

Preparation and evaluation of some new liquid crystal as antioxidant for base stocks

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Abstract

Four liquid crystal compounds of the form, 2-Sec-butyl-4-[(4-x-phenyl) diazenyl] phenyl-4-(octadecyloxy) benzoate symbolized as I18a, I18b, I18c and I18d were prepared in which the substituent (X) was taken CH₃O-, CH₃-, Br- and -NO₂ respectively. Characterization of prepared compounds is done using FT-IR, ¹H-NMR, Mass Spectroscopy and Elemental Analysis. Their mesophase behavior was investigated by Differential Scanning Calorimetry (DSC). Their antioxidant efficiency for Egyptian lubricating base oil was tested. The oxidation processes were monitored using the change in the Total Acid Number (TAN). The obtained results showed that the efficiency of these compounds was ranked as follows I18d > I18c > I18b > I18a.

Keywords: Liquid crystals; lubricating oil; TAN; antioxidants; DSC.

Introduction

The most important parameter that affects the lube oil degradation is its oxidation stability [1]. Oxidation products are the primary cause of metal corrosion, viscosity increasing, and sludge formation in lubrication systems [2]. An investigation of the chemical nature of these products was undertaken to provide a better understanding of primary oxidation and the subsequent behavior of these primary oxidation products [1,2].

Oil deterioration results in a loss of lubrication, with the signals showed by the appearance of sludge. Efforts aimed to reduce 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 oxidation products [3]. Although qualitative information is available, which reports the presence of acids, aldehydes, ketones, esters, and lactones in the oxidates of used crankcase lube oils, information on the extent of oxidation is scanty [4,5],[5-7].

Today, many efforts have been made: papers, conference recommendations, or books and inventions in an attempt to use monomeric liquid crystals whether as lubricants or as additives for lubricating oils. The improvement of the efficiency

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of lubricants is of important it is estimated that 50% of the energy consumption is wasted as friction [8,9].

Liquid crystals (LCs) are soft materials that spontaneously form several types of ordered structures and thermally change their physicochemical properties [10]. Since the time of their discovery, liquid crystals have been very extensively investigated. The exploration of liquid crystals included molecules with different shapes (rod-like, disc-like). Also, there are different possibilities of substitution and combination of linking units in designing the new molecular structures [11]. The ordered liquid crystals have received much attention, as potential lubricants, due to the long-range orientation of their molecules [9 and 12-17]. Most liquid crystals, studied nowadays, are thermotropic phases constituted by polar neutral organic molecules [18]. The goal of our present work is to prepare new monomeric (LCs), azo phenol derivatives, and applying them as good antioxidants.

Experimental

Raw material

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

Preparation of azo phenol derivatives

The preparation of 2-Sec-butyl-4-[(4-x-phenyl) diazenyl] phenyl-4-(octadecyloxy) benzoate took place through three steps according to Scheme 1.

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

4-(Octadecyloxy) benzoic acid was prepared from ethyl 4-hydroxybenzoate and the appropriate 1-bromooctadecane; the ester was then

technological and economic relation as saponified to the corresponding acids using alcoholic potassium hydroxide applying the method described previously [19].

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

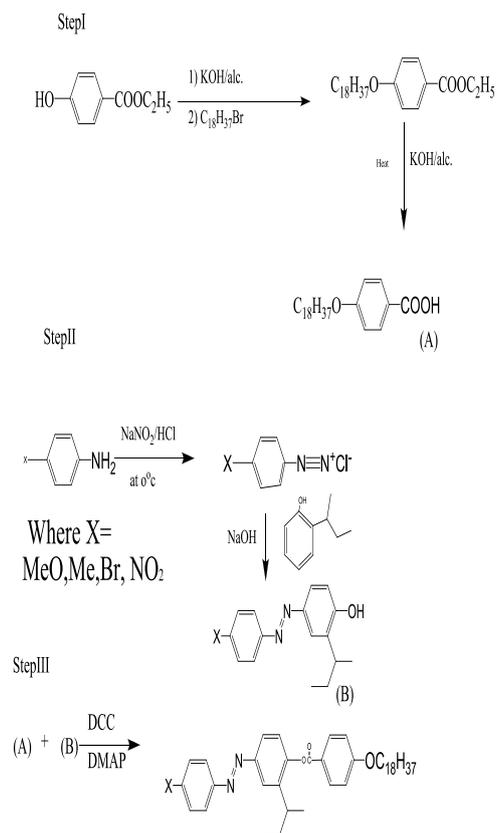
Two azo phenols were prepared as reported previously [20].

