ISSN: 0975-833X

Available online at http://www.journalcra.com

International Journal of Current Research
Vol. 5, Issue, 05, pp.1111-1117, May, 2013

INTERNATIONAL JOURNAL OF CURRENT RESEARCH

RESEARCH ARTICLE

THE EFFECT OF SOME BENZOTHIAZOLE DERIVATIVES AS ANTIOXIDANTS FOR BASE STOCK

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ARTICLE INFO

Article History:
Received 12th January, 2013
Received in revised form
20th March, 2013
Accepted 14th April, 2013
Published online 12th May, 2013

Key words:
Benzothiazoles, Alkyl amines,
Base Stocks,
Oxidation stability and
Total Acid Number.

ABSTRACT

The oxidation stability of base stocks in the presence of some synthesized Benzothiazoles derivatives, 2-(benzothiazol-2-ylthio)-N-butylacetamide (Ia), 2-(benzo-thiazol-2-ylthio)-N-octyl-acetamide (Ib) and 2-(benzothiazol-2-ylthio)-N-dodecylaceta-mide(Ic), as oxidation inhibitors has been studied. The structures of these prepared compounds are elucidated by the common tools of analysis, Elemental analysis, I.R. and ^{1}H-NMR spectroscopy. The oxidation reaction of these compounds with one of the base stocks that used in the formulation of the local lubricating oil was investigated, using the change in Total Acid Number (TAN), Viscosity, and Infra-Red (IR) spectroscopy. The data obtained, reveals that these prepared compounds gave good results. The efficiency order is shown as follows Ib and Ic > Ia.

INTRODUCTION

The deterioration of lubricants often leads to the buildup of insoluble deposits or sludge and an increased viscosity during use. The understanding of lubricant oxidation still remains at the empirical level due to extremely complex process, involving primary oxidation products formation and subsequent conversion to higher molecular weight oil soluble products (1). Widely accepted mechanistic routes suggest free radical reaction (2). In order to avoid or temporally delay these problems, lubricants need to possess superior oxidation stability. Therefore, antioxidants are the key additives that protect the lubricant from oxidative degradation, allowing the oil to meet the demanding requirements for use in industrial applications (3). In order to meet the latest technical, economical and environmental requirements the lowest possible level of sulfur and phosphorus content of any additive has to be used in the formulation of industrial oil (4,5). It is well known that most of heterocyclic compounds which have compact structure possess antioxidant, anticorrosion and antiwear properties (6-8). Amer et. al. (9) studied the effect of some synthesized thiazoles as antioxidant additives for Egyptian lubricating oils. They studied, the effect of the concentration of the most effective antioxidant in order to obtain the optimum concentration recommended to be used. They concluded that increasing the additive concentration led to a decrease in the oxidative products. Because mineral lubricating oils are usually used in air, oxidative chemical reactions can take place. The rate of these oxidative chemical processes varies greatly with the nature of lubricating oils, the extent of processing in refining, the temperature and the presence of metallic catalyst (10,11). The antioxidant activities of some poly-functionalized phenols linked to heterocyclic derivatives were evaluated by (12).

Experimental

All reagents (purchased from Merck Co., Aldrich and Fluka chemical Co.) were of analytical grade and used without further purification.

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The tested base stock was delivered from Alexandria Petroleum Company. The physicochemical characteristics of the base stock are tabulated in Table-1

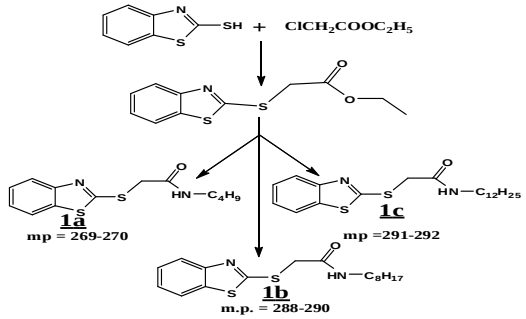
Table 1. Physicochemical Characteristics of the Base Stock

