

The Effect of Some Liquid Crystals as Antioxidants for Base Oil

¹Ashraf. M. Ashmawy, ²Doaa.I.Osman, ³El- Sayed.M.Elnaggar, ⁴Maher.I.Nessim

^{1,3}Chemistry Department, Faculty of Science (boys), AL-Azhar University, 11884, (EGYPT)

^{2,4}Egyptian Petroleum Research Institute, Evaluation and Analysis Department

Abstract: Two liquid crystalline compounds, namely of 2-sec-butyl-4-(4-methoxyphenyl) diazenyl) phenyl 4-(dodecyloxy) benzoate(I12a), and 2-sec-butyl-4-((4-nitrophenyl)diazenyl)phenyl 4-dodecyloxy)benzoate (I12b) were prepared. These compounds were characterized by elemental analysis, Infrared (IR), and Mass Spectroscopy. Their mesophase behavior was investigated by Differential Scanning Calorimetry (DSC). They were tested as antioxidants for Egyptian base oil. The oxidation was monitored using the change in the Total acid number (TAN) and viscosity. The data showed that of I12b is more efficiency than I12a.

Keywords: liquid crystals, viscosity, TAN, DSC and antioxidants.

I. INTRODUCTION

Mineral Base oils are the major components of lubricants, represent usually 85% or more of the formulation. These mineral oils produced from petroleum crude oil by various processing steps. They are complex mixtures of hydrocarbons that are commonly classified as paraffinic, paraffinic-naphthenic, aromatic, and aromatic-asphaltic, depending on their saturate, aromatic, resin and asphaltene contents[1, 2].

Engine lubricants are used to reduce friction between the moving parts within an engine. Engine lubricant oils also serve as coolants, corrosion protectors, and help in removing contaminants and debris from the engine interior [3, 4]. Lubricants aged and degraded as the machine operates, this is due to oxidation as well as thermal and mechanical decomposition. Lubricant oils may then lose some of their functions, which may, in turn, lead to machine damage or even catastrophic failure. Oxidation is lead to the degradation of hydrocarbon-based oils and can be influenced by several factors such as high engine temperature, the exposure to oxygen, and metallic wear debris [3, 5].

Oil deterioration results in a loss of lubrication, with the signals shown by the appearance of sludge and varnish. Efforts aimed at reducing sludge formation may extend the life span of the lubricant and prevent failure in service. The latter, however, cannot be achieved without the understanding of the processes of sludge formation and the nature of the oxidized products. Although qualitative information is available, which reports the presence of acids, aldehydes, ketones, esters, and lactones in the oxidates of used lube oils, information on the extent of oxidation is scanty [6, 7]. Consequently, antioxidant additives became highly required to decrease oil oxidation, with a secondary effect of reducing corrosion of certain types of sensitive bearing materials. Antioxidants can generally be considered as free radical inhibitors of peroxide decomposers, and may vary in chemical structures [1, 8]. Concentration and efficiency of antioxidant effect on the lubricating life time[6, 7].

Liquid crystals have demonstrated unusual lubricating properties in many cases [1-6] due to their ordered state. Thermotropic Liquid crystals has long been accepted that the presence of an adsorbed close-packed molecular monolayer can prevent direct contact between the surfaces and produce a dramatic friction reduction, while surface chemistry controls wear behavior. The fact that liquid crystal molecules can give rise to surface-aligned ordered layers explains the

interest in their use as lubricants or lubricant additives from the first studies on the effect of Liquid crystals (LCs) on the lubricating properties of mineral oils[9-15]. The formation of ordered fluid films is the base of the use of LCs in lubrication. Some LCs derived from azo- or cyanoaryls which were initially developed for display applications but have also been studied as lubricants or lubricant additives.

