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FULL LENGTH ARTICLE

Preparation and evaluation of some benzimidazole derivatives as antioxidants for local base oil

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KEYWORDS

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Alkyl amines;
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Oxidation stability;
Total acid number

Abstract Some benzimidazole derivatives, 2(1-H benzo(d)imidazole-2-y1)thio) N-butyl acetamide Ia, 2(I-H benzo(d)imidazole-2-yl)thio) N-octylacetamid Ib and 2(I-H benzo(d)imidazole-2-yl) thio) N-dodecylactamide Ic were prepared and studied as antioxidants for base stock. The structure of these compounds was elucidated by elemental analysis, IR and ^{1}H NMR spectroscopy. The inhibition efficiency of the prepared compounds was determined by studying the oxidation stability of the local base oil via the change in total acid number (TAN), viscosity and infrared (IR) spectroscopy.

1. Introduction

Motor oil engine is the oil used for lubrication of various internal combustion engines. The main function of motor oil is to lubricate the moving parts; it also cleans, inhibits corrosion, improves sealing and cools the engine parts by carrying heat away from moving parts [1].

The deterioration of lubricating oil often leads to the buildup of insoluble deposits or sludge and consequently the viscosity increases during use. In order to avoid these problems, lubricants need to possess superior oxidative stability. The degradation of lubrication oil resulting in increase in acidity and viscosity reduces the efficiency of the system [2]. Usually lubricating oils operate at higher severities of temperatures and pressure, therefore it's required to improve thermal and oxidative stability and excellent temperature-viscosity characteristics allowing the oil to meet the demanding requirements for use in industrial application [3]. Therefore addition of antioxidants is the suitable way to protect the lubricant from oxidative degradation during industrial application [4].

Sulfur and phosphorous contents of any additive must be used with the lowest level in the formulation of industrial oil [5,6]. Most of heterocyclic compounds which have compact structure possess antioxidant, anticorrosion and antiwear properties [7–9]. Amer et al. [10] studied the effect of some synthesized thiazoles as antioxidant additives for Egyptian lubricating oils. They studied the effect of concentration of the most effective antioxidant in order to obtain the optimum concentration to be used. They concluded that increasing the additive concentration led to a decrease in oxidative products. The

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antioxidant activities of some poly-functionalized phenols linked to heterocyclic derivatives were evaluated [11].

2. Experimental

All reagents (purchased from Merk Co., Aldrich and Fluka Chemical Co.) were of analytical grade and used without further purification. The tested base stock was delivered from Alexandria petroleum Company. The physicochemical characteristics of the base stock are tabulated in Table 1.

2.1. Preparation of additives (Ia–c)

The additives were prepared [12] according to the pathway outlined in Scheme 1.

2.1.1. Preparation of the ester ethyl-2((I-H benzo(d)imidazole-2-yl) thio acetate)

In a 250-cc round-bottomed flash are placed 15.02 g. (0.1 moles) of 2-mercapto-benzoimidazole (I) and 12.25 g of ethyl chloroacetate (0.1 mol). This mixture is then refluxed for three hours in ethanol. The ester is then collected and recrystallized from n-pentane (with a 70% yield) and its melting point is measured (136–138 °C).

Table 1 Physicochemical characteristics of base stock.

Test	Test method	Result
Density at 15.5 °C, g/L	ASTMD4052	0.8916
Pour point, °C	ASTMD97	−3
Viscosity 40 °C	ASTMD-445	170.5
100 °C	ASTMD-445	15.03
Viscosity index (VI)	ASTMD-2270	86
Total acid number (TAN)	ASTMD-664	0.025
Sulfur content, wt%	ASTMD-4294	0.53
Carbon residue wt%	ASTMD-524	0.7
Ash content, wt%	ASTMD-482	0.004
Wax content, wt%	UOP 46	0.85
Copper corrosion	ASTMD-190	Ia
Water content, ppm	ASTMD-1744	50

2.1.2. Preparation of additives, 2((I-H benzo(d)imidazol-2-yl) thio) N-alkyl acetamide (Ia–c)

In a 100-cc conical flask are placed 11.8 g. (0.05 mol) of ester and (0.05 mol) of N-alkyl amines, (N-butylamine (a), N-octylamine (b) and N-dodecylamine (c). The mixture is cooled to zero °C in ethanolic KOH for one hour. The products (Ia–c) were filtered and recrystallized from ethanol. The compounds were characterized by elemental analysis, IR and ^{1}H-NMR spectrophotometric techniques.