TEST	TEST METHOD	RESULT
Density At 15.5 ^{0}C, g / L	ASTM D – 4052	0.8916
Pour Point, ^{0}C	ASTM D - 97	-3
Viscosity 40 ^{0}C	ASTM D - 445	170.5
Viscosity 100 ^{0}C	ASTM D - 445	15.03
Viscosity Index (VI)	ASTM D - 2270	86
Total Acid Number (TAN)	ASTM D - 664	0.025
Sulfur Content, wt %	ASTM D - 4294	0.53
Carbon Residue, wt %	ASTM D - 524	0.7
Ash Content, wt %	ASTM D - 482	0.004
Wax Content, wt %	UOP 46	0.85
Copper Corrosion	ASTM D-190	I a
Water Content, PPM	ASTM D-1744	50

I-Preparation of additives (Ia-c): The additives were prepared according to the path outlined in scheme1

i)Preparation of the ester [ethyl-2-(benzothiazol-2-ylthio-) acetate] : In a 250-cc. round bottomed flask are placed 16.7 g. (0.1 moles) of 2-mercapto-benzothiazole (I) and 12.25g of ethyl chloroacetate (0.1mole). 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 (43-45^{o}C).

ii)Preparation of [ethyl-2-(benzothiazol-2-ylthio)-N-alkyl ace-tamide] (Ia-c) additives: In a 100-cc. conical flask are placed 11.05 g. (0.05 mole) of (I) and (0.05 mole) of n-alkyl amines, [(n-butyl amine (a), n-octyl amine (b) and n-dodecyl amine (c)]. The mixture is cooled to zero ^{o}C in ethanolic KOH for one hour. The products (Ia-c) were filtered off and recrystallized from ethanol. The compounds were characterized by elemental analysis, IR and ^{1}H-NMR spectrophotometry techniques.



Scheme 1

II-OXIDATION STABILITY STUDY

i)The oxidation test was carried out at 120 ^{o}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 liter/hour for maximum 96 hours. The characterized 2-mercaptobenzothiazole and its derivatives (Ia-c) compounds were added in different concentrations, ranging from 200 to 1000 ppm. The oil sample after, 24, 48, 72 and 96 hours of oxidation time were analyzed for their viscosity, total acid number and infra-red spectroscopy.

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).

FT-IR SPECTROSCOPY

Infra-red spectra of the oxidized samples at different periods were recorded on FT-IR Spectrophotometer, Model 960M000g, ATI Mattson Infinity Series, USA. A thin film of the sample, 5 mm thickness and 13 mm diameter. 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 4cm and scan rate 32 cm/min. Elemental analyses were carried out in the Micro analytical 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).

RESULTS AND DISCUSSION

Lubricating oils produced by solvent refining of high boiling petroleum distillates consisted mainly of long chain hydrocarbon molecules. These organic species were subjected to deterioration by oxidation, especially at high temperatures and in the presence of air and metal (13). The lube oils suffered from auto-oxidation, as a result of contact with air at elevated temperatures for long periods and in contact with metals, to form oxygenated products which increased the oil viscosity and motor metal corrosion. Many types of organic heterocyclic compounds were used as antioxidant additives for lubricating oils [e.g. thiazoles derivatives] (14-18). In continuation to our previous results in the field (19,20) we prepared some newly heterocyclic compounds (Ia-c) and their antioxidation activities for some Egyptian base stocks were evaluated. The synthetic procedure adapted to obtain the targeted compounds was depicted in Scheme 1. These compounds were characterized by elemental analysis (Table 2), infrared spectroscopy, (Table3) and NMR-Chemical Shift, (Table 4).

Evaluation of the Prepared Compounds as Antioxidants:

It is obvious from the obtained results that the absence of the additive increased the oxidative products with time. In 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, 7, 8 and 9 and Figures 1, 2, 3 and 4, reveals the prepared compounds exhibit good oxidation resistances compared with the fresh oil. The Tables and Figures also show that the TAN and Viscosity increase with increasing the oxidation time even in the presence 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.

I-Effect of additive concentration

It was interesting to study the effect of concentration of the prepared additives. Thus, 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 number, viscosity and intensity of carbonyl group were studied. The data in the Tables reveals that the most effective concentration in all cases is 400 ppm i.e. the total acid number and the viscosity decrease by increasing the concentration of the additives.

Effect of Time

The process of thermal degradation of engine lubricants proceeds by two mechanisms, namely oxidation and thermal decomposition. Mineral oil is very complex in nature due to the presence of large variety of molecular types and functional groups. This complex structure makes the oxidation reactions extremely hard to understand.

