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DEPOSIT CONTROL AGENTS FOR LUBRICATING OIL

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Abstract

Different Mannich base compounds based on polyisobutylene succinic anhydride (PIBSA) were prepared. The structures of the prepared compounds were confirmed using Fourier Transform Infrared Spectroscopy (FTIR), Proton Nuclear Magnetic Resonance (^{1}H-NMR) and Gel Permeation Chromatography (GPC) for determination of molecular weight. The efficiency of the prepared compounds as antioxidants and detergents/dispersants were studied. It was found that the efficiency of the prepared compounds as dispersants increases with increasing the number of NH group. It was found that Mannich base compounds are more efficient as dispersants than that before Mannich base formation, and the efficiency of the prepared compounds as antioxidants increases by increasing the number of NH group. The Mannich base formation leads to enhanced efficiency as antioxidants than compounds before Mannich base.

Keywords: Lubricating Oil Additives; Mannich base; Antioxidants; Detergents and Dispersants.

1. Introduction

The term lubricating oil is generally used to include all those classes of lubricating materials that are applied as fluids [1]. The development of the modern engine and transmission technologies would have been impossible without advanced lubricant additives chemistry and lubricant formulation. 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 requirements [2-4].

Lubricant additives are compounds or mixtures when incorporated into a base lubricating fluid, supplement its natural characteristics and improve their field service performance in the existing application. The additives must not interfere with each other. Moreover, the materials used are normally more chemically reactive than the base oil [5-6]. Additives are added to the base oil in suitable proportions to produce finished oil according to the desired performance levels meeting the international classification [4].

Additives that reduce oil oxidation are called antioxidants, e.g., aromatic amines, hindered phenols, sulphurized phenols, and zinc dithiophosphates. Antioxidants act to retard oxidation of the lubricating oil, thus preventing the formation of corrosive products.

Detergent additives act to prevent an accumulation of sludge in the crankcase [7]. Detergents are an integral part of any engine oil formulation. Detergents are typically metal salts of organic acids, containing a surface active polar group which can react with metal surfaces to form a protective film that keeps metal surfaces of an engine clean. In addition to cleaning, detergents also neutralize acidic combustion and oxidation products, thereby, minimize corrosion, rust and deposit formulation in the engine [8]. The most widely used types of metallic detergents are the phenates, sulphonates, and salts of phosphorus acids [9].

Dispersants are additives which disperse sludge formed in engines operated at relatively low temperature [10]. The key function of a dispersant in an industrial or automotive lubricant formulation is to reduce oil thickening caused by accumulation and agglomeration of soot particles. Dispersants are major components of fully formulated automotive lubricants which maintain cleanliness by suspending dirt that result from oxidation of a lubricant, degradation of the lubricant additives, or incomplete combustion. Dispersants are relatively high molar mass polymers (1000-5000 MW) composed of non-polar hydrocarbon chains and a polar "head group" that typically contains oxygen and nitrogen. Hydrocarbon chains effectively ensure solubility of a polar head group in a non-polar hydrocarbon continuous phase (base oil), leading to the formation of inverse micelles [11]. There are four different types of ashless dispersants: (1) succinimide, (2) succinate esters, (3) Mannich types and (4) phosphorus types [4].

In the present work different Mannich base compounds based on polyisobutylene succinic anhydride (PIBSA) were prepared and evaluated as antioxidant and detergents/dispersants for lube oil.

2. Experimental

2.1. The reaction of (PIBSA) with trimethylol propane (TMP)

In a three-necked flask fitted with reflux condenser, mechanical stirrer, and thermometer, one mole of PIBSA and one mole of trimethylol propane (TMP). In the presence of xylene solvent and catalyst (p-toluene sulphonic acid) 0.5% of total weight. The mixture was refluxed at 130°C for 3 hrs., and then extracted of xylene from the product group (A) by rotary, their designation shown in Table 1.

Table 1. The designation of the group (A).