Several families of thermotropic LCs, 4,4'-dialkyl- and dialkoxyazobenzenes, 4,4'-diakylazoxy- benzenes and cyanoaryls, have been studied as commercial oil additives [16]. The goal of our present work is to prepare new azo phenol liquid crystals and applying them as antioxidants for Egyptian base oil.

II. EXPERIMENTAL

Raw material:

Samples of Hydro finished base oil (HBS) were delivered from Co-operative Petroleum Company, Cairo, Egypt. All other reagents were purchased from Merck, Aldrich and Fluka chemical companies.

Synthesis of additives:

The preparation of I12a&I12b took place through three steps according to scheme one.

Step one: Preparation of 4-(dodecyloxy) benzoic acid

4- (dodecyloxy) benzoic acid was prepared from ethyl 4-hydroxybenzoate and the appropriate 1- bromododecane; the ester was then saponified to the corresponding acids using alcoholic potassium hydroxide, by the method described previously[17].

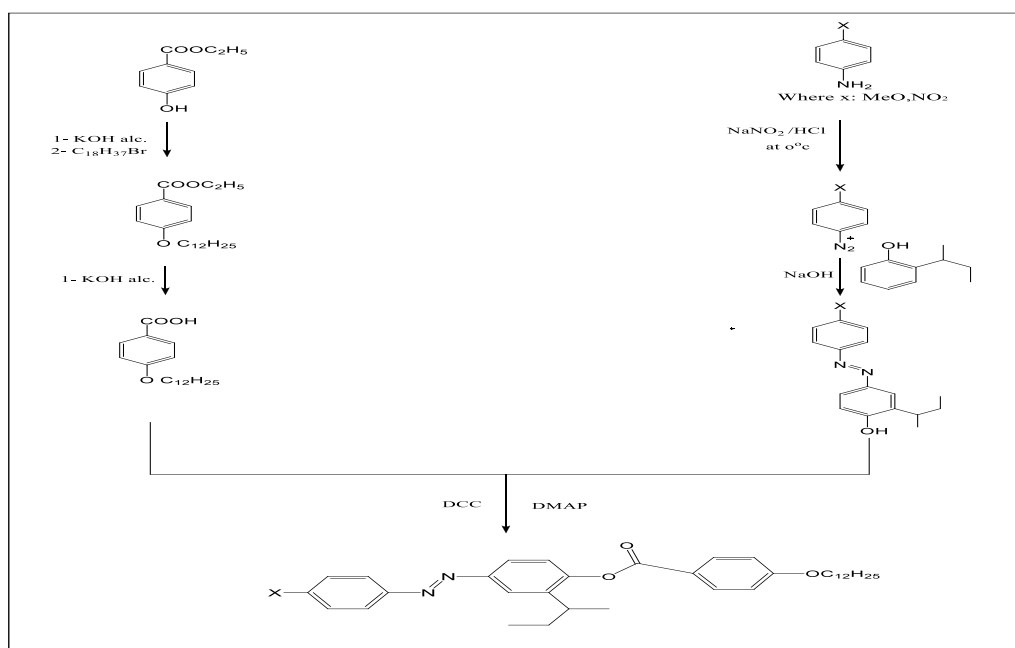
Step two: Preparation of 4-(4-Substituted phenyl azo) phenol

Two azo phenols were prepared as reported previously by Nessim [18].

Step three: 4-(dodecyloxy) benzoic acid with 4-(4-Substituted phenyl azo) phenol

One molar equivalent of both the 4-(4-substituted phenyl azo) phenol and 4-(dodecyloxy) benzoic acid were dissolved in methylene dichloride. To the resulted solution, Dicyclohexyl carbodiimide (DCC) and 4-(Dimethylamino) pyridine (DMAP) were added as a catalyst, and the solution was left to stand overnight with stirring at room temperature. The solution was filtered off and the solute was distilled off and the residue recrystallized by acetic acid [19].

The synthesis route used to prepare these additives is depicted in Scheme 1.