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

One molar equivalent of both the 4-(4-substituted phenyl azo) phenol and 4-(octadecyloxy) 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, the solute was distilled off and the residue recrystallized by acetic acid [21].

Characterization of the prepared compounds

The chemical structure of the prepared compounds were well-established by Elemental analyses using CHNS-932 (LECO) Vario Elemental Analyzers, IR; using A Perkin-Elmer FT-IR type 1650 spectro-photometer "; Model "Vector 22", Nuclear Magnetic Resonances (NMR), using ¹H-NMR (type varian 300 MHz) with the TMS as internal standard zero compound, Mass spectroscopy was one using direct inlet unit (D1-50) of SHIMADZU GC/MS-QP5050A, and calorimetric investigation was made 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 1-2 mg.



Scheme 1. Preparation of additives (I18_a-118_d)

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 stock in the static mode, and copper and iron wires were used as catalysts. The base oil samples were subjected to oxidation at 120 °C with a pure oxygen with flow rate (0.1 liter/hour) up to 96

h. The prepared compounds were added with different percents. The change in total acid number (TAN) of oil samples were examined (after 24, 48, 72 and 96 h) according to ASTM test methods D-664.

Results and discussion

The physico-chemical properties of local base stock used in this study are represented in Table 1.

Table 1.

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

Characterization of compounds I18_{a-d}

The chemical structure of compounds I18_{a-d} were elucidated using the following results which are shown.

Elemental analysis

Elemental analysis was performed for the synthesized azophenols I18_{a-d}, and obtained in Table 2.

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 I18_{a-d}

Infrared absorption bands for compounds I18_{a-d} 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-C18). Moreover, it can be noted that, the ester C=O absorption bands are not greatly affected by the nature of the substituents (MeO-, Me-, Br- or 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-, Me-, Br- or NO₂-. Thus, in the electron withdrawing (NO₂-) substituted derivative I18d, conjugative interaction takes place between NO₂- and the lone pair of the ester oxygen, *via* the phenylazo moiety (Figure 6). Table 2 shows the elemental analysis of the newly prepared compounds, I18_{a-d}.

Table 2. Elemental analysis of the newly prepared compounds, I18_{a-d}

Pd.	Analysis calculation(found)							
	C%		H%		Br%		N%	
	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.	Calc.	Obs.
I18 _a	76.79	76.54	9.21	8.92	-	-	4.26	4.81
I18 _b	78.7	76.95	9.44	9.05	-	-	4.37	5.03
I18 _c	69.77	69.39	8.14	8.01	11.32	10.88	3.97	4.12
I18 _d	73.29	73.96	8.55	9.12	-	-	6.25	6.35

Table 3. Infrared spectra of I18_{a-d}

Cpd.	Stretching of Vibrations, (ν) in cm ⁻¹						
	CH aromat ic	CH aliphatic	N=N	C=O	C-O-C	Br	NO ₂
I18 _a	2916	2849	1436	1732	1241	-	-
I18 _b	2917	2849	1467	1734	1252	-	-
I18 _c	2917	2849	1467	1735	1252	658	-
I18 _d	2918	2849	1517	1724	1254	-	1344