2.2. Oxidation stability study

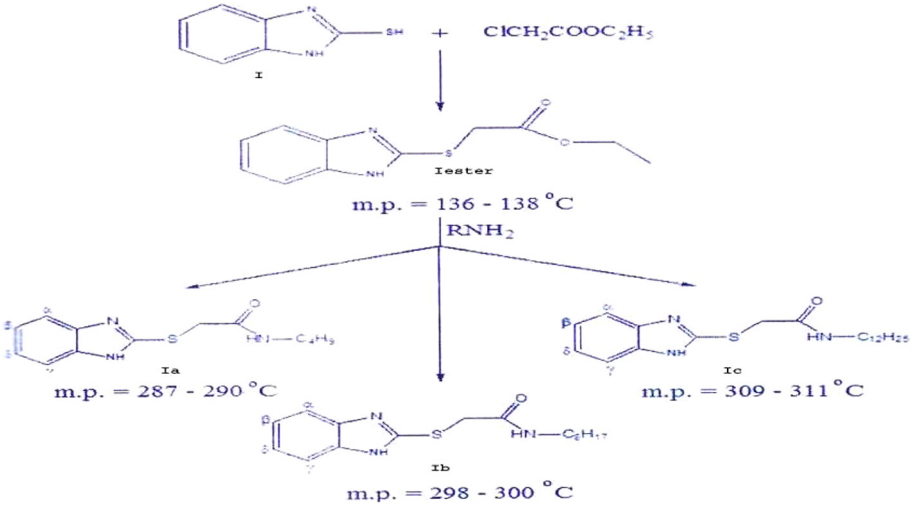
The oxidation test was carried out at 120 °C, according to ASTM D-943 standard method. The oxidation cell in the static mode contained 250 ml. base stock, and activated copper and iron wires catalysts. The base stock sample was subjected to oxidation with pure oxygen (99.95%) at a flow rate of 0.1 L/h for maximum 96 h. The characterized 2-mercaptobenzimidazole and its derivative (Ia–c) compounds were added in different concentrations, ranging from 200 to 1000 ppm. The oil sample after, 24, 48, 72 and 96 h of oxidation times were analyzed for their viscosity, total acid number and infra-red spectroscopy.

2.2.1. Total acid number (TAN), and viscosity

Total acid number and viscosity were carried out according to ASTM standard test methods (D-664 and D-445, respectively).

2.2.2. FT-IR spectroscopy

Infra-red spectra of the oxidized samples at different periods were recorded on FT-IR Spectrophotometer, Model 960 M00g, ATI Mattson Infinity Series, USA. A thin film of the sample, 5 mm thickness and 13 mm diameter and spacers with 0.025 mm thickness (path length) were used. The spectra of the studied samples were measured in the range of 4000–400 cm^{-1} with a suitable scan resolution 4 cm and scan rate 32 cm/min. Elemental analyses were carried out in the Micro Analytical



Scheme 1 Preparation of additives (Ia–c).

Center, the center publication for research, Cairo, Egypt. By Elementary Viro El Microanalysis, ^{1}H-NMR spectra recorded on a Varian 300 MHz (Germany 1999) using TMS as internal standard (Cairo University).

3. Results and discussion

Lubricating oils consisted mainly of long chain hydrocarbons which were produced by solvent refining of high boiling petroleum distillates. The oxidation of these organic species caused deterioration especially at high temperatures and in the presence of air and metals [13].

Auto-oxidation, as a result of contact with air at elevated temperatures for long times in contact with metal forming oxygenated compounds, increased the oil viscosity and motor metal corrosion. Antioxidant additives as organic heterocyclic compounds were used for lubricating oils (e.g. thiazoles derivatives) [14–18]. We prepared some newly heterocyclic compounds (Ia–c) and their anti-oxidation activities for some Egyptian base stocks were evaluated. These compounds were characterized by elemental analysis (Table 2), infra-red spectroscopy, (Table 3) and ^{1}H-NMR-chemical shift, (Table 4).