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

Cpd.	$C_{calc.}$%	$C_{obs.}$%	$H_{calc.}$%	$H_{obs.}$%	$N_{calc.}$%	$N_{obs.}$%	$S_{calc.}$%	$S_{obs.}$%	$O_{calc.}$%	$O_{obs.}$%
Ia	55.71	55.48	5.71	5.92	10.00	9.89	22.86	23.02	5.72	5.69
Ib	60.71	60.35	7.14	7.38	08.33	8.14	19.05	19.35	4.77	4.78
Ic	64.29	64.13	8.16	8.52	07.14	7.22	16.33	16.47	4.08	3.66

Table 3. Infra Red Spectral results of (Ia-c)

Cpd.	STREACHING ν (Cm^{-1})					
	NH	OH	CH2	C=O	CONH	C=N
Ia	3335	3547	2925	1706	1598	1646
Ib	3338	3538	2928	1705	1596	1642
Ic	3336	3542	2927	1706	1596	1645

Table 4. Chemical Shifts (δ) of Ia-c

Cpd.	 *(d)*	 *(m)*	 *(m)*	 *(d)*	*SCH_2C Methylene (s)*	*NCH2 Methylene (t)*	*NH Amide (s)*	*-(CH_2)- (m)*	*CH_3 (t)*
Ia	*7.86*	*7.52*	*7.4*	*7.80*	*4.38*	*3.97*	*7.25*	*1.61*	*0.83*
Ib	*7.94*	*7.51*	*7.38*	*7.84*	*4.31*	*4.03*	*7.27*	*1.61*	*0.91*
Ic	*7.88*	*7.49*	*7.37*	*7.81*	*4.31*	*4.02*	*7.27*	*1.47*	*0.87*

Our experiments were carried out at 24, 48, 72 and 96 hours. As stated before, increasing the oxidation time, always increase both of the total acid number and the 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 the viscosity of the oil by increasing the oxidation time is due to the formation of sludge and other higher molecular weight compounds.

Effect of substituted alkyl groups

As it is clear from Scheme 1, we started by the compound [2-Mercaptobenzo-thiazole (I)] and then this compound was reacted with ethyl chloroacetate to obtain (ethyl-2-(benzothiazol-2-ylthio) acetate). Ethyl-2-(benzothiazol-2-ylthio)acetate reacted with N-alkyl amines, [(N-butylamine (a), N-octylamine (b) and N-dodecylamine (c) respectively] to obtain "Ia-c". It is clear that, from the data shown in the Tables 6, 7, 8 and 9, we noticed that the most effective substituted groups are shown with Ib and Ic (octyl- and dodecyl- respectively). 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 increase antioxidant properties of the additives.

Total acid number and viscosities

The data of the variations of both total acid numbers and viscosities of the oxidized base stock are tabulated in Tables (6 – 9). These data are graphically shown in Figures 1 to 8. The variations of the total acid numbers and viscosities of the fresh base stock are also included. As oxidation is the most predominant reaction of lubricant in service, it is responsible for numerous lubricant problems. These problems including viscosity increase, varnish, sludge and sediment formation, additive depletion, base oil breakdown, filter plugging, loss in foam control, acid number (AN) increase, rust formation and corrosion. The data of the oxidation of base stock shown in the tables and figures indicate that the viscosity and acid numbers always increase by oxidation time and controlled by the additive added. The data showed that the fresh base stock has no resistance to oxidation. The addition of additives showed a noticeable decrease in both viscosities and total acid numbers. It is clear that the best results showed when using the additives Ib and Ic after 96 hours at concentration 400ppm.

Table 5. Assignments for Absorptions Associated withBase Stock Oxidation(♀)

REGION,cm^{-1}	ASSIGNMENTS
3600 to 3000	Mainly Hydroxyl Species
2800 to 2200	Hydrogen Bonded Hydroxyl
1850 to 1600	Mainly Carbonyl Compounds
1850 > 1800	Probably Lactones and Anhydrides
1800 > 1745	Probably Lactones (5-Membered), Anhydrides and Peroxy Acids
1745 > 1700	Esters, Acids, Ketones, Aldehydes, etc.
1700 > 1600	Carboxylates and Conjugated Compounds
1270 to 1000	Mainly Oxygenated Compounds – Alcohols, Glycols, Ethers, Lactones, Sulfates etc.