Abbreviation	Prepared compounds	Abbreviation	Prepared compounds
Group (A), Trimethylol Propane.		Mannich base of the group (A).	
A	PIBSA + TMP	A_{1M}	A_1+ HCHO + dodecyl phenol
Amination of group (A)		A_{2M}	A_2+ HCHO + dodecyl phenol
A_1	A + ethylene diamine	A_{3M}	A_3+ HCHO + dodecyl phenol
A_2	A + diethylene triamine	A_{4M}	A_4+ HCHO + dodecyl phenol
A_3	A + triethylene tetramine		
A_4	A + tetraethylene pentamine		

2.2. Amination of group (A)

In three-necked flask fitted with mechanical stirrer, thermometer, Dean-stark and reflux condenser, one mole of the compound after reaction with TMP, with one mole of different amine (ethylene diamine, diethylene triamine, triethylene tetramine, and tetraethylene pentamine), the mixture dissolved in approximately 30 ml of toluene and heated to 120°C to 2 hrs. That produces four different compounds, their designation is shown in Table 1.

2.3. Mannich base preparation of group (A)

In a three-necked flask fitted with mechanical stirrer, thermometer, Dean-stark and reflux condenser, one mole of the aminated compounds "have different amines" with an equal amount of dodecyl phenol, formalin solution (formaldehyde) and 5% of total weight of the reactant NaOH 10% (soln.). The mixture was refluxed at 100-105°C for 3 hrs the reaction was continued as previous. Therefore, we will have another four products, their designation shown in Table 1.

2.4. Characterization of the prepared compounds

The prepared compounds were characterized by FTIR-spectroscopy using FTIR spectrophotometer type [Mattson-Infinity series bench top 961], ^{1}H NMR spectroscopy using ^{1}H NMR type

[300 M.Hs. spectrophotometer W-P-300, Bruker] and the molecular weights of the prepared compounds were determined by Gel Permeation Chromatograph (GPC) Water model 600E.

2.5. Solubility test

The solubility of the prepared compounds was investigated by dissolving the prepared compounds (additives) in lube oil (free from any additives) (SAE 30). In a conical flask, 2 g of the prepared compounds was added to a previously weighted lube oil (100g) and the mixture was allowed to stand overnight. This time was enough to procure the required swelling for the additive. 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^{o}C and at this point, the mixture was agitated by a Teflon covered magnet for 20 minutes.

3. Evaluation of the prepared compounds as lube oil additives

3.1. Evaluation as antioxidants

The lube oil samples as well as its blends with 2% by weight of each of the prepared additives were subjected to sever oxidation condition in the presence of copper and iron strips at 165.5^{o}C for 72 hrs using the Indiana test method of oxidation [12]. The oxidation stability of the lube oil blends was determined by taking samples at 24 hrs intervals to 72 hrs. These samples were tested for:

3.1.1. Variation of viscosity ratio V/Vo

The variation of viscosity ratio (V/Vo) has been determined using IP 48/86 methods, where: V=kinematic viscosity at 40^{o}C of the sample after oxidation; Vo=kinematic viscosity at 40^{o}C of the sample before oxidation.

3.1.2. Change in total acid number (ΔTAN)

The change has been calculated according to IP 177/83 methods, where: ΔTAN= (total acid number of the sample after oxidation – total acid number of the sample before oxidation).

3.2. Evaluation as detergents/dispersants

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

$$\%\ dispercancy = \frac{diameter\ of\ the\ black\ spot\ x\ 100}{diameter\ of\ the\ total\ spot}$$

The efficiency of dispersants has been classified as follows:

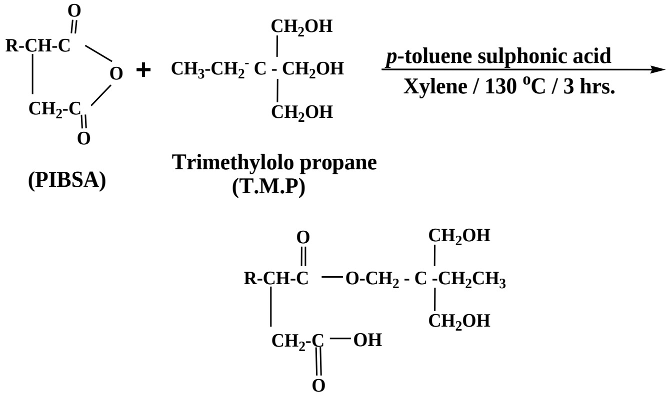
- Up to 30%: no dispersancy;
- 30-50%: medium dispersancy;
- 50-60%: good dispersancy;
- 60-70%: very good dispersancy;
- Above 70%: excellent dispersancy.

4. Results and discussions

The reaction of PIBSA with trimethylol propane (TMP.) to produce a product (A), Scheme 1.