3.1. Evaluation of the prepared compounds as antioxidants

The result showed that, in the absence of the additive increased the oxidative products with time but with the presence of the prepared additives, the oxidation products also increased but at a rate much less than those in the absence of the additives. The data shown in Tables 6–9 and Figs. 1–4 reveal that the prepared compounds are good oxidation resistances compared with the fresh oil. The data also show that the TAN and viscosity increase with increasing the oxidation time even in the presence of additive of additive compounds. This means that the oxidation of the oil may lead to the formation of carboxylic acids and many oxidative products. In all cases the formation of such compounds is always less than that formed on subjected the fresh oil in the absence of additives.

Table 5 Assignments for absorption associated with base stock oxidation (♀).

Region, cm^{-1}	Assignments
3600–3000	Mainly hydroxyl species
2800–2200	Hydrogen bonded hydroxyl
1850–1600	Mainly carbonyl compounds
1850 > 1800	Probably lactones and anhydrides
1800 > 1745	Probably lactones (5-membered), proxy acids, anhydrides
1745 > 1700	Easter, acids, ketones, aldehydes, etc.
1700 > 1600	Corboxylates and conjugated compounds
1270–1000	Mainly oxygenated compounds, alcohols, glycols, ethers, lactones, sulfates, etc

(♀) From John P. Coals and Lynn C. Setti. Infra-red spectroscopy as a tool for monitoring oil degradation, aspects of lubricant oxidation, ASTM STP 916, W.H. Stadt-Miller and A.N. Smith, Eds. American Society for Testing and Materials, Philadelphia, pp. 57–78, 1986.

3.1.1. Effect of additive concentration

The study of the effect concentration of the prepared additives was carried out. Four different concentrations, 200 ppm, 400 ppm, 500 ppm and 1000 ppm of each additive were used (the determined concentration calculated on the bases of the effective element, "sulfur" in the molecule) and the total acid

Table 2 Elemental analysis data of (Ia–c).

Cpd.	Ccalc.%	Cobs%	Hcalc%	Hobs%	Ncalc	Nobs%	Scalc%	Sobs%
Ia	59.32	59.14	06.46	06.57	15.97	16.04	13.17	12.42
Ib	63.95	63.57	07.83	07.95	13.17	13.09	10.03	10.14
Ic	67.20	67.20	08.80	08.67	11.20	11.38	08.53	08.44

Table 3 Infrared spectral results of (Ia–c).

Cpd.	NH	OH	CH_2	C═O	CONH	C═N
Ia	3328	3465	2930	-	1648	1579
Ib	3274	3553	2922	-	1638	1588
Ic	3281	3540	2918	-	1637	1592

Table 4 Chemical shifts (δ) of (Ia–c).

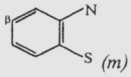
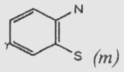
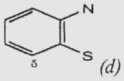
Cpd.					SCH_{2C} methylene (s)	NCH_2 methylene (s)	NH amide (s)	—(CH_2)—	CH_3
Ia	7.42	7.26	7.26	7.42	4.19	3.57	12.08	1.37	0.80
Ib	7.40	7.13	7.13	7.40	4.31	3.97	12.05	1.36	0.85
Ic	7.36	6.96	6.96	7.36	4.31	3.86	11.75	1.32	0.87

Table 6 Variation of total acid number, viscosity and carbonyl group of compound I with oxidation time and concentration.

	Total acid number × 10^2				Viscosity × 10^2				Intensity of carbonyl × 10^4			
	24	48	72	96	24	48	72	96	24	48	72	96
Fresh	75	140	190	231	1613	1642	1670	1741	915	1394	1520	1703
200	53	88	125	165	1578	1623	1636	1651	788	960	1156	1415
400	47	76	99	141	1568	1614	1630	1642	703	920	991	1386
500	46	72	90	125	1566	1610	1627	1635	698	898	974	1162
1000	35	55	83	108	1550	1579	1620	1631	671	794	948	995

Table 7 Variation of total acid TAN, viscosity and carbonyl group of compound ia with oxidation time and concentration.

	TAN × 10^2				Viscosity × 10^2				Intensity of carbonyl × 10^4			
	24	48	72	96	24	48	72	96	24	48	72	96
Fresh	75	140	190	231	1613	1642	1670	1741	915	1394	1520	1703
200	23	27	51	72	1531	1537	1576	1608	580	633	775	906
400	08	24	40	61	1508	1535	1559	1586	496	575	689	811
500	06	10	33	53	1505	1514	1548	1587	481	509	670	791
1000	55	78	96	134	1580	1617	1629	1637	803	930	985	1125

Table 8 Variation of total acid number, viscosity and carbonyl group of compound Ib with oxidation time and concentration.