(♀)From John P. Coats and Lynn C. Setti."Infrared 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, 1986, pp. 57 – 78.

Table 6. Variation of Total Acid Number, TAN, Viscosity and Carbonyl Group of Compound (I) with Oxidation Time and Concentration

	Total acid Number x 10 2				Viscosity x 10 2				Intensity of carbonyl x 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	76	139	192	228	1615	1641	1673	1738	921	1361	1515	**1682**
400	74	136	187	220	1611	1638	1668	1733	903	1355	1486	**1664**
500	73	133	184	214	1609	1636	1664	1725	896	1342	1482	**1651**
1000	71	131	181	203	1605	1635	1662	1719	880	1318	1466	**1618**

Table 7.Variation of Total Acid Number, TAN, Viscosity and Carbonyl Group of compound (Ia) with Oxidation Time and Concentration

	Total acid Number x 10 2				Viscosity x 10 2				Intensity of carbonyl x 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	35	71	92	117	1550	1606	1625	1630	673	896	973	**1156**
400	31	53	68	88	1548	1578	1593	1622	668	789	822	**954**
500	64	23	167	186	1590	1632	1655	1665	810	1315	1436	**1482**
1000	70	28	174	193	1603	1634	1659	1672	874	1327	1448	1550

Table 8. Variation of Total Acid Number, TAN, Viscosity and Carbonyl Group of compound (Ib) with Oxidation Time and Concentration

	Total acid Number x 10 2				Viscosity x 10 2				Intensity of carbonyl x 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	61	82	97	1579	1587	1620	1628	671	802	943	**984**
400	22	31	54	77	1533	1547	1577	1614	606	667	795	**927**
500	58	19	150	181	1580	1629	1649	1600	759	1171	1422	**1461**
1000	66	126	169	190	1593	1633	1656	1669	521	1293	1440	**1516**

Table 9. Variation of Total Acid Number, TAN, Viscosity and Carbonyl Group of compound (Ic) with Oxidation Time and Concentration

	Total acid Number x 10 2				Viscosity x 10 2				Intensity of carbonyl x 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	24	57	74	90	1534	1579	1614	1625	611	788	907	**975**
400	20	51	65	81	1531	1573	1590	1620	582	776	813	**938**
500	49	105	143	165	1570	1525	1643	1657	712	1041	1405	**1452**
1000	62	121	160	188	1583	1631	1652	1666	807	1261	1435	**1493**

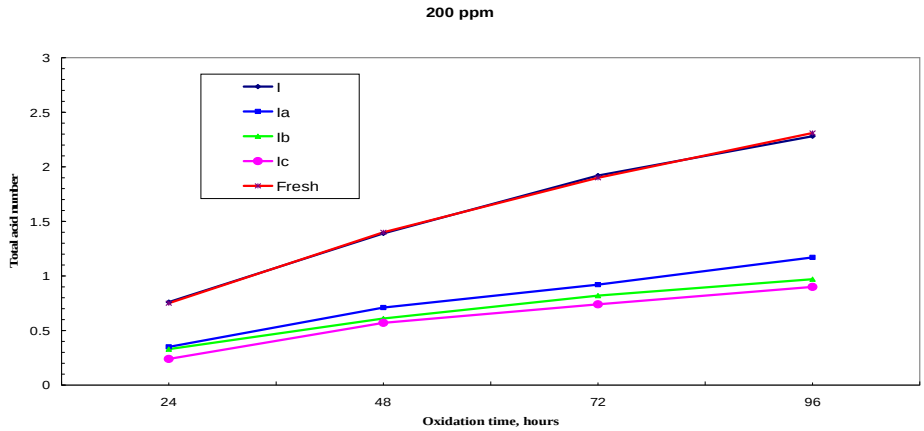


Figure 1. Variation of Total Acid Number (TAN) of base oil without and with 200 ppm I and Ia-c additives