The IR spectrum of the prepared product (A) given in Fig. (1), indicate the presence of broad band at 3200-3600cm^{-1} for OH group, the disappearance of two bands of anhydride group and appear of carboxylic –C=O at 1732cm^{-1}, and the presence of – C–O group at the range of 1000-1250cm^{-1}.

The ^{1}H-NMR spectrum of the prepared product (A) given in Fig. 2, indicates the presence of a band centered at 1.2ppm corresponding to the methylene group of polyisobutylene, the presence of a band at 2.5ppm corresponding to methylene bonded to the carbonyl group ($-CH_2-C=O$), and the band at 3.9ppm for ($O=C-O-CH_2$), and the presence of band at 5.2ppm corresponding (OH) group and the carboxylic group (COOH) appear at 10.5-12ppm (out of range).



Scheme 1, product A

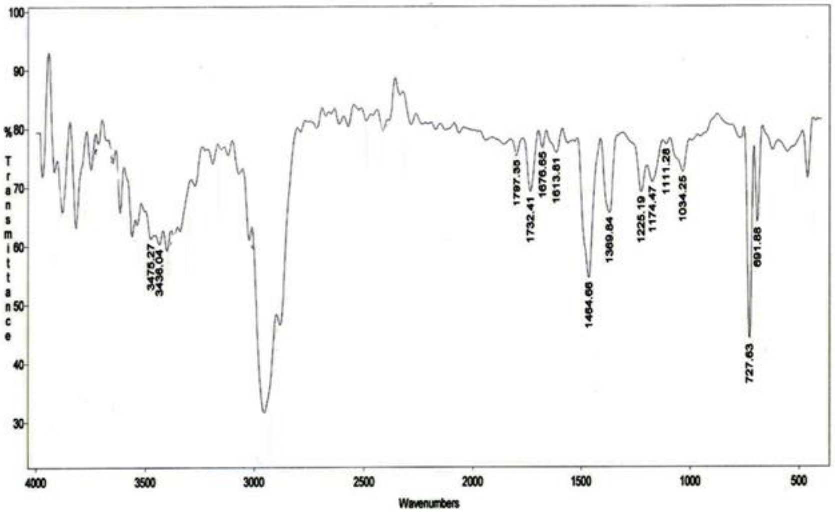


Figure 1. IR spectrum of compound (A)

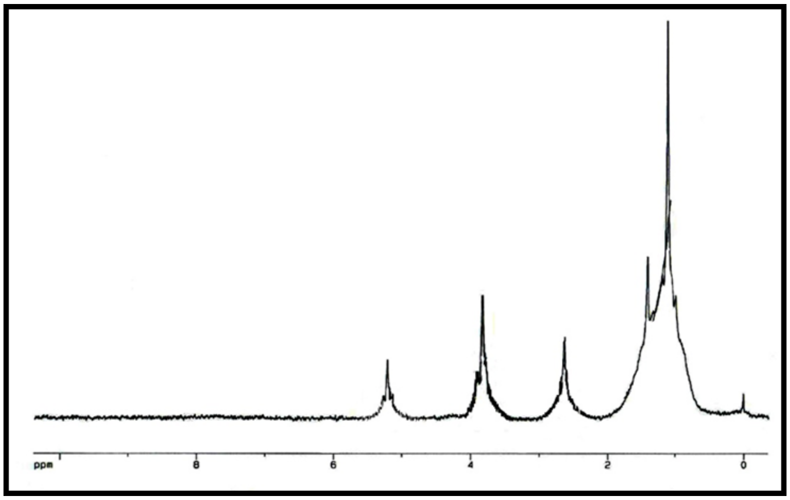


Figure 2. 1H NMR spectrum of compound (A)

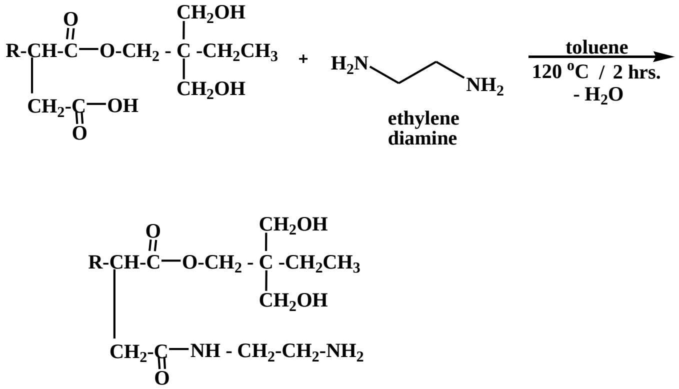
The determined mean molecular weights of the prepared product (A), was in a good accord with the theoretical molecular weight, the data are present in Table 2.