Characterization of the prepared compounds:

Elemental analyses using CHNS-932 (LECO) Vario Elemental Analyzers, IR; using A Perkin-Elmer FT-IR type 1650 spectro-photometer and Mass spectroscopy, using direct inlet unit (D1-50) of SHIMADZU GC/MS-QP5050A were used to ensure the structure of the prepared compounds. The mesophase behavior was investigated using a polymer laboratories differential scanning calorimeter, PL-DSC, England, with nitrogen as a pure gas. Typical heating and cooling rates were 20 K/min., and sample masses were 1-2mg.

Evaluation of the prepared compound as antioxidant:

Evaluation of the prepared compounds as antioxidants was carried out according to ASTM D-943 method. Where the cell contained 200 ml base oil in the static mode, and copper & iron wires were used as catalysts. The base oil samples were subjected to oxidation at 120 oC with pure oxygen flow rate (0.1 liter/hour) up to 96 hours. The prepared compounds were added with different percents. The change in the total acid number (TAN) and viscosity of oil samples were examined (after 24, 48, 72 and 96 hours) according to ASTM test methods (D-664 and D- 445), respectively).

III. RESULTS AND DISCUSSION

The physico-chemical properties of local base stock used in this study represent in table (1).

Test	Result	ASTM
Density @ 15.5 °C, g / L	0.817	D-1298
Pour Point, °C	Zero	D-97
Viscosity at 40 °c	52.34	D-445
Viscosity at 100 °c	7.41	D-445
Viscosity Index (VI)	92	D -2270
Total Acid Number	0.067	D - 664
Sulfur Content, wt %	0.34	D -4294
Color	2.5	D -1500
Ash Content, wt %	0.003	D - 482
Copper Corrosion	I a	D - 130
Flash point, °C	220	D - 92
Aniline point °C	100.5	D - 611
Molecular Weight	468.9	-

A. Characterization of compounds I12a and I12b:

The chemical structures of compounds I12a and I12b were elucidated as the following:

Elemental analysis:

Elemental analysis was performed for the synthesized azophenols derivatives I12a and I12b and the Obtained results are shown in Table (2).

Cpd.	Analysis calculation(found)					
	C%		H%		N%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
I12a	75.49	75.76	8.45	7.89	4.89	5.23
I12b	71.52	70.90	7.22	8.22	7.15	7.52

The data obtained from table (2) shows that the calculated values of the elements were in good compatibility with that measured.

Infrared spectra of compounds I12a,I12b:

Table (3): Infra-Red spectra of I12a,b.

Cpd.	$\nu_{C=O}$	ν_{C-O}	ν_{NO_2}
I12a	1735.48	1251.55	-
I12b	1744.85	1250.80	1514.94

Infrared absorption bands for compounds I12a and I12b are given in table (3). From Table 3, small shifts were observed in the carbonyl absorption bands with the effect of the alkoxy-chain length (O-C₁₂). Moreover, it can be noted that, the ester C=O absorption bands are not greatly affected by the nature of the substituents (MeO-, NO₂-). This can be attributed to their weak effect on the polarization of the ester C=O group through the phenylazo group. Nonetheless, the ester oxygen absorption bands are affected by the electronic nature of MeO-, NO₂-. Thus, in the electron withdrawing (NO₂-) substituted derivative I12b, conjugative interaction takes place between NO₂- and the lone pair of the ester oxygen, via the phenylazo moiety (Figure 1,2).

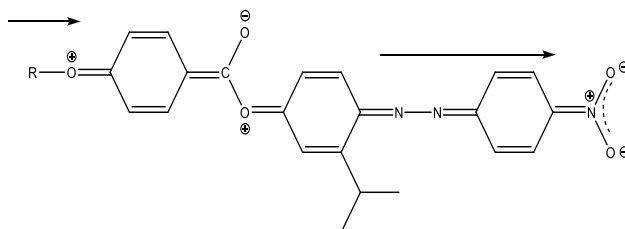


Fig. (1): Conjugative interaction within the nitro substituted homologue I12a.