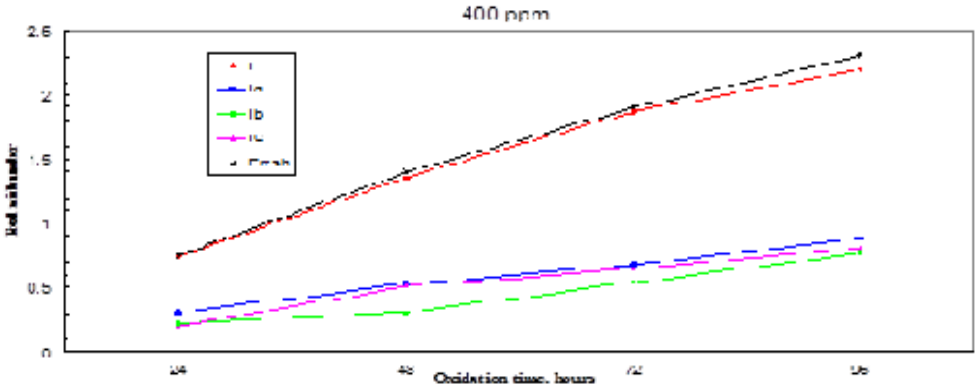


Figure 2. Variation of Total Acid Number (TAN) of base oil without and with 400 ppm I and Ia-c additives

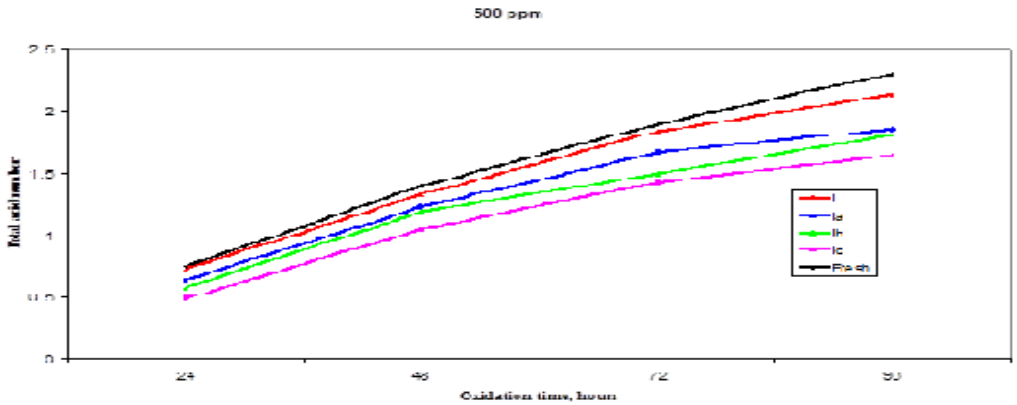


Figure 3. Variation of Total Acid Number (TAN) of base oil without Additive and with 500 ppm I and Ia-c Additive

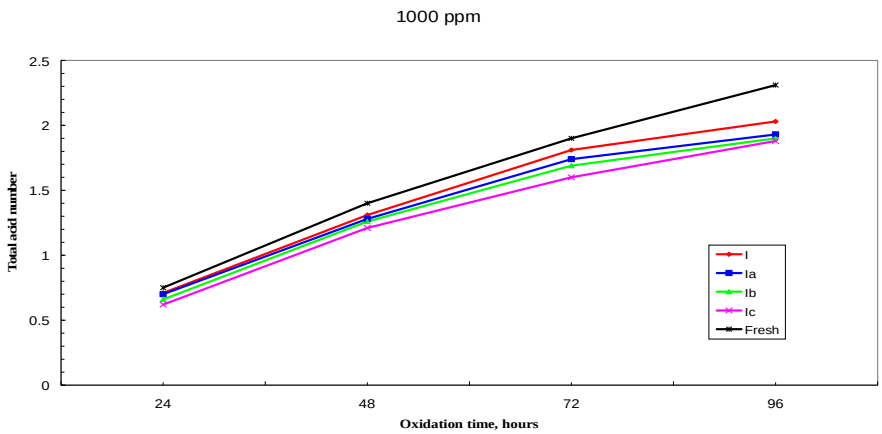


Figure 4. Variation of Total Acid Number (TAN) of base oil without and with 1000 ppm I and Ia-c additives