Table 2. Theoretically and determined the mean molecular weight of product (A).

Compound	Theoretical MW.	Determined MW
A	1232.18	1234

4.1. Reaction of the prepared product (A) with different ethylene polyamines

The prepared product (A) reacted with different polyethylene polyamine (ethylene diamine, diethylene triamine, triethylene tetramine, tetraethylene pentamine), Scheme 2 to produce four different compounds [A_1, A_2, A_3 and A_4].



Scheme 2. Product (A_1)

The IR spectrum of the prepared compound (A_1) after amidation given in Fig. 3 indicates the presence of a broad band at 3200-3600 cm^{-1} for NH and OH group. The appearance of C=O of an amide at 1649 cm^{-1}. C=O of ester appears at 1732 cm^{-1}. The C-O band appears at rang of 1000-1250 cm^{-1}.

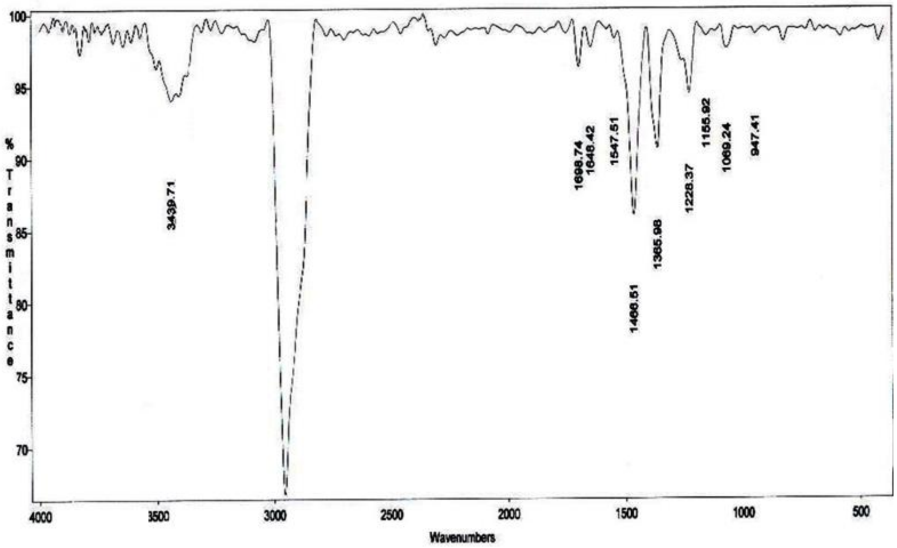


Figure 5. Infrared spectrum of the prepared product (A3M)

The ^1H NMR spectrum of the prepared product (A_2) given in Fig. 4 indicates the presence of a band centered at 1.2ppm corresponding to methylene group of polyisobutylene, the band at 2.5ppm arises from methylene bonded to the carbonyl group ($-CH_2-C=O$) and the proton of OH group, the band at 3.9ppm for proton ($O=C-O-CH_2$), and the band at 3.3ppm for amide, and the band at 7.2ppm for ($-NH_2$).

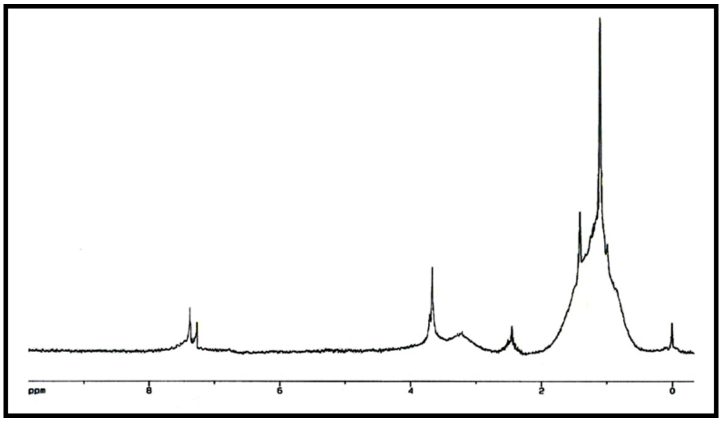


Figure 6. 1H NMR of the prepared product (A2M)