Mass spectroscopy

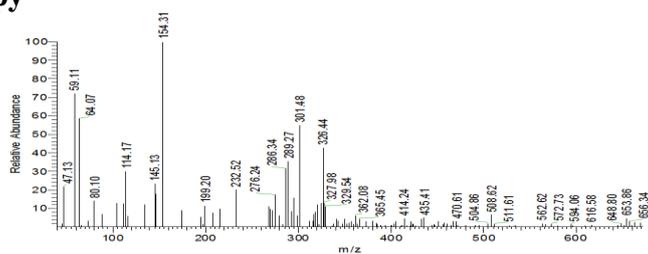


Figure 1. Mass spectra of the prepared compound (I18a)

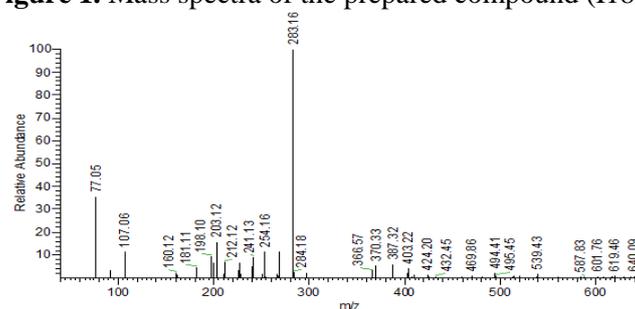


Figure 2. Mass spectra of the prepared compound (I18b)

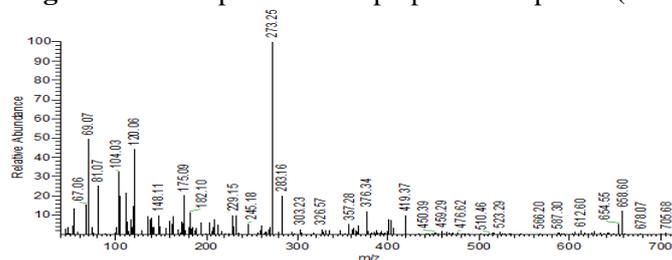


Figure 3. Mass spectra of the prepared compound (I18c)

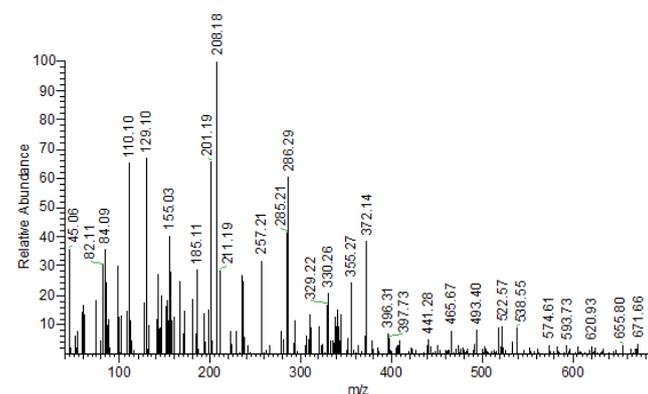


Figure 4. Mass spectra of the prepared compound (I18d)

Table 4. Chemical shifts of compound I18_a

H ⁺ Types	a (d)	b (d)	c(d)	d(s)	e(d)	f(d)	g(d)	h(t)
Chemical shift	8.122	8.07	8.03	7.947	7.853	7.453	7.147	4.32
H ⁺ Types	I(m)	j(m)	k(d)	k-(t)	l(t)	m(m)	n(m)	o(t)
Chemical shift	4.105	3.305	1.738	1.622	1.402	1.357	1.237	0.943

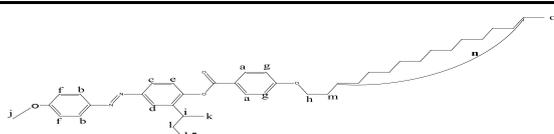
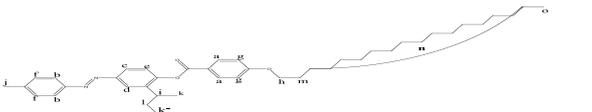
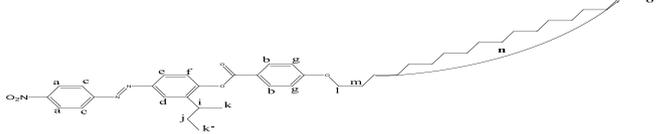