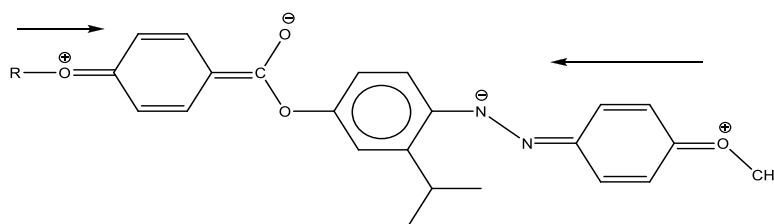


Fig.(2): Conjugative interaction within the methoxy substituted homologue I12b.

Where: R= C₁₂ H₂₅-

Mass spectroscopy:

m/z Cpd.cal.	Molecular formal	m/z obs.	m/z calc.
I _{12a}	C ₃₆ H ₄₈ N ₂ O ₄	572.43	572.78
I _{12d}	C ₃₅ H ₄₅ N ₃ O ₅	587.34	587.49

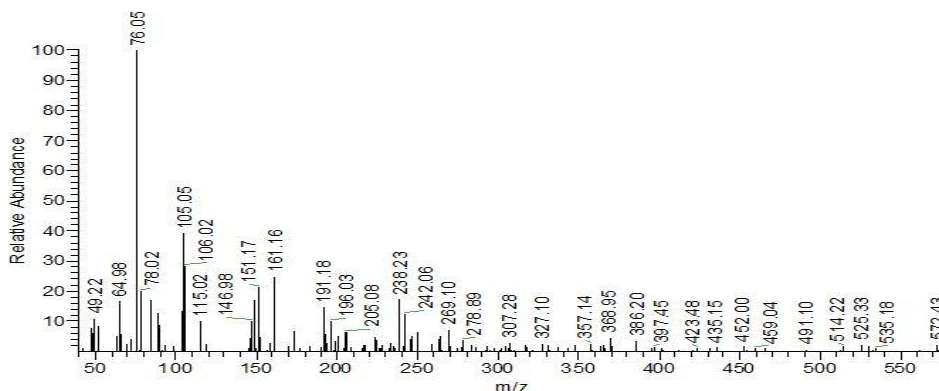


Fig. (3): Mass spectra of the prepared compound (I_{12a}).

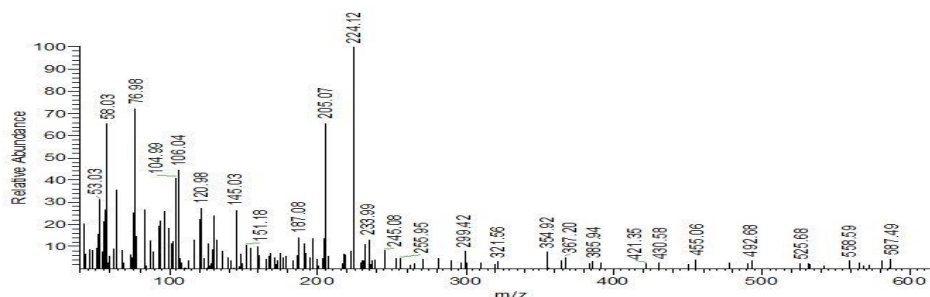


Fig. (4): Mass spectra of the prepared compound (I12b).

From the previous figures (3, 4), we noted that the molecular ion peaks were in accordance with the calculated molecular weight for I12a and I12b.

Differential Scanning Calorimetry (DSC):

In order to investigate the effect of substituents on the phase behavior of the investigated compounds, the DSC analyses for compounds I12a and I12b were carried out. The transition temperatures observed are summarized in table (4). Original DSC curve are given in figure 5 and figure 6.