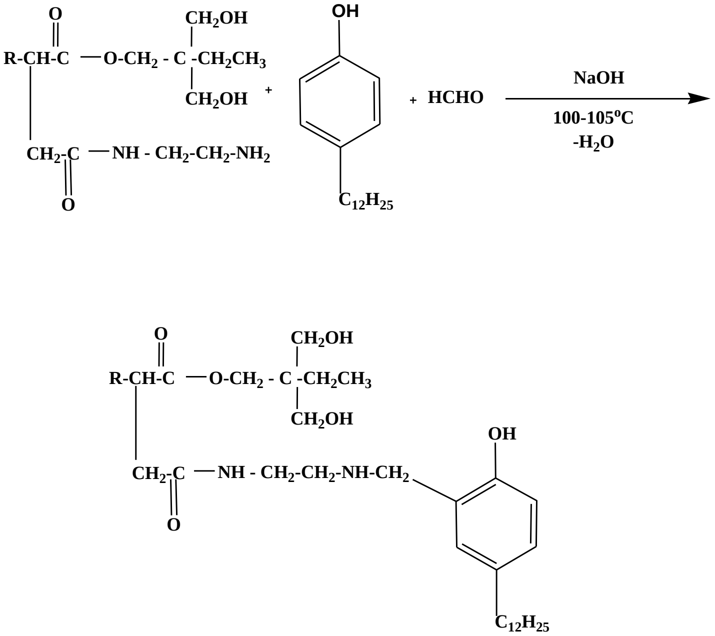
The determined mean molecular weights of the prepared products [A_1, A_2, A_3 and A_4] have been found to very near from that calculated theoretically that shown in Table (3).

Table 3. Theoretically and determined mean molecular weights of the group [A] after amination.

Compounds	Theoretically MW	Determined MW
A_1	1274.28	1276
A_2	1317.17	1320
A_3	1360.42	1362
A_4	1403.49	1405

4.2. Mannich base reaction for the prepared products [A]

Mannich base prepared by condensation of dodecyl phenol and formaldehyde with the prepared compounds(A_1, A_2,A_3,A_4), which give four different products [A_{1M}, A_{2M}, A_{3M} and A_{4M}] as the difference of ethylene polyamine respectively.



Scheme (3) (A_{1M})

The determined mean molecular weights of the prepared products [A_{1M}, A_{2M}, A_{3M} and A_{4M}] have been found to very near from that calculated theoretically that shown in Table 4.

Table 4. Theoretically and determined mean molecular weights of group [A] after Mannich base

Compounds	Theoretically MW	Determined MW
A_{1M}	1548.28	1550
A_{2M}	1591.17	1593
A_{3M}	1634.42	1637
A_{4M}	1677.49	1680

The IR spectrum of the prepared compound [A_{3M}] after Mannich base given in Fig. 5 indicate the presence of a broad band at 3200-3600 cm^{-1} for NH and OH group. The appearance of C=O of an amide at 1649 cm^{-1}.C=O of ester appears at 1732 cm^{-1}. The C-O band appears at rang of 1000-1250 cm^{-1}. C=C of alkenes appears at 1600-1680 cm^{-1}. C=C aromatic appears at 1475 and 1600 cm^{-1}.

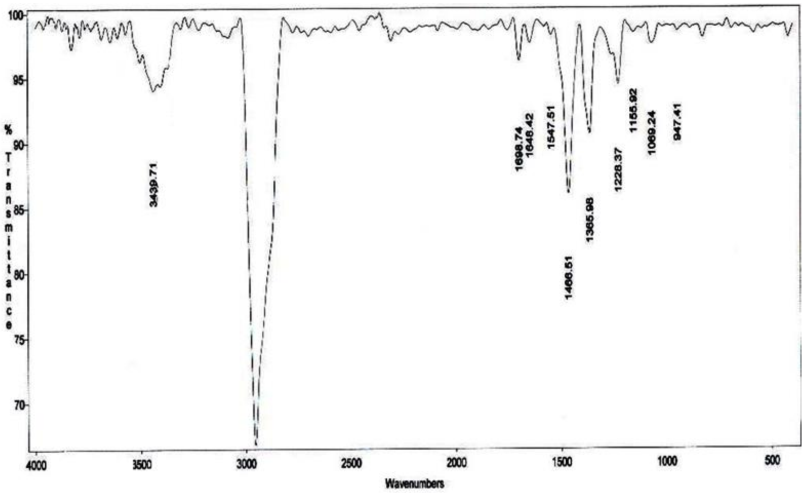


Figure 5. Infrared spectrum of the prepared product (A3M)

