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To cite this article: A.Y. El-Naggar, R. A. El-Adly, T. A. Altalhi, A. Alhadhrami, F. Modather, M. A. Ebiad & A. Salem (2017): Oxidation stability of lubricating base oils, *Petroleum Science and Technology*, DOI: [10.1080/10916466.2017.1403450](https://doi.org/10.1080/10916466.2017.1403450)

To link to this article: <https://doi.org/10.1080/10916466.2017.1403450>



Published online: 26 Dec 2017.



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Oxidation stability of lubricating base oils

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ABSTRACT

The oxidative stability of three base lubricating oils of different grades light, medium and heavy oils (B1, B2 and B3, respectively) was studied at oxidative times 50, 100 and 150 hours. The quality of base oils under investigation were evaluated on the basis of total acid number, vaporization loss, kinematic viscosity and quantity of sludge formed. Also, the chemical composition of the studied lubricating oils was achieved via capillary gas chromatography. The comparative study of the oxidative performance of the base oils showed that the higher degrees of heavy oil than light one. The increase in the oxidation time led to increases of the evaporation loss and lubricant viscosity. Analysis of a lubricant's oxidation stability therefore contributes to a better understanding of its effectiveness under normal operating conditions and its suitability for formulating automotive lubricants. The aim of this work is the study the Potential life of lubricant oils inside engine motor at different oxidative times in view of their oxidation stability.

KEYWORDS

base lubricating oils; capillary gas chromatography; chemical composition; oxidation stability; oxidative times; total acid number

1. Introduction

The lubricating oils are generally petroleum oils of different compositions according to their biomarkers, (El-Sabagh et al. 2017). The rheological behavior, chemical composition and physicochemical properties of base mineral oils were explored for assessing the reliability for production of lubricating oils, (El-Adly et al 2013). Four categories of engine oils, virgin, used, recycled and oil extracted from multi-component resin were identified using capillary gas chromatography (El-Naggar and R. A. El-Adly, 2013). Formulation of automotive lubricating oil is a complicated process. The modern engine lubricant is a carefully designed blend of base oils and performance enhancing additives, such as pour point depressants, antioxidants, dispersants and detergents,

(Pedersen and Ronningsen 2003). Regardless of the complexity, the lubricating oil formulator must assess the performance of the base oil and the additives, and finally balance the performance and the cost, prior to the full-scale engine testing of the oil. Because engine testing is an expensive process, a number of bench tests have been developed to screen out the lubricating oil throughout the formulation process, (Perez 2000). Many of these bench tests are time Consuming, man-power intensive, empirical, show poor reproducibility and require a large investment in specialized equipment and skilled operators, and may be advantageously replaced by conventional thermal analysis techniques, (Siyuan and James 2016 and Gamlin, et al 2002). The thermal degradation process of mineral base lubricating oils was studied by thermal, spectroscopic and rheological analysis, (Santos et al 2007). On other hand, paraffinic hydrocarbons distribution in petroleum compounds was investigated using Gas chromatography, (El-Naggar

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A. Y. 2006 and EL Nady et al 2012). Several methods have been developed to evaluate oxidation of a lubricant. Thermal analytical methods are important and effective, (Walker and Tsang 1980, Bolesław K. 1995, Zeman, et al 1984 and Kowalski 1995). In this work, the oxidative behaviour of three grades from base lubricating oils, light, medium and heavy oils, were studied at oxidative time 50, 100 and 150 hours. Also, the changes in paraffinic composition of these oils after oxidation times were determined.

2. Experimental

2.1. Base oil

Three types of base oils, light, medium and heavy were designated B1, B2 and B3, respectively. These types of base oil were obtained from raw lubricant distillates of mixed crude oils from Al-Ameria petroleum refinery. The physico-chemical characteristics of these oils were carried out as reported elsewhere, (El-Sabagh et al 2015). In this respect, insoluble product and resin content were evaluated according to ASTM D-893 method. This method involves dissolving the oxidized oil sample in pentane, then washing and drying the residue to evaluate the pentane insoluble. The procedure is repeated on the residue using benzene, the difference in the residue being referred to as the resin content of the oxidized oil.