Table (4): Transition temperatures (in °c) and enthalpy of transitions (in KJ/Mole) for compounds I12a,I12b as determined by DSC.

Cpd.	Heating				Cooling	
	Tm	ΔH	TC	ΔH	Tm	ΔH
I12a	58.1	20.26	122.2	18.97	72.5	8.54
I12b	102.41	89.50	-	-	52.20	94.31

Where Tm= solid- smectic. Tc= smectic -isotropic transition.

In order to investigate the effect of terminal substituents (X) on the mesophase behavior of compounds I12a and I12b the number of carbon atoms in the alkoxy substituent kept constant (C₁₂H₂₅O-). The substituent x varied between CH₃O- and NO₂-. Table 4 compares the transition temperatures of the four compounds I12a and I12b.

It is well recognized that the stability of the mesophase would be augmented by an increase in the polarity of the mesogenic part of the molecule. Thus in the nitro analogue, the polarity of the mesogenic portion as a whole, Figure 3 should be increased, which stabilized the mesophase. This heuristics is in accordance with the observed results, Table 4, that the nitro analogue has the highest clearing (Tc) temperature. On the contrary, the molecule of the methoxy analogues Figure 2, are expected to possess lower dipolar character that would lead to derivatives with lower Tc values.

Evaluation of the synthesized compounds as antioxidants:

Using Change in TAN:

Organic acids are produced during oxidation. These acids are detectable as an increase in the TAN number which quantifies acid concentration by measuring the volume of an alkaline (potassium hydroxide) reagent that is required to neutralize the acid in the oil. The TAN test doesn't discriminate acids generated by oxidation from those that are ingested as contaminants from the process. Also, some additives like anti-wear, extreme pressure and some rust inhibitors, are acidic.

Table (5): Variation of total acid number, TAN with oxidation time and concentration.

Time (Hrs)	Total Acid Numbers, mg KOH / g Sample x 10 ²						
	Base oil	Base oil + I12a			Base oil + I12b		
		100	250	500	100	250	500
24	37	34	32	28	7.1	5.2	4.3
48	79	69	64	58	22	15	13
72	162	78	69	63	43	35	31
96	201	164	142	123	70	65	40

They produce a high initial TAN that can diminish as the additive is depleted. The total acid number is an analytical test to determine the deterioration of lubricants the more acidic a lubricant, the more degradation occurs. As a fluid degrades, the levels of corrosive acids increase, along with the danger of component failure.

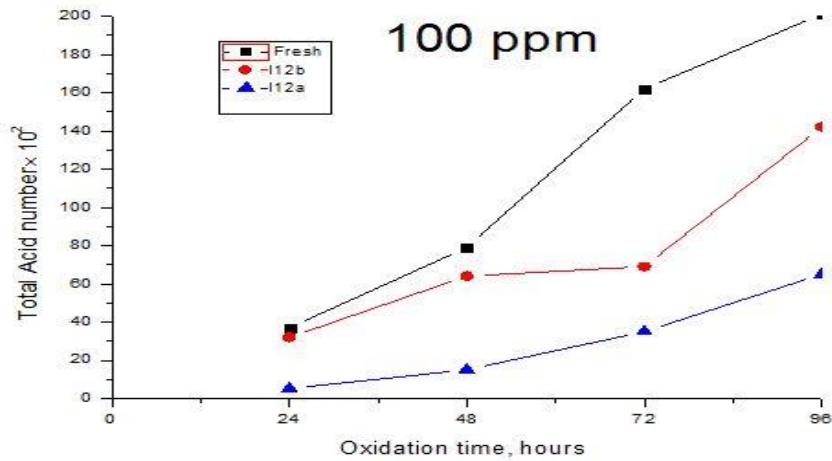


Fig. (5): Variation of Total Acid Number (TAN) of base oil without and with 100 ppm I12a,12b additives.