The ^1H NMR of the prepared product [A_{2M}] given in Fig. 6 illustrate the presence of a band centered at 1.2ppm corresponding to the methylene group of polyisobutylene, the band at 3.8ppm for the (O=C–O - CH_2), protons and the band at 7.5ppm for protons of benzene ring, the band at 2.4 ppm for (-CH_2-C=O) and OH proton, and the band at 3.3ppm for amide proton.

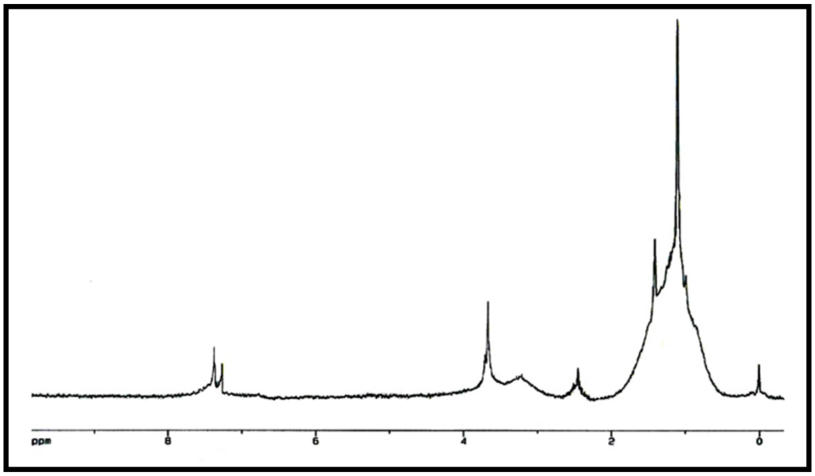


Figure 6. 1H NMR of the prepared product (A2M)

4.3. Evaluation of the prepared compounds as lube oil additives

4.3.1. As antioxidants

All the prepared products [A_1, A_2, A_3 and A_4] were added to a sample of "SAE-30" lubricating free from any additives, and undergo sever oxidation as illustrated previously will obtained and tested their oxidation stability expressed as increase in viscosity ratio (V/Vo) and change in total acid number (ΔTAN) were determined and compared with lube oil sample free from additives. Results are given in Table 5 and Fig. 7, 8.

Table 5. Oxidation stability of group (A) before the Mannich base of lube oil with 2 % wt. additives after different oxidation hours

Sample	(ΔTAN) time, hour				(V/Vo) time, hour			
	0	24	48	72	0	24	48	72
A_1	0	1.92	4.28	6.13	1	1.13	1.207	1.28
A_2	0	1.52	4.19	4.92	1	1.12	1.203	1.26
A_3	0	1.3	3.009	4.80	1	1.10	1.17	1.25
A_4	0	1.00	2.04	3.18	1	1.09	1.16	1.24
Blank	0	3.5	6.02	10.52	1	1.35	1.86	3.74

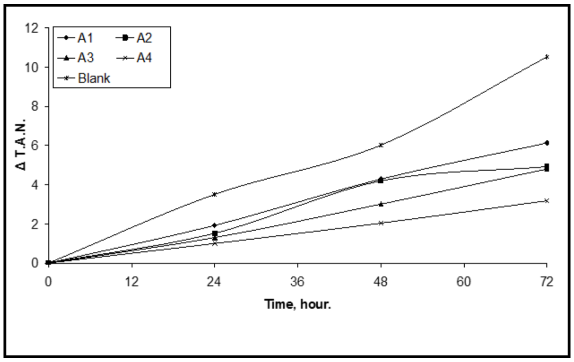


Figure 7. Variation of ΔTAN with oxidation time of lube oil without and with additives [A1 - A4]

