/dispersant for lubricating oil.

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## 2. Experimental

### 2.1. Synthesis of propoxylated amines

One mole of propylene oxide (PO) and one mole of different types of tertiary amine (triethanolamine, 2-(dibutylamino)ethanol and n,n-dimethyloctadecylamine) and Two mole of water in were mixed in three-round bottom flask equipped with a mechanical stirrer and thermometer. The reaction mixture was maintained at temperature  $120\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  with continuous stirring for about 4 h, then cooled to the ambient temperature. The products were obtained (A, B and C) and their designation shown in Table 1.

### 2.2. Esterification of propoxylated amines with different organic acids

The reaction was carried out in three-round bottom flask equipped with a mechanical stirrer, efficient condenser and thermometer. In the flask was placed one

mole of the prepared propoxylated amines and one mole of different organic acids (stearic acid, dodecylbenzenesulphonic acid and di-n-butylthiophosphoric acid). The reactants which mixed with an equal weight of xylene and heated gradually to  $130\text{ }^{\circ}\text{C} \pm 5\text{ }^{\circ}\text{C}$  with continuous stirring for about 4 h using a well-controlled thermostat. The extent of reaction was followed by monitoring the amount of liberated water to give products; therefore we have 9 different products, their designation shown in Table 1.

### 2.3. Characterization of the prepared compounds

#### 2.3.1. Infrared spectroscopic analysis

The prepared compounds were characterized by using FT-IR.

Spectrometer Model Type “Nicolet iS10 FT-IR Spectrometer,”—made in USA.

Spectral resolution: better than  $0.4\text{ cm}^{-1}$ , non-apodized, and sample prepared as disk.

Room temperature, KBr optics, DTGS detector,  $4\text{ cm}^{-1}$  spectral resolutions.

Maximum speed: 40 spectra per second at  $16\text{ cm}^{-1}$  resolution.

#### 2.3.2. Determination of molecular weights

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

#### 2.3.3. Proton magnetic resonance analysis

The prepared compounds were characterized by  $^1\text{H}$  NMR spectroscopy.

**Table 1**  
The designation of prepared compounds.

abbreviation	Prepared compounds
<b>A</b>	<b>Triethanolamine + PO + H<sub>2</sub>O</b>
A <sub>1</sub>	A + Stearic acid
A <sub>2</sub>	A + Dodecylbenzenesulphonic acid
A <sub>3</sub>	A + Di-n-butylthiophosphoric acid
<b>B</b>	<b>2-(Dibutylamino)ethanol + PO + H<sub>2</sub>O</b>
B <sub>1</sub>	B + Stearic acid
B <sub>2</sub>	B + Dodecylbenzenesulphonic acid
B <sub>3</sub>	B + Di-n-butylthiophosphoric acid
<b>C</b>	<b>N,N-Dimethyloctadecylamine + PO + H<sub>2</sub>O</b>
C <sub>1</sub>	C + Stearic acid
C <sub>2</sub>	C + Dodecylbenzenesulphonic acid
C <sub>3</sub>	C + Di-n-butylthiophosphoric acid

Using  $^1\text{H}$  NMR type [300 M.Hs. spectrophotometer W-P-300, Bruker].

### 2.3.4. Solubility test

The solubility of the prepared compounds was investigated by dissolving the compounds in free additive base oil (SAE 30) from “Cooperation Company for petroleum”. In a conical flask, 2 g of compounds was added to previously weight base oil (100 g) and the mixture was allowed to stand overnight. The conical flask was immersed in an oil bath placed on a thermostated hot plate fixed over a magnetic stirrer. The temperature of the oil bath was then raised to  $60\text{ }^{\circ}\text{C}$  and at this point the mixture was agitated by a Teflon covered magnet for 20 min.

### 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 severe oxidation condition in the presence of copper and iron strips at  $165.5\text{ }^{\circ}\text{C}$  for 72 h using the Indiana test method of oxidation [12]. The oxidation stability of the lube oil blends were determined by taking samples at 24 h intervals to 72 h. These samples were tested for:

2.4.1.1. *Variation of viscosity ratio  $V/V_0$* . The variation of viscosity ratio ( $V/V_0$ ) has been determined using IP 48/86 method,

where:  $V$  = Kinematic viscosity at  $40\text{ }^{\circ}\text{C}$  of sample after oxidation.

$V_0$  = Kinematic viscosity at  $40\text{ }^{\circ}\text{C}$  of sample before oxidation.

The prepared compounds were evaluated using Koehler laboratory bath Model K2337800000, made in USA.

2.4.1.2. *Change in total acid number ( $\Delta\text{TAN}$ )*. The change has been calculated according to IP 177/83 method, where.

$\Delta\text{TAN}$  = (total acid number of sample after oxidation – total acid number of sample before oxidation).

The prepared compounds were evaluated using Potentiometric Titration Workstation (Mono buret), “TitraLab 960,” made in France.

2.4.1.3. *Optical density using infrared techniques*. The infrared spectra of oxidized oils have been determined in the range of the carbonyl group absorbance ( $1500\text{--}1900\text{ cm}^{-1}$ ). The spectra have been superimposed upon that of unoxidized oil. The absorbance (A) has been calculated according to

$$A = \log I/I_0$$

Where  $I$  is % transmittance of the oil after oxidation and  $I_0$  is the transmittance of the oil before oxidation.

#### 2.4.2. As detergents/dispersants.

2.4.2.1. *Spot method [12,13]*. 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 measure as follows:

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

The efficiency of dispersants has been classified as follows:

- Up to 30%: no dispersancy.
- 30–50%: medium dispersancy.
- 50–60%: good dispersancy.

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