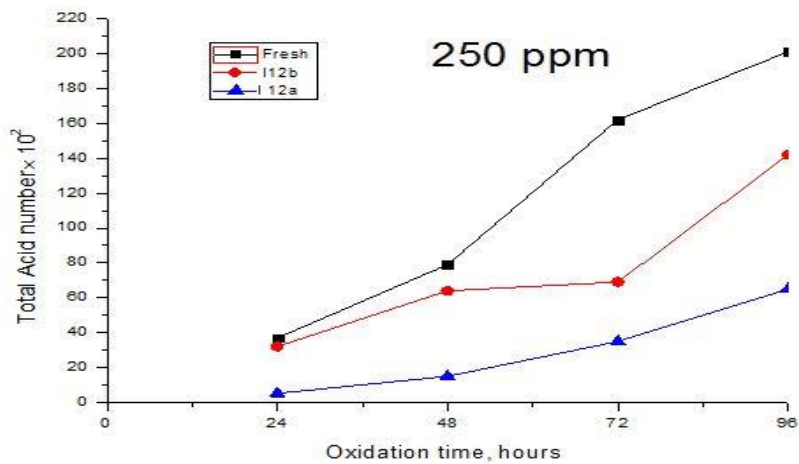


Fig. (6): Variation of Total Acid Number (TAN) of base oil without and with 250 ppm I12a,12b additives.

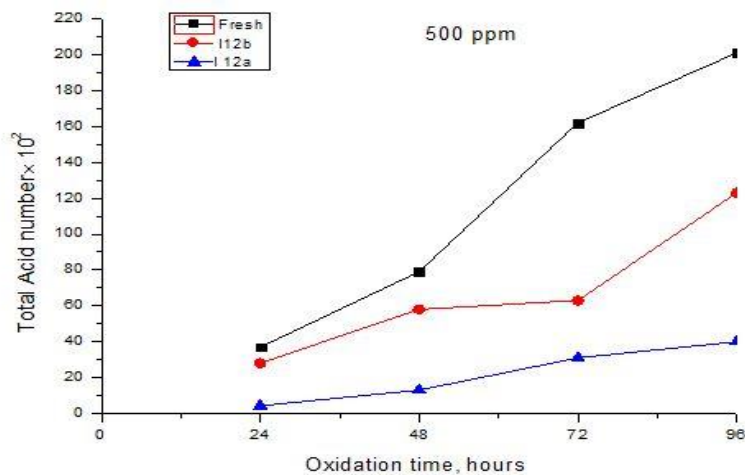


Fig. (7): Variation of Total Acid Number (TAN) of base oil without and with 500 ppm I12a, 12b additives.

Looking in Table 5 and Figures 5 -7, this is concluding the following:

Generally, the total acid number decreased by the addition of the synthesized compounds. This is clear from data of the oxidized base stock without additives and the data obtained after the addition of the two compounds. The data obtained after the addition of both additives [(I12a) and (I12b)] showed the decrease of the total acid number by increasing the dose of the compounds. The data obtained showed that the compound (I12b) is more effective than the compound (I12a). With the (I12a) the TAN decreased by the addition of 100 ppm, after 24 hours from 0.37 mg KOH / g sample to 0.34 mg KOH / g sample and from 0.79 mg KOH / g sample to 0.69 mg KOH / g sample after 48 hours. After 72 hours and 96 hours the decreased showed 0.78 mg KOH / g sample and 1.64 mg KOH / g sample respectively. On the other hand, by adding the same dose 100 ppm the (I12 b) showed 0.071, 0.22, 0.43 and 0.70 mg KOH / g sample after 24, 48, 72 and 96 hours respectively. Addition of 250 ppm and 500 ppm decreased the TAN from 0.37 to 0.32 and 0.28 mg KOH / gm sample in case of (I12a) after 24 hours. While addition of same concentrations of (I12b) showed decrease in TAN after the same period to 0.052 mg KOH / gm sample and 0.043 mg KOH / gm sample. As we see from the table, the (I12b) is more effective as anti-oxidant. It causes depression in the TAN in comparison with that caused by the addition of (I12a). From the Table one can notice that 500 ppm of both compounds showed the best results.