2.2. Oxidation test

Oxidation characteristic of base oils under investigation was carried out according to modified ASTM d 943. The tested samples were oxidized at 150°C using copper coil as catalyst and flow rate 5 liter per hours for 50, 100 and 150 hours. After testing, the density, viscosities at 400C and 100°C, total acid number (TAN) and flash point of the tested oil samples were determined using ASTM methods D 1480, D 445, D 664 and D 92, respectively. The rate of oxidation was measured by the increase in total acid number and viscosity

2.3. Gas chromatography analysis

The three grades of base lubricating oil samples after oxidation times were analyzed using Agilent 6890 plus HP gas Chromatograph, equipped with flam ionization detector (FID), using fused silica capillary column HP-1 of 30 meter length and 0.35 mm internal diameter. The elution of the recycled lubricating oil was achieved with temperature programming from 80 to 300°C at temperature rate of 5°C min⁻¹. Nitrogen (oxygen-free) was used as carrier gas, flow rates was measured uncertain marker was used to correct the dead volume from the end of the column with a soap bubble flow rate. The injector and detector temperatures were 250 and 300°C respectively. The nature of the base lube oils and the chemical nature of these oils can drastically alter the profiles of the chromatographic obtained. The rate of oxidation was measured by the increase UCM compounds and change in paraffinic distributions

3. Results and Discussion

The physicochemical properties are necessary to study the general relationships governing the change in base oil composition in the operation. Research along this line is being conducted elsewhere (4, 5). Thermal degradation of base oils by oxidative mechanisms is potentially a very serious problem such as, increase total acid number, formation of polymers leading to sludge and viscosity changes. It is necessary to monitor simultaneously the change in physicochemical properties of base mineral oils, that is determined by this method can be used to determine the change in product viscosity, TAN and sludge content. Thermal oxidative analysis of the quality of the studied base oils for automotive engine, and certain relationships in oil properties that have been established on this basis. Accordingly, experimental data in Table 1, show the physicochemical properties of base mineral oils after thermally oxidative

Table 1. Physico-chemical properties of oxidized base oil for different time.

Oxidation time, (hr) Characterization	50			100			150		
	B1	B2	B3	B1	B2	B3	B1	B2	B3
Specific gravity @ 15°C	0.8801	0.8812	0.8815	0.8809	0.8818	0.8820	0.8813	0.8825	0.8840
Evaporization loss, wt%z	3.0	2.5	2	4.5	3.5	3.2	7.5	5	4.5
Kinematic viscosity, Cst									
@40°C	55	106	130	84	141	148	95	195	217
@100°C	7	11	11	10	13	14.5	10	18	19
Viscosity index	93	94	95	93	94	94	94	93	94
Pour point, °C	-3	-3	-3	0	0	0	3	3	3
Sludge content	0.2	0.3	0.5	1.3	1.5	2	2.5	3.1	4.2
Flash point, °C	180	186	193	185	195	205	190	210	220

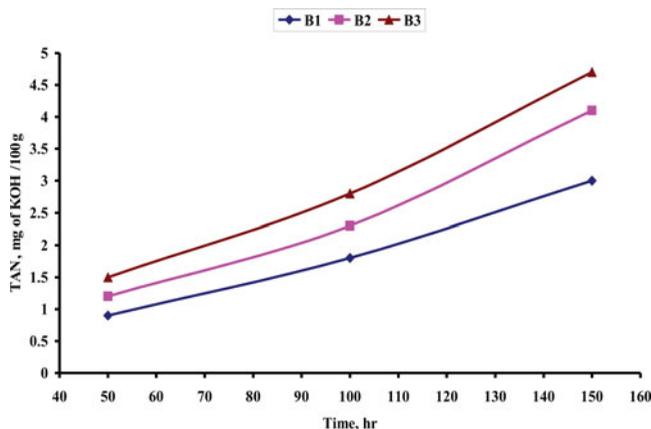
at 120°C for 50,100 and 150 hr were carried out using ASTM/ IP standard methods analysis. Comparing with the three base oils (B1, B2 and B3) the B3 is characterized by relatively higher content of both carbon residue and sludge leading to higher flash point at all oxidation times. Also, it may be of interest to point out that the kinematic viscosity at all oxidation times for B3 having highest values over B1 and B2. This reveal that at increasing oxidation time the viscosity of the B3 increases as a result of the polycondensation of the oxygenated products formed in the oxidation phase. Further polycondensation and polymerization reactions of these high molecular weight intermediates form products which are no longer soluble in the hydrocarbon.

Experimental data of evaporation loss of base oils under investigation are presented in Table 1. These data indicates that the thermo-oxidative treatment leads to a degradation of mineral oils increased with increasing oxidation time for all oils. On other hand, sludge content is increased of these oils with increasing oxidation time. It could be explained due to the polymerization reaction, with formation of high molecular weight products. It may also be observed that the increase oxidation time leads to an enlargement and consequently, an increase in the resinous compounds.