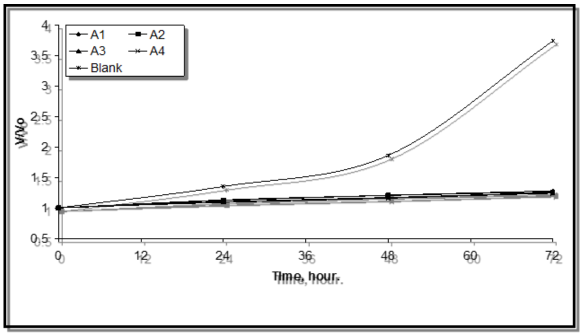


Figure 8. Variation of V/Vo oxidation time of lube oil without and with additives [A1 - A4]

It was found that the prepared compounds act as oxidation inhibitors which reduce the quantity of oxygen reacting with oil by forming inactive soluble compounds and by passiving metal bearing surfaces to retard the oxidation rate. Trimethylol propane esters exhibit several advantages as lubricating fluids. For example, TMP esters show excellent thermal stabilities, good friction reducing properties and acceptable anti-wear properties the presence of amino groups in their structures represent good character of oil antioxidants by donation of a labile hydrogen from such groups as OH or NH to stabilize the chain radicals, by destroy the peroxide radicals, and thus the oxidation chain is broken [14].

It was found that compound A_4 is the best as lube oil antioxidants, followed by A_3, A_2 and then compound A_1 comes later. The good efficiency of compound A_4 compared with the other is due to that it contains more number of NH groups in its structure.

4.3.2. As detergents/dispersants

All the prepared compounds [A_1, A_2, A_3 and A_4] have been added to lube oil samples in concentration of 2 wt.%, as the method illustrated previously. Results given in Table 6, show clearly that the prepared compounds have excellent dispersancy power (82-93%) for the sludge and soil particles formed during lube oil oxidation compared with the lube oil only. 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 neutralize some of the acidic products of oxidation due to their basic nature. The hydrogen bonding is one of the mechanisms proposed to explain the ability of metal organic or ashless motor oil dispersants to keep the engine clean [15]. That the compounds we prepared are riches in the OH group so it can be forming hydrogen bonds with the polar liquids.

Table 6. Percentage of dispersion (spot test method) of lube oil sample and its blends with additives (A) before the Mannich base, after different oxidation times (hrs.).

Sample	Percentage of dispersion, time (hours)		
	24	48	72
Blank	35	33	32
A_1	82	84	85
A_2	84	87	88
A_3	89	90	91
A_4	90	92	93

It is reasonable to assume that dispersants will form hydrogen bonds with hydroxylic compounds found in engine crankcases. This action will contribute to engine cleanliness by preventing the reaction of such sludge, varnish, and rust precursors as the alcohols, acids and hydroxyl acids, and by minimizing the agglomeration and deposition of sludge particles [15].

4.4. Evaluation of group [A] after Mannich base

4.4.1. As antioxidants

All the prepared products [A_{1M}, A_{2M}, A_{3M} and A_{4M}] were added to a sample of "SAE-30" lubricating of free from any additives, and undergo sever oxidation conditions illustrated previously and their oxidation stability expressed as increase in viscosity ratio (V/Vo) and total acid number (ΔTAN) were determined compared with lube oil sample free from additives. Results are given in Table 7 and Fig. 9, 10.

Table 7. Oxidation stability of group (A) after the Mannich base of lube oil with 2 % wt. additives after different oxidation hours

Sample	(ΔTAN) Time, hour.				(V/Vo) Time, hour.			
	0	24	48	72	0	24	48	72
A_{1M}	0	1.02	3.98	5.26	1	1.10	1.14	1.19
A_{2M}	0	0.35	3.12	3.94	1	1.09	1.12	1.17
A_{3M}	0	1.03	2.79	3.28	1	1.09	1.11	1.16
A_{4M}	0	0.95	2.60	2.40	1	1.00	1.00	1.10
Blank	0	3.5	6.02	10.52	1	1.35	1.86	3.74

All the prepared compounds impart better oxidation resistance properties to the lube oil compared with the undoped oil and the same group before Mannich base preparation. This may be attributed to the presence of amine groups and the alkyl phenol that condensed with an amine to contain aromatic amine. The amines groups have inhibitors function by donation of a labile hydrogen from such groups as OH or NH to stabilize the chain radicals, i.e. these inhibitors destroy the peroxide radicals, and thus the oxidation chain is broken. The presences of the amine group in the structure of the prepared compounds neutralize some of the acidic products of the lube oil oxidation. In the other hand, the phenolic antioxidants are especially considered because they can directly seize peroxy radicals formed during oxidative degradation, thus breaking the auto-oxidation chain reaction [16-17].