Using Change In Viscosity:

As carboxylic acid byproducts of oxidation dimerize (or associate), the medium density of the molecules increases. This results in increased viscosity. Viscosity can be measured using kinematic or absolute methods.

Table (6): Variation of viscosity with Oxidation Time and Concentration of additive

Time, Hours	Kinematic Viscosity, @40 °C, Cst.						
	Base oil	Base stock + I-12 a			Base stock + I-12 b		
		100	250	500	100	250	500
24	69.40	68.77	68.20	68.07	55.45	55.01	40.01
48	75.20	69.50	69.09	68.60	59.10	58.01	42.01
72	81.40	70.16	70.00	69.01	64.80	59.51	51.01
96	96.20	71.20	70.30	69.90	65.00	61.51	60.60

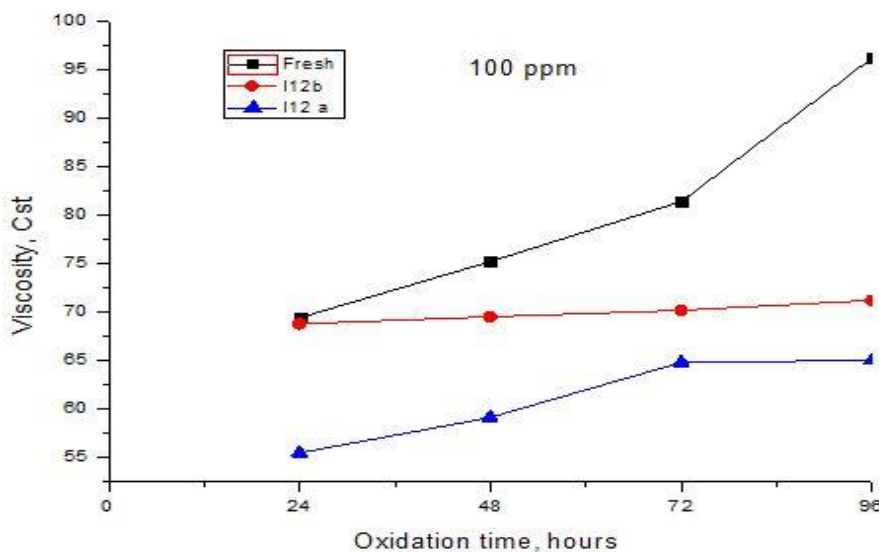


Fig.(8): Variation of Viscosity of Compounds without and with 100 ppm I12a,12b additives..

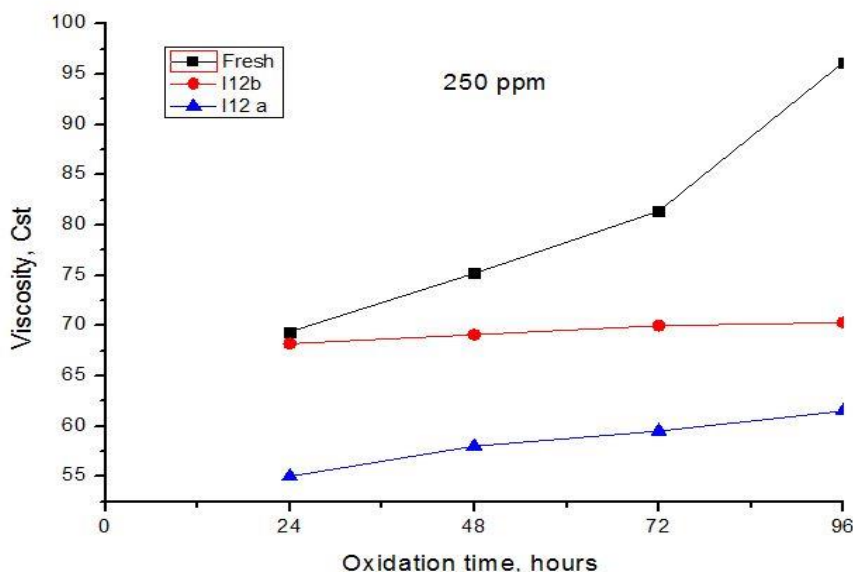


Fig. (9): Variation of Viscosity of Compounds without and with 250ppm I12a,12b additives..