	TAN × 10^2				Viscosity × 10^2				Intensity of Carbonyl × 10^4			
	24	48	72	96	24	48	72	96	24	48	72	96
Fresh	75	140	190	231	1613	1642	1670	1741	915	1394	1520	1703
200	33	58	51	72	1547	1587	1619	1628	642	801	921	987
400	22	56	40	61	1533	1547	1607	1627	615	792	902	975
500	58	50	33	53	1580	1629	1605	1624	582	774	889	970
1000	66	124	96	134	1593	1633	1650	1662	813	1312	1436	1486

Table 9 Variation of total acid number TAN, viscosity and carbonyl group of compound Ic with oxidation time and concerntration.

	TAN 10^2				Viscosity × 10^2				Intensity of carbonyl × 10^4			
	24	48	72	96	24	48	72	96	24	48	72	96
Fresh	75	140	190	231	1613	1642	1670	1741	915	1394	1520	1703
200	34	62	86	113	1549	1587	1624	1631	679	811	951	995
400	33	60	82	97	1546	1585	1620	1629	677	803	950	982
500	25	52	74	93	1535	1576	1609	1626	620	780	901	973
1000	73	131	177	192	1608	1636	1661	1673	905	1326	1453	1563

number, viscosity and intensity of carbonyl group were studied. The data show that the most effective concentration in all cases is 500 ppm i.e. the total acid number and the viscosity decrease by increasing the concentration of the additives.

3.1.2. Effect of time

There are two mechanisms namely oxidation and thermal decomposition during thermal degradation of engine lubricants. Mineral oil is very complex due to the presence of a large variety of molecular types and functional groups which makes the oxidation reactions extremely hard to understand. Our experiments were carried out at 24, 48, 72 and 96 h. As stated before, increasing the oxidation time, always increases both of total acid number and viscosity. The increase in TAN is due to the formation of appreciable amounts of oxygenated compounds especially acidic ketonic and alcoholic compounds. The increase in viscosity of oil by increasing the oxidation time is due to the formation of sludge and other higher molecular weight compounds.

3.1.3. Effect of substituted alkyl groups

From Scheme 1, and the data shown in Tables 6–9, we noticed that the most effective substituted group was shown with Ib and Ic (octyl and dodecyl amine respectively).

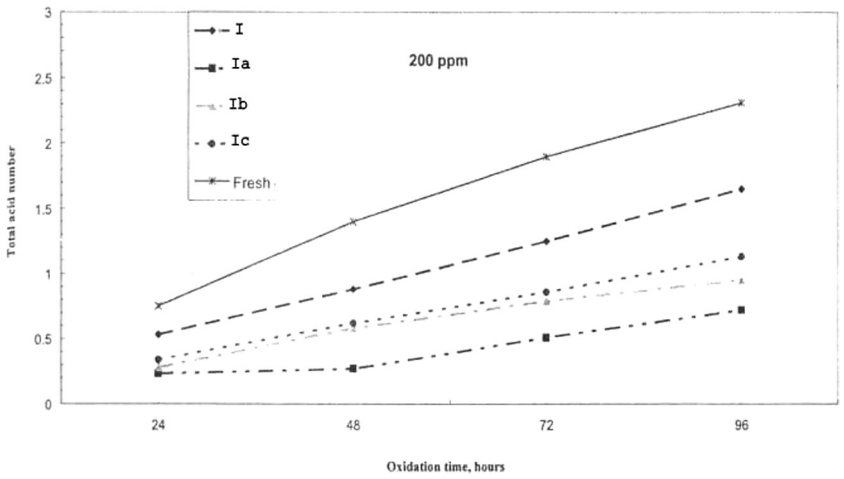


Fig. 1 Variation of total acid number (TAN) of compounds I Ia through Ic without additive and with 200 ppm additive.