Table 5. Chemical shifts of compound I18_b

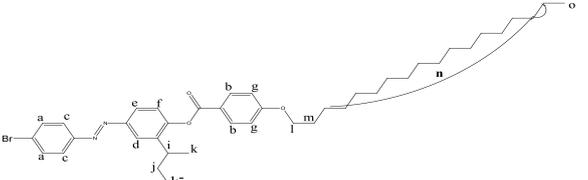
H ⁺ Types	a(d)	b(d)	c(d)	d(s)	e(d)	f(d)	g(d)	ht)
Chemical shift	8.012	7.810	7.751	7.703	7.601	7.131	6.553	4.125
H ⁺ Types	I(m)	j(m)	k(d)	k-(t)	l(t)	m(m)	n(m)	o(t)
Chemical shift	3.502	3.290	1.902	1.810	1.639	1.501	1.221	0.577


Table 6. Chemical shifts of compound I18_c

H ⁺ Types	a(d)	B(d)	c(d)	d(s)	e(d)	f(d)	g(d)	
Chemical shift	8.463	8.129	7.886	7.656	7.438	7.186	7.053	
H ⁺ Types	I(m)	j(m)	k(d)	k-(t)	l(t)	m(m)	n(m)	o(t)
Chemical shift	4.264	4.045	2.201	1.913	1.716	1.422	0.980	0.606


Table 7. Chemical shift of compound I18_d Where (s) single,(d) doublet,(t) triplet and (m) multiplet

H ⁺ Types	a(d)	b(d)	c(d)	d(s)	e(d)	f(d)	g(d)	
Chemical shift	8.383	8.109	7.891	7.951	7.152	7.012	6.914	
H ⁺ Types	I(m)	j(m)	k(d)	k-(t)	l(t)	m(m)	n(m)	o(t)
Chemical shift	5.553	3.868	3.352	3.261	3.097	1.561	1.091	0.789



Differential scanning calorimetry (DSC)

In order to investigate the effect of terminal substituents (X) on the mesophase behavior of compounds I18_{a-d}, the number of carbon atoms in the alkoxy substituent were kept constant (C₁₈H₃₇O-). The substituent x varied between CH₃O-, CH₃-, Br- and NO₂-. Table 8 compares the transition temperatures of the four compounds (I18_{a-d}).

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 6), which should be increased stabilized the mesophase. This heuristics is in accordance with the observed results, (Table 8), in which the nitro analogue has the highest clearing (T_c) temperature. On the contrary, the molecules of the methoxy and methyl analogues (Figure 7) are expected to possess lower dipolar character that would lead to derivatives with lower T_c values.

Table 8. Comparison of the transition temperatures of the compounds (I18_{a-d})

Cpd.	T _{s-s}	T _m	T _{A-N}	T _c
I18 _a	9.43	49.55	-	62.16
I18 _b	16.96	38.88	-	51.50
I18 _c	18.25	41.39	50.23	56.00
I18 _d	-	46.86	-	78.42

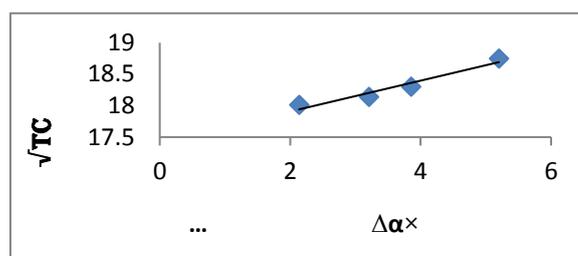


Figure 5. Dependence of T_c on the polarizability anisotropy $\Delta\alpha \times$ of the Car-x bonds for series I18a-d.