The physicochemical properties of the studied base oils are strongly inter-correlated, viscosity, pour point, carbon residue content and evaporation loss. They also strongly correlated with percentage of the asphaltene and resin (sludge) content.

Total acid number is used as a guide in the quality control of lubricating oil. It is also used as a measure of lubricant degradation in service. Figure 1 presents the TANs data of the three oils after thermal oxidation for 50,100 and 150 hours. TANs have increased in the following order B3>B2> B1 as shown in Figure 1.

These data indicate that the amount of oxidation products and acidic substances in case B3 higher than B2 and B1. This view confirmed by the sludge content (Table 1) of the three base oils after tests, which


Figure 1. Variation of TAN with thermal oxidation time of base oils (B1, B2 and B3).

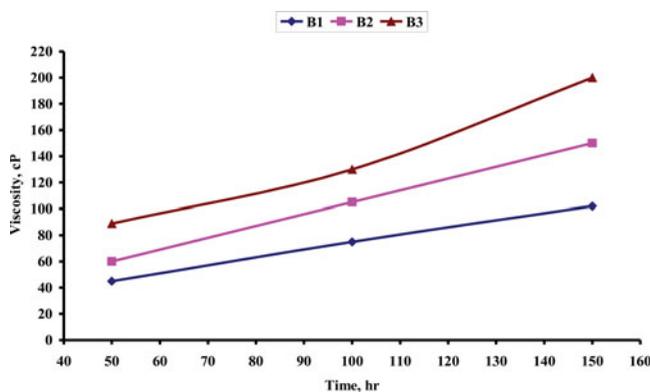


Figure 2. Variation of dynamic viscosity with thermal oxidation time of base oils (B1, B2 and B3).

supports the low thermo-oxidation stability of oils B3 and B2 compared with B1. From these results, it is clear that the developed procedure is capable of differentiating between base mineral oils within a short measuring time (150 hours). The combination of TAN and sludge content can help greatly in evaluating the thermo-oxidation stabilities of base mineral oils.

Apparent viscosities of base oils under investigation results are presented in Figure 2. It may be observed that the three base oil (B1, B2 and B3) show an increase in dynamic viscosity with oxidation time. This data may be due to evaporate loss of lower viscosity components. This evaporation may be related to thermal oxidative degradation. On this way, the sludge content for B1, B2 and B3 are increasing with increasing oxidation time as presented in Table 1. According to literature data (Perez JM. 2000) carboxylic acids and ketones are formed after thermal oxidation, leading to the formation of hydrogen bonding and dipole-dipole interaction. As result, higher intermolecular forces are formed, increasing oil viscosity. On the other hand, oxidation products are detected and determined through total acid number for all samples after thermo-oxidative time. This way, we believe that viscosity variation may not be related to oxidative compounds. Another possibility is a polymerization reactions, these reactions could be explained on the basis of free- radical mechanism, which may also lead to a viscosity increase, due to the formation of high molecular weight products.

Also, the oxidation phase becomes diffusion controlled as hydrocarbon viscosities increase from progressive polycondensation of higher molecular weight products, causing varnish and sludge formation. These finding results are in good agreement with the results reported by (El-Nagggar A. Y. and Eladly R. A. 2013).

Inspection and correlation of the data of the physicochemical properties listed in Table 1, Figures 2 and 3 show that the light base oil (B1) has a higher thermo oxidation stability than oil B2 and B3. On other hand, B1 is characterized by relatively higher content of evaporation loss compared with B2 and B3. The selection of components for lubricating oil formulation requires knowledge of the most suitable crude sources for the base oils, the type of refining required, the types of additive necessary, and the possible effects of the interactions of these components on the properties of the finished lubricating oil.

3.1. GC data of the three oils after oxidation

The capillary gas chromatography of the three base lubricating oils of different grades light, medium and heavy oils after oxidation were given in Tables 1–3 and Figure 1. It has been found that each oil has two important parts the first is the paraffines over the second part which is a hump and these two parts are differ in percentages for light, medium and heavy lubricating oils. The hump represents the unresolved complex mixture and contains polycyclic aromatic hydrocarbons, naphthens and resins. All samples have a wide range of paraffines from Heptadecanes (C_{17}) to Tetracontanes (C_{40}) but with different low percentages. Hexacosanes (C_{26}) is the predominate carbon number along the carbon number distribution

Table 2. Hydrocarbon compositions of the studied lubricating oil at three different interval times of oxidation.