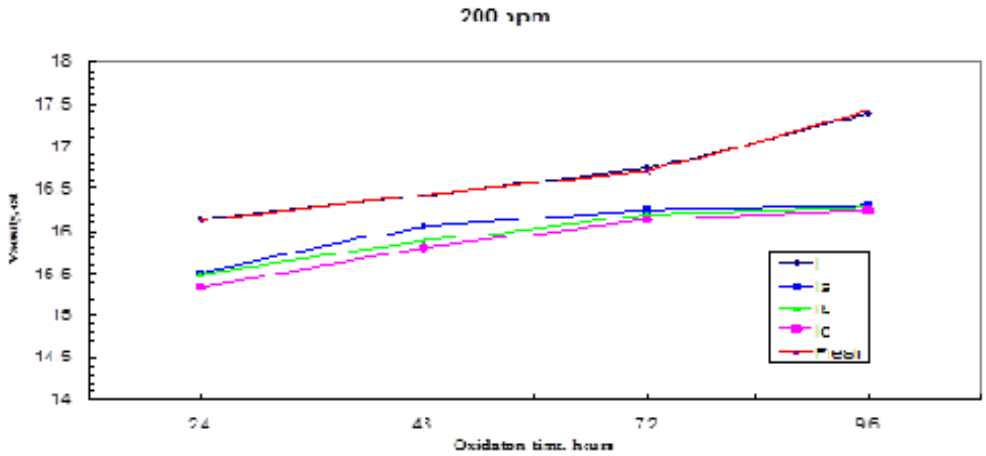


Figure 5. Variation of Viscosity of base stock without and with 200 ppm I and Ia-c additives

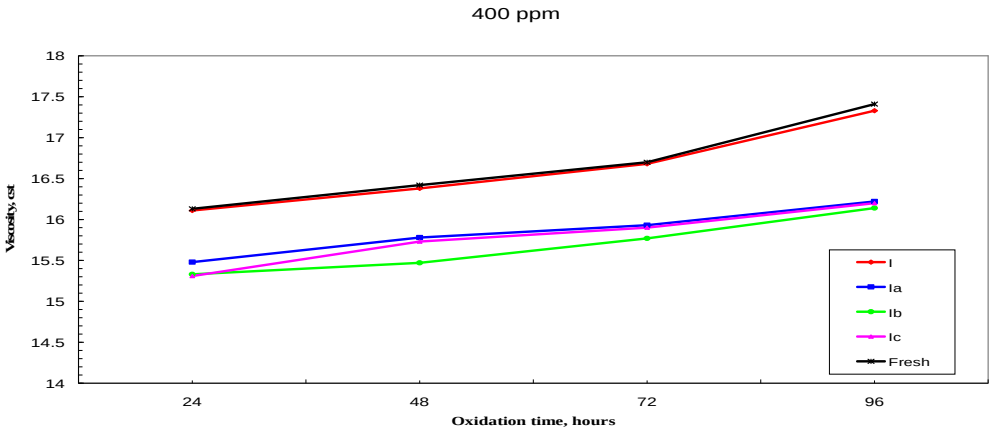


Figure 6. Variation of Viscosity of base stock without and with 400 ppm I and Ia-c additives

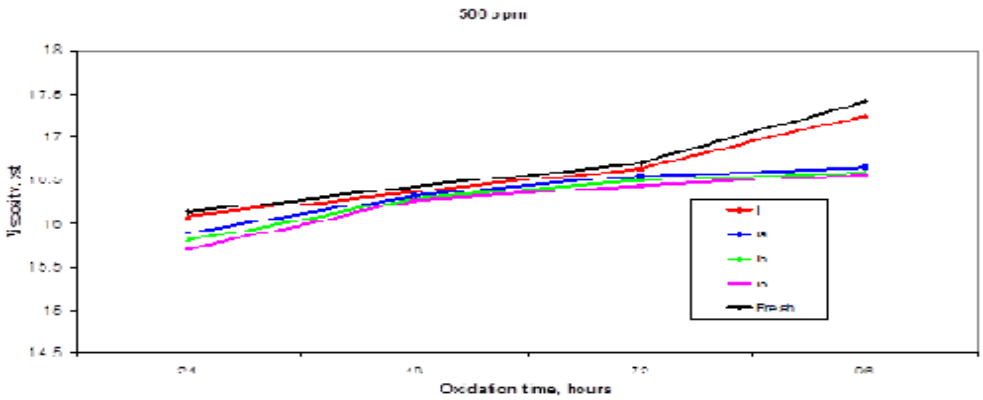


Figure 7. Variation of Viscosity of base stock without and with 500 ppm I and Ia-c additives