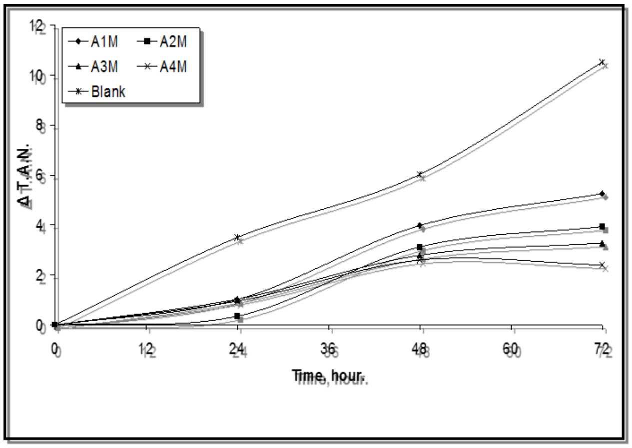


Figure 9. Variation of ΔTAN with oxidation time of lube oil without and with additives [A1M - A4M]

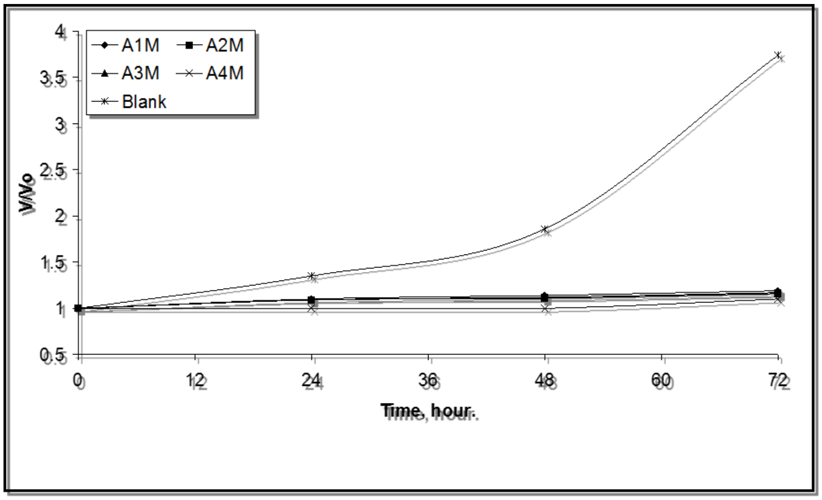


Figure 10. Variation of V/Vo with oxidation time of lube oil without and with additives [A1M - A4M]

It was found that compound A_{4M} is the best as lube oil antioxidants, followed by A_{3M}, A_{2M} and then compound A_{1M} comes later. The efficiency of compound A_{4M} compared with the other is due to that it contains more number of NH groups in its structure.

4.4.2. As detergents/dispersants

The prepared additives [A_{1M}, A_{2M}, A_{3M} and A_{4M}] have been added to lube oil samples in the concentration of 2 % Wt., the method illustrated previously. Results given in Table 8, show clearly that the prepared compounds have excellent dispersancy power (84-96%) for the sludge and soil particles formed during lube oil oxidation compared with the lube oil only.

Table 8. Percentage of dispersion (spot test method) of lube oil sample and its blends with additives (A) after Mannich base, after different oxidation times (hrs).

Sample	Percentage of dispersion, time (hours).		
	24	48	72
Blank	35	33	32
A_{1M}	84	86	88
A_{2M}	89	91	92
A_{3M}	90	92	93
A_{4M}	93	95	96

Data also show that compound A_{4M} gives excellent dispersancy power during the periods of 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 neutralize some of the acidic products of oxidation due to the presence of the Mannich base structure.

5. Conclusions

Different Mannich base compounds based on polyisobutylene succinic anhydride (PIBSA) were prepared. The structures of the prepared compounds were confirmed. All the prepared compounds were found to be soluble in lube oil.

The efficiency of the prepared compounds as antioxidants and detergents/dispersants were studied. It was found that the additives have the excellent power of dispersion and detergency. The efficiency of the prepared compounds as dispersants increases with increasing the number of NH group. The Mannich base compounds are more efficient as dispersants than compounds before Mannich base formation. The efficiency of the prepared compounds as antioxidants increases by increasing the number of NH group. The Mannich base formation leads to enhanced efficiency as antioxidants than compounds before Mannich base.

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