Components	Interval Times of oxidation of light lubricating oil			Interval Times of oxidation of middle lubricating oil			Interval Times of oxidation of heavy lubricating oil		
	50 (hours)	100 (hours)	150 (hours)	50 (hours)	100 (hours)	150 (hours)	50 (hours)	100 (hours)	150 (hours)
Heptadecanes	0.119	0.077	0.011	0.090	0.027	0.005	0.000	0.000	0.000
Octadecanes	0.846	0.675	0.231	0.698	0.240	0.126	0.000	0.000	0.000
Nonadecanes	2.269	1.882	1.014	0.992	0.287	0.138	0.000	0.000	0.000
Icosanes	4.161	3.467	1.889	1.889	1.007	0.440	0.000	0.000	0.000
Eneicosanes	4.912	3.910	3.155	2.519	1.779	0.900	0.000	0.000	0.000
Dodeicosanes	5.123	4.624	3.807	2.881	2.071	1.259	0.000	0.000	0.000
Tricosanes	4.825	5.049	4.049	3.446	2.696	1.477	0.000	0.000	0.000
Tetraicosanes	6.270	6.084	4.488	4.238	3.488	2.404	0.000	0.000	0.000
Pentaicosanes	6.965	7.070	5.237	4.997	4.667	3.106	0.200	1.140	0.684
Hexaicosanes	8.333	8.116	6.778	5.623	5.658	3.814	0.264	1.325	0.772
Heptaicosanes	7.993	7.705	7.163	6.423	6.494	5.235	0.525	1.960	1.139
Octaicosanes	7.573	7.579	7.758	7.099	7.211	6.596	0.888	2.233	1.557
Nonaicosanes	7.283	7.146	8.305	7.941	8.033	7.706	1.229	2.841	1.988
Tricosanes	6.838	6.662	7.874	8.463	8.540	8.984	1.988	3.846	2.757
Entricosanes	5.675	6.178	7.195	8.960	8.939	10.238	4.363	5.774	5.003
Dodetricontanes	4.393	5.365	6.775	9.643	9.738	11.306	8.052	7.794	8.283
Tritricontanes	3.432	4.417	5.550	7.738	7.943	8.984	10.450	9.607	9.754
Tetratricontanes	3.005	3.246	4.247	4.992	5.577	7.302	11.695	10.794	11.191
Pentatricontanes	2.469	2.834	3.578	3.402	4.607	6.107	12.522	11.703	12.594
Hexatricontanes	2.148	2.297	2.959	2.643	3.868	4.403	13.840	13.243	13.728
Hepatricontanes	1.778	1.778	2.274	1.780	2.674	3.249	11.309	10.224	10.481
Octatricontanes	1.855	1.257	1.660	1.190	1.677	2.511	9.648	7.764	8.283
Nonatricontanes	0.921	1.046	1.298	0.896	1.101	1.954	6.630	5.340	6.366
Tetracontanes	1.48	1.54	1.658	1.46	1.68	1.75	6.40	4.41	5.42
Total	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00	100.00
Paraffines	3.97%	3.07%	2.32%	2.57%	1.82%	1.61%	1.61%	1.15%	0.90%
UCM	96.03%	96.93%	97.68%	97.42%	98.18%	98.39%	98.39%	98.85%	99.09%
Mol WT	369.5	375.113	388.7	394.378	406.482	422.407	422.407	471.5	478.5

in the middle lubricating oil after 50 and 100 hours interval times of oxidation, nonacosanes (C_{26}) is the predominate one after 150 hours of oxidation.

With respect to the light lubricating oil, the total paraffinic hydrocarbons for the three intervals times 50, 100 and 150 (hours) are 3.97%, 3.07% and 2.32% respectively as given in Table 1. High oxidation time accompanied with both low paraffinic hydrocarbon percentage and high heavy fraction of hydrocarbons. This means that lubricating oil at high oxidation time becomes high molecular weight due to the degradation of light hydrocarbons and formation of polymeric compounds.

Hydrocarbon compositions of middle lubricating oil at three different interval times of oxidation were given in Table 2. Generally the total paraffinic hydrocarbons in middle lubricating oil are lower than that in light lubricating oil. Dodetricontanes (C_{32}) is the predominate carbon number along the carbon number distribution of the middle lubricating oil after all interval times of oxidation. Table 3 gives the hydrocarbon compositions of heavy lubricating oil at three different interval times of oxidation; this oil has the lowest percentages of paraffinic hydrocarbons which decrease with increasing interval times of oxidation. Most composition of heavy lubricating oil is unresolved complex mixture including poly aromatic and poly