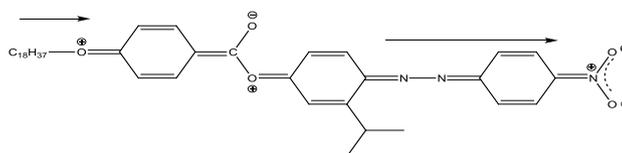


Figure 6. Conjugative interaction within the nitro substituted homologue I18d.

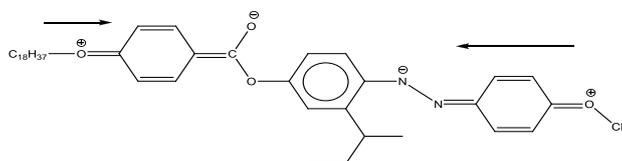


Figure 7. Conjugative interaction within the nitro substituted homologue I18a.

In order to investigate the effect of terminal substituents (X) on the mesophase behavior of compounds I18a-d, the number of carbon atoms in the alkoxy substituent were kept constant ($C_{18}H_{37}O-$). The substituent x varied between CH_3O- , CH_3- , Br- and NO_2- . Table 8 compares the transition temperatures of the four compounds (I18a-d).

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 6), which should be increased stabilized the mesophase. This heuristics is in accordance with the observed results, (Table 8), in which the nitro analogue has the highest clearing (T_c) temperature. On the contrary, the molecules of the methoxy and methyl analogues (Figure 7) are expected to

possess lower dipolar character that would lead to derivatives with lower T_c values.

Evaluation of the synthesized compounds as antioxidants using change Total Acid Number (TAN)

The total acid number (TAN) defined the amount of potassium hydroxide in milligrams that is needed to neutralize the acids in one gram of oil. It is important to evaluate the amount of additive reduction, acidic contamination and oxidation of lubricant degradation. It is an important quality measurement of crude oil used as a guide in the quality control of lubricating oil formulations. It is also sometimes used as a measure of lubricant degradation in service. The TAN value indicates the crude oil refinery and the potential of corrosion problems. Testing for TAN is essential to maintain and protect equipment, and

also prevent damage in advance. TAN testing is a measure of both the weak organic acids and strong inorganic acids present within oil. The total acid number is an analytical test to determine the deterioration of lubricants. The more acidic a lubricant is, the more degradation occurs. As a fluid degrades, the levels of corrosive acids increase along with the danger of component failure.

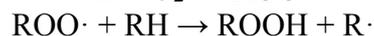
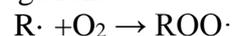
The TAN value itself cannot be used to predict the corrosive nature of an oil, as the test only measures the amount of acid in a sample, not the specific quantities of different acidic compounds in the sample. Two samples might have the same TAN value, but one has high levels of corrosive acids while the other has much lower levels of the same corrosive acids. An increase in viscosity and the formation of gums and resins are two other negative effects which can be attributed to an increased TAN value. A rise in TAN is indicative of oil oxidation due to time and/or operating temperature. Trend as well as absolute values should be used to monitor TAN levels.

The synthesized antioxidants were added to the base stock. The obtained blends were subjected to severe oxidation conditions at 120 °C. Samples were taken at specific time intervals (24, 48, 72 and 96 h) of oxidation. Usually the total acid number (TAN) of the oil increases by increasing the oxidation time. The increment of TAN values is due to the oxidation processes which produce peroxides. These peroxides undergo further reaction to form a variety of oxygenated compounds such as alcohols, aldehydes and ketones. The TAN is affected by the formation of carboxylic acids after prolonged oxidation and it also increases with increasing carbonyl formation which deteriorates the lubrication ability of the oil [22,23].