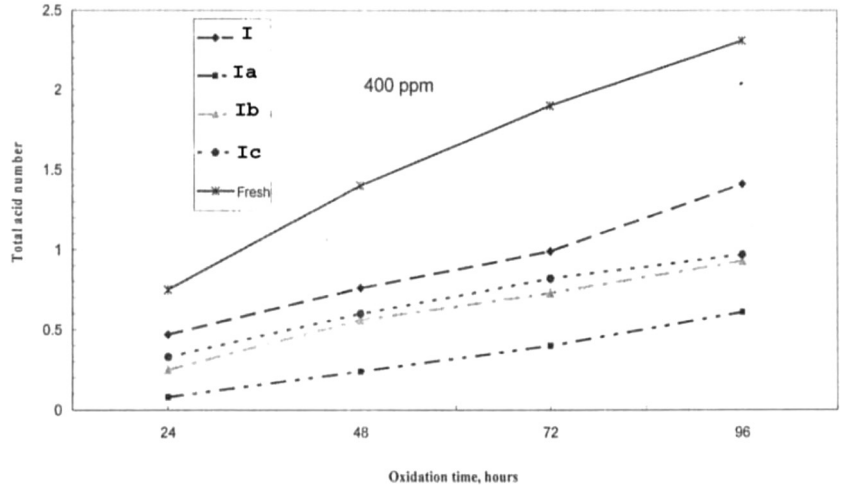


Fig. 2 Variation of total acid number (TAN) of compounds I Ia through Ic without additive and with 400 ppm additive.

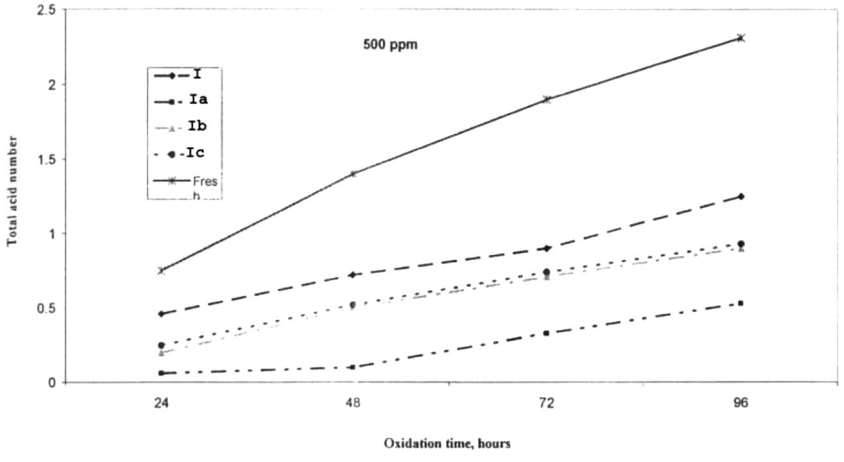


Fig. 3 Variation of total acid number (TAN) of compounds I Ia through Ic without additive and with 500 ppm additive.

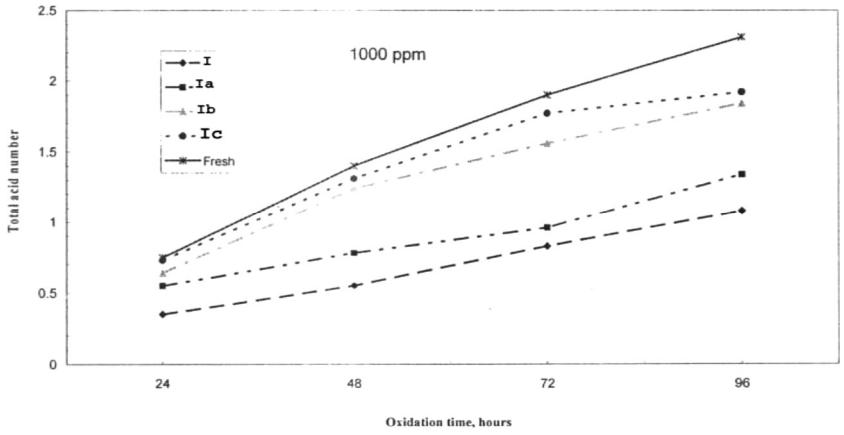


Fig. 4 Variation of total acid number (TAN) of compounds I Ia through Ic without additive and with 1000 ppm additive.