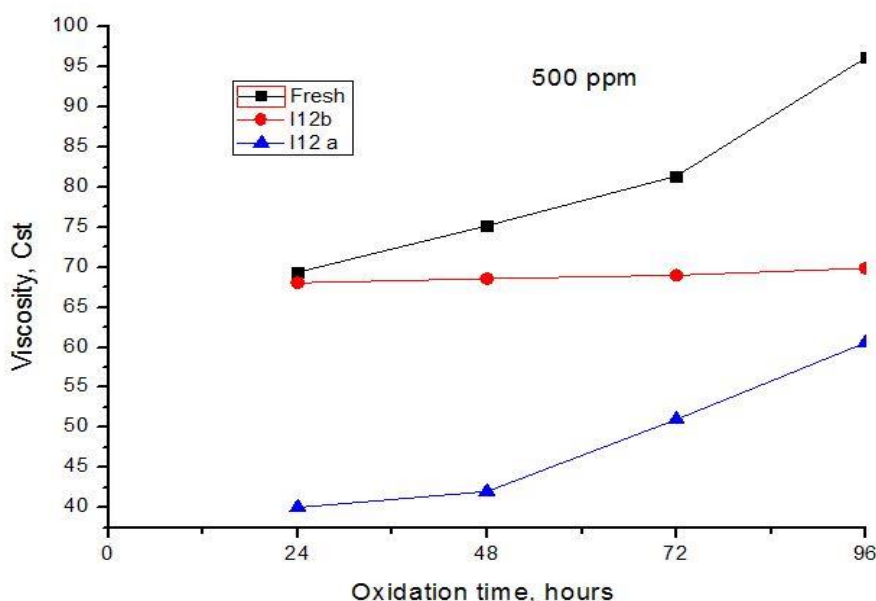


Fig.(10): Variation of Viscosity of Compounds without and with 500 ppm I12a,12b additives.

From the data in Table (6), and Figures 8 - 10 one can noted that:

The viscosity of the oxidized base stock always increases by increasing the oxidation period. Adding the synthesized compounds to the base stock caused appreciable increasing in the viscosities of the base stock. For example, by increasing the oxidation period from 24 hours to 96 hours, the viscosity changed from 69.40 Cst and 96.20 Cst without additive to 68.77 Cst and 71.20 by adding 100 ppm of I-12 a respectively. At the same time, addition of the same concentration from I12 b, the viscosity changes to 55.45 Cst and 65.00 respectively.

By increasing the concentration of the added compounds from 100 ppm to 500 ppm, the viscosity decreases to from 69.40 to 40 after 24 hours at 100 ppm and from 0.712 Cst to 0.61cst at 500 ppm after 96 hours. The table also revealed that the compound I12 b is more effective than I12 a.

IV. CONCLUSION

From the data obtained from this study we can concluded that:

The base oil showed bad results when oxidized without additive, that it gives sharp increase in both total acid number and viscosities. The addition of the two additives showed decrease in the total acid number and viscosities as compared to the base oil without additives.

Generally the compound I12b is more effective gave good results than the compound I 12a.

The concentration 500 ppm is the most effective concentration among the concentrations we are used.

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International Journal of Novel Research in Engineering and Science

Vol. 3, Issue 2, pp: (36-45), Month: September 2016 - February 2017, Available at: www.noveltyjournals.com

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