1. Initiation:



2. Propagation:



3. Termination:

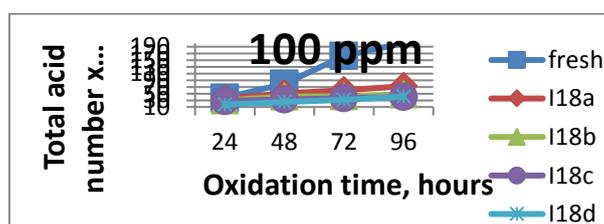
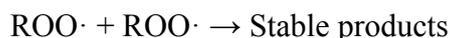
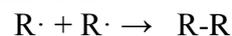


Figure 8. Variation of Total Acid Number (TAN) of base oil without and with 100 ppm I_{18a-d} additives

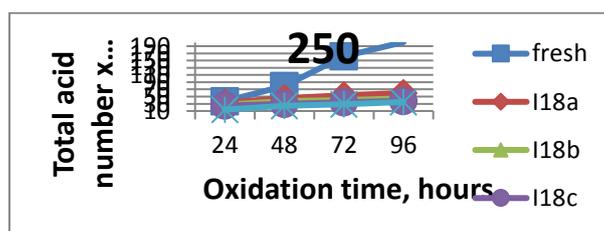


Figure 9. Variation of Total Acid Number (TAN) of base oil without and with 250 ppm I_{18a-c} additives

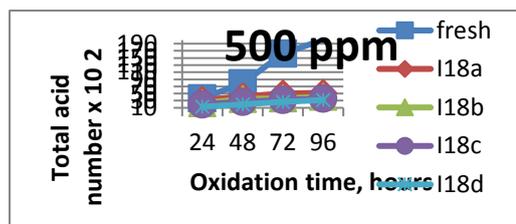


Figure 10. Variation of Total Acid Number (TAN) of base oil without and with 500 ppm I18a,-d additives

Looking at the table, we can see that the Base oil +I_{18a} shows TAN at 100 ppm after 24 hour, Base oil + I_{18b} shows the same at 500 ppm after 48 hours while the Base oil + I_{18d} shows the same after 96 hours. Using 500 ppm from 18a after 24hours, 100 ppm from 18c after 48 hours or 500 pm after 72 hours and 500ppm from 18d after 96 hours, accordingly, one can notice that TAN of .032 mg KOH/g from the table 9, figures 8:10, it can be observed that, generally, the TAN of the oxidized base stock was increased by increasing the duration time. First of all, after 24 hours, the TAN decreases by increasing the concentration of the additive added from each of the four used compounds.

The Base oil + I_{18d} showed the best results.

Increasing the oxidation period to 48, 72 and 96, the TAN also decreases by increasing the concentration dose of any used additive. Again, the Base oil + I_{18d} gave the best results.

Looking at the table, we can see that the Base oil +I_{18a} shows TAN at

100 ppm after 24 hour, Base oil + I_{18b} shows the same at 500 ppm after 48 hours while the Base oil + I_{18d} shows the same after 96 hours. Using 500 ppm from 18a after 24hours, 100 ppm from 18c after 48 hours or 500 pm after 72 hours and 500ppm from 18d after 96 hours, accordingly, one can notice that TAN of .032 mg KOH/g sample was obtained from each. Although the I_{18c} gave the best condition, TAN of 0.20 mg KOH/g sample, using 500 ppm after 24 hours, showed less efficiency as compared to I_{18d} at 48, 72 and 96 h.

The obtained results after 24 hours from 18a using 100 ppm, after 48 hours from 18b using 500 ppm and from 18d after 96 hours using 250 ppm are the same (TAN 0. 35 mg KOH/g sample). But, although it's more economical to use low concentration from the additive added, it is more efficient to use high concentration to run more operating time. So, the 18d is more efficient because it gave the same results after long operating period.

Table 9. Variation of total acid number, TAN with and without additives

Time (Hrs)	Base Stock *	Base Stock + Additive x 10 ²													
		Base oil + 18a				Base oil + 18b				Base oil + 18c				Base oil + 18d	
24	37	100	250	500	100	250	500	100	250	500	100	250	500		
48	79	35	33	32	30	27	33	28	25	20	17	14	13		
72	162	51	46	42	41	38	35	32	30	27	25	24	20		
96	201	70	54	50	42	40	37	36	34	32	31	29	27		
		72	60	52	48	45	41	40	38	36	41	35	32		

Conclusion

The results obtained in this work indicate the following results:

1. Four prepared compounds had properties of liquid crystals.
2. In our study, Liquid crystals give more efficiency as antioxidant.