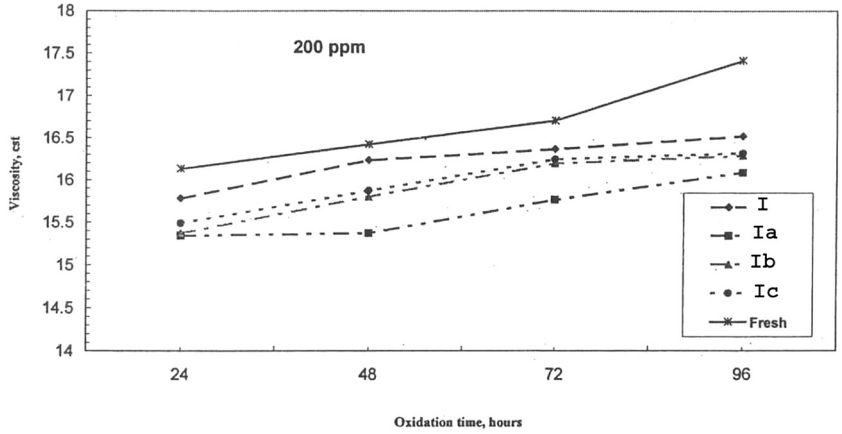


Fig. 5 Variation of viscosity of compounds I Ia through Ic without additive and with 200 ppm additive.

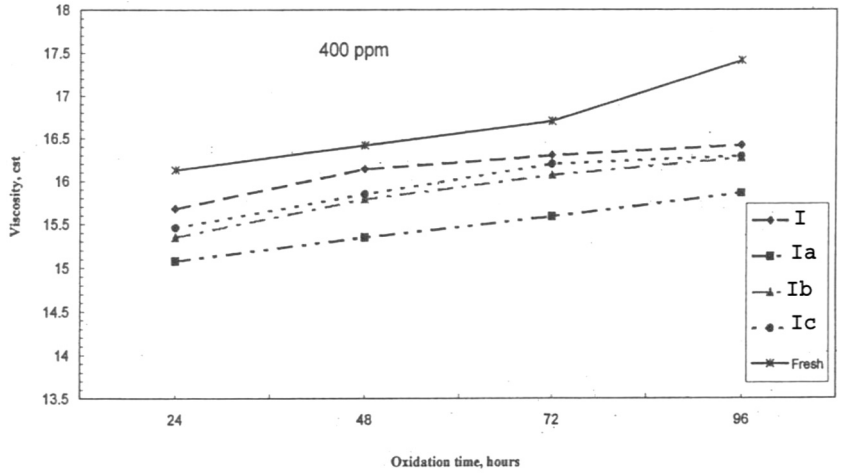


Fig. 6 Variation of viscosity of compounds I Ia through Ic without additive and with 400 ppm additive.

This may be attributed to the effect of the long chain carbon atom which increases the solubility of the additive in the mineral oil which intern increases antioxidant properties of the additives.

3.2. Total acid number and viscosities

The data of the various acid numbers and viscosities of the oxidized base stock are shown in Tables 6–9 and Figs. 1–8. There

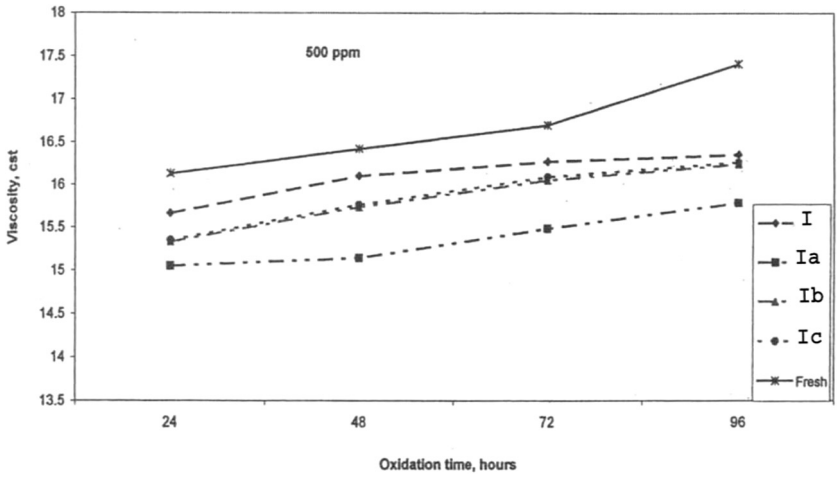


Fig. 7 Variation of viscosity of compounds I Ia through Ic without additive and with 500 ppm additive.