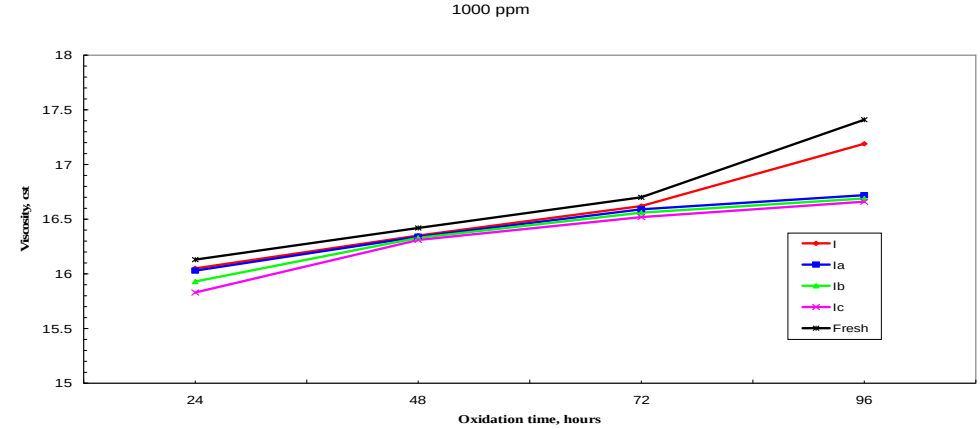


Figure 8. Variation of Viscosity of base stock without and with 1000 ppm I and Ia-c additives

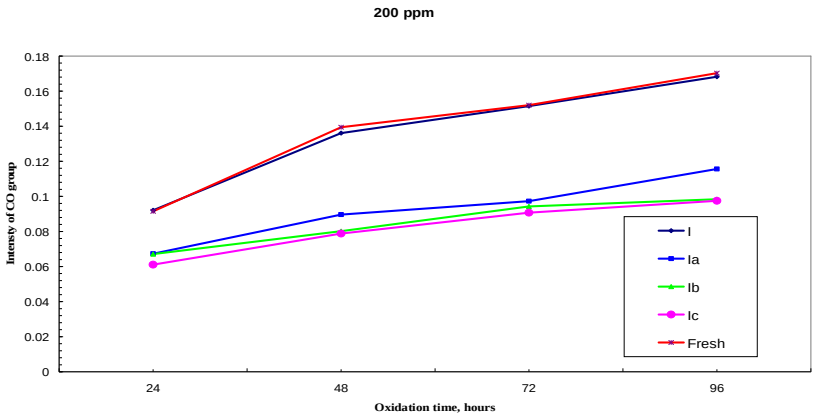


Figure 9. Variation of Carbonyl Group Intensity of base oil without and with 200 ppm I and Ia-c additives

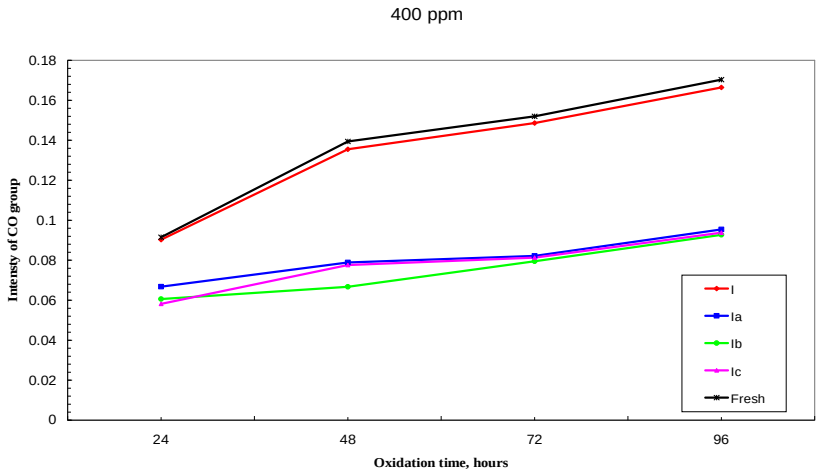


Figure 10. Variation of Carbonyl Group Intensity of base oil without and with 400 ppm I and Ia-c additives