3. The prepared antioxidants proved to be successful in enhanced the oxidation stability of the base stock.

4. The above (Total Acid Number) data reveal that the most effective concentration is (500 ppm).

From the previous data we noted that, the inhibition efficiency of the two prepared antioxidants is ranked as follows I18d > I18c > I18b > I18a.

References

- [1] M.D. Johnson, S. Korcek, M. Zinbo, *Industrial & engineering chemistry research*, 26, **1987**, 1754-1757.
- [2] S.K. Naidu, E.E. Klaus, J.L. Duda, *Industrial & engineering chemistry product research and development*, 23, **1984**, 613-619.
- [3] F. Egharevba, A.U. Maduako, *Industrial & engineering chemistry research*, 41, **2002**, 3473-3481.
- [4] E. Abner Jr, Lubricant deterioration in service, CRC Handbook of Lubrication, Citeseer, **1983**, pp. 517-532.
- [5] G. Offunne, A. Maduako, C. Ojinnaka, *Tribology International*, 22, **1989**, 401-404.
- [6] G. Ofunne, A. Maduako, C. Ojinnaka, *Tribology International*, 23, **1990**, 407-412.
- [7] E. Klaus, L. Cho, H. Dang, SAE Technical Paper, **1980**.
- [8] F.J. Carrion, G. Martinez-Nicolas, P. Iglesias, J. Sanes, M.D. Bermudez, *Int J Mol Sci*, 10, **2009**, 4102-4115.
- [9] M.D. Bermúdez, W. Brostow, F.J. Carrión-Vilches, J.J. Cervantes, D. Pietkiewicz, *Polymer*, 46, **2005**, 347-362.
- [10] T. Hirose, H. Takai, M. Watabe, H. Minamikawa, T. Tachikawa, K. Kodama, M. Yasutake, *Tetrahedron*, 70, **2014**, 5100-5108.
- [11] R.I. Nessim, M.M. Naoum, S.Z. Mohamed, M.I. Nessim, *Liquid Crystals*, 31, **2004**, 649-654.
- [12] G. Biresaw, D. Zadnik, *Tribology and the Liquid-Crystalline State*, **1989**, 83-90.
- [13] M.-D. Bermúdez, G. Martínez-Nicolás, F.-J. Carrión-Vilches, *Wear*, 212, **1997**, 188-194.
- [14] S. Mori, H. Iwata, *Tribology international*, 29, **1996**, 35-39.
- [15] Y. Kimura, K. Nakano, T. Kato, S. Morishita, *Wear*, 175, **1994**, 143-149.
- [16] M. Shen, J. Luo, S. Wen, J. Yao, *Tribology & Lubrication Technology*, 58, **2002**, 18.
- [17] K. Nakano, *Tribology Letters*, 14, **2003**, 17-24.
- [18] P. Iglesias, M. Bermudez, F. Carrion, G. Martinez-Nicolás, *Wear*, 256, **2004**, 386-392.
- [19] M.M. Naoum, G.R. Saad, R.I. Nessim, T.A. Abdel-Aziz, H. Seliger, *Liquid crystals*, 23, **1997**, 789-795.
- [20] M.I. Nessim, A.A. Bassoussi, D.I. Osman, H.F.Khalil, A.M.Ashmawy, *International Journal of Current Research*, 6, **2014**, 9203-9216.
- [21] S.Z. Mohammady, R.I. Nessim, O.R. Shehab, M.M. Naoum, *Liquid Crystals*, 32, **2005**, 477-482.
- [22] H. Omrani, A.E. Dudelzak, B.P. Hollebone, H.-P. Looock, *Analytica chimica acta*, 811, **2014**, 1-12.
- [23] M. Rashed, M. Kalam, H. Masjuki, H. Rashedul, A. Ashraful, I. Shancita, A. Ruhul, *RSC Advances*, 5, **2015**, 36240-36261.

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