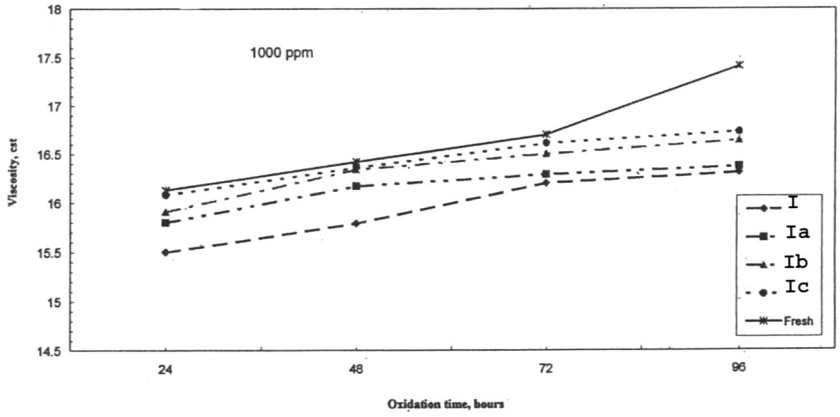


Fig. 8 Variation of viscosity of compounds I Ia through Ic without additive and with 1000 ppm additive.

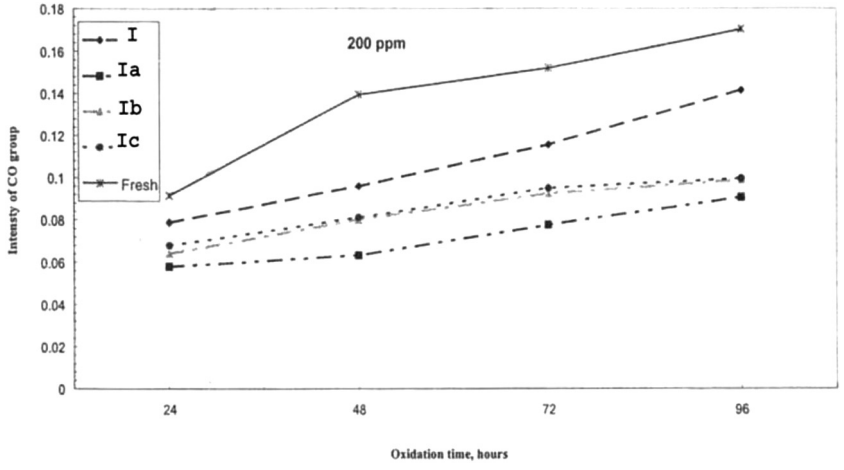


Fig. 9 Variation of carbonyl group intensity of compounds I Ia through Ic without additive and with 200 ppm additive.

are numerous lubricant problems caused by oxidation during lubricant reaction. These problems are viscosity increasing, varnish, sludge and sediment formation, additive depletion, base oil break down, loss in foam, acid number (AN) increasing, rust formation and corrosion. The data of the oxidation of the base stock shown in the tables and figures revealed that the viscosity and acid numbers always increase by oxidation time and controlled by the additive added. The data showed that

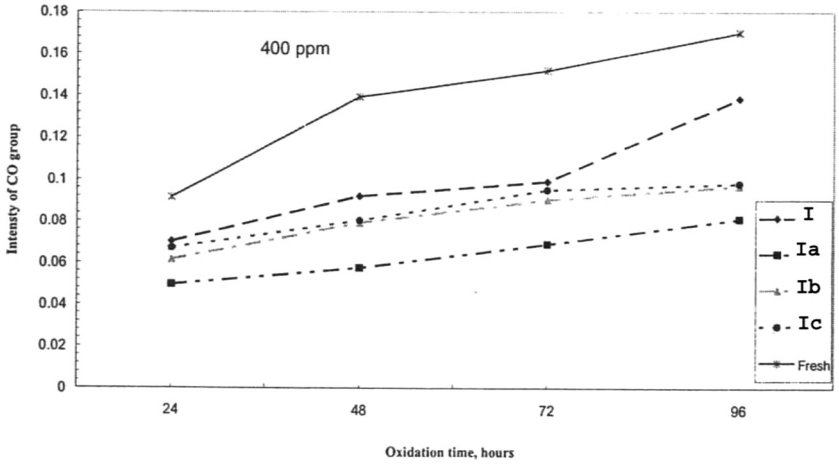


Fig. 10 Variation of carbonyl group intensity of compounds I Ia through Ic without additive and with 400 ppm additive.

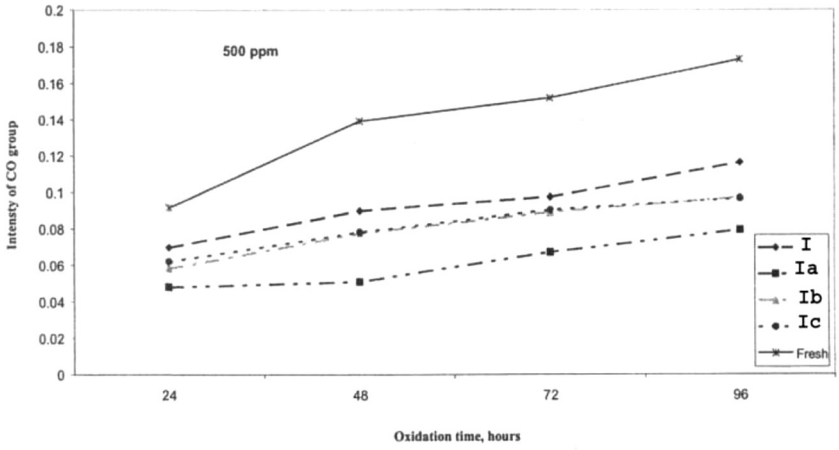


Fig. 11 Variation of carbonyl group intensity of compounds I Ia through Ic without additive and with 500 ppm additive.

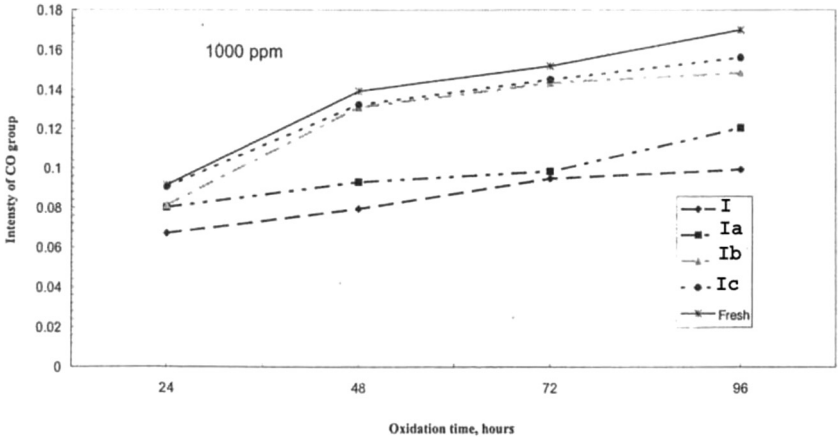


Fig. 12 Variation of carbonyl group intensity of compounds I Ia through Ic without additive and with 1000 ppm additive.

the fresh base stock has no resistance to oxidation but by adding additives, a noticeable decrease in both viscosities and total acid numbers. All additives gave best result and the order of the compounds was as follows Ia > Ib > Ic > Fresh sample.

3.3. Infrared studies

Infrared absorption spectroscopy can be applied for the investigation of the structure of petroleum and its fractions includ-

ing their functional groups. Also it is a widely used technique for analysis of lubricating oils. It provides useful molecular information about the change in a lubricant and the mechanical compartment being lubricated. The chemical degradation of an oil lubricant may be defined by number of processes; the most important of them is the oxidation process. At elevated temperatures oil exposed to oxygen, will be oxidized to form varieties of oxygenated compounds. These compounds are (C═O) such as Esters, Ketones and Carboxylic acids. Carboxylic acids contribute to the acidity of oil which becomes more acidic causing corrosion and an increase of viscosity degree. The regions of characteristic absorption from the sets of oxidation tests were indicated by infra-red spectroscopy.

A summary and assignment of regions are in Table 5. The data of the change in intensity of the carbonyl group, as indication of the total acid number, are in Tables 6–9 and Figs. 9–12. The best results are in the order Ia > Ib > Ic > Fresh sample.

4. Conclusions

The results obtained in this work indicate the following:

- Increasing the oxidation time always increases the total acid number, the viscosity and the intensity of the carbonyl group.
- The synthesized additives (Ia–c) proved to be successful in controlling the oxidation stability of the delivered base stock.
- The oxidation inhibition efficiency of these compounds depends on their structure.
- The data reveal that, the most effective concentration of these compounds is at 500 ppm.
- The order of increasing inhibition is shown as follows Ia > Ib > Ic.

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