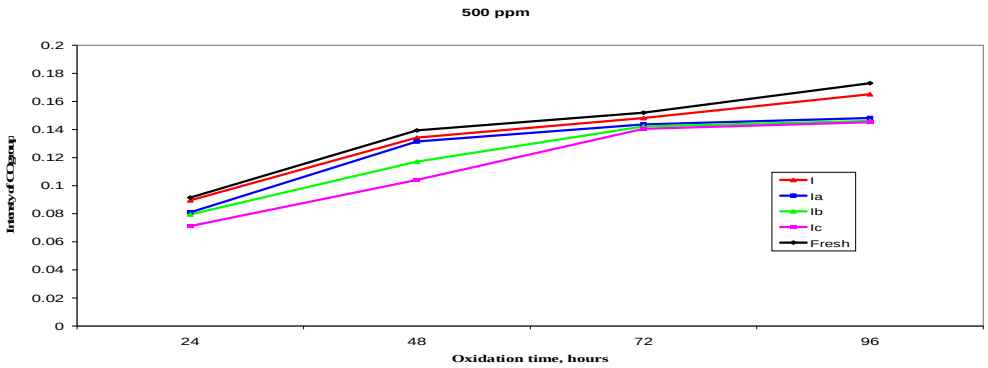


Figure 11. Variation of Carbonyl Group Intensity of base oil without and with 500 ppm I and Ia-c additives

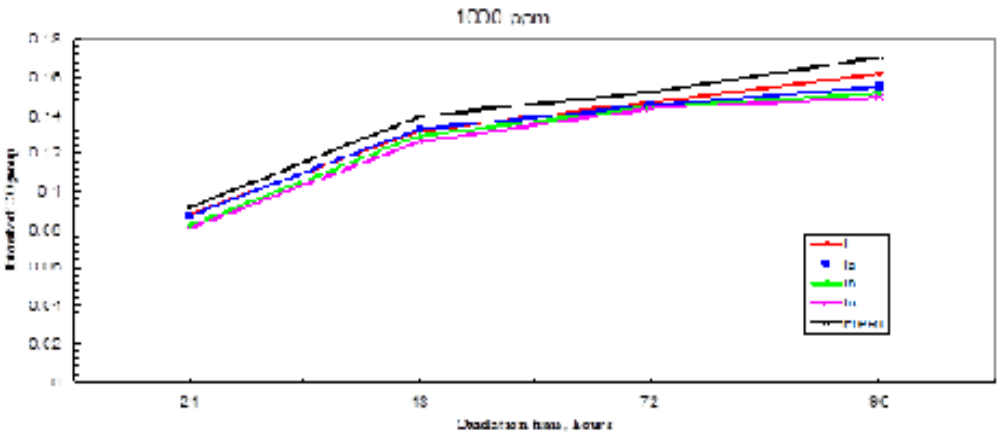


Figure 12. Variation of Carbonyl Group Intensity of base oil without and with 1000 ppm I and Ia-c additive

Infrared Studies

The use of infrared spectroscopy for routine monitoring of oil-lubricated components, breakdown products and contaminants have not been widely used in the past, although infrared studies of lubrication oils themselves have been performed for several years. The reason for this is that older dispersive infrared spectrometers would take several minutes to generate a spectrum of the used oil and then additional time would be needed to reduce and interpret spectral data. The chemical degradation of an oil lubricant may be defined by a number of processes; the most important of them is the oxidation process. At elevated temperature, oil exposed to oxygen, will be oxidized to form varieties of oxygenated compounds. The majority of these are carbonyl compounds (C=O) such as Esters, Ketones and carboxylic acids. Some of these compounds are dissolved by the oil or remain suspended owing to dispersive additives in the oil. Carboxylic acids contribute to the acidity of oil and deplete its basic reserve as neutralization takes place. The net effect of prolonged oxidation is that chemically, the oil becomes acidic causing corrosion, while physically an increase in viscosity occurs. The increase in viscosity however, may be masked by other factors such as fuel dilution. Examination of the infrared spectra from the sets of oxidation tests has indicated that there were regions of characteristic absorptions, but there are subtle differences in the observed absorption profile. These represent spectral changes due to oxidation and serve to define the main regions changed as the process of oxidation continues. A summary and assignment of these regions are given in Table-5. The data of the change in the intensity of the carbonyl group, as indication of the total acidity, are shown in Tables 6-9 and graphically shown in Figures 9-12. Again additives Ib and Ic show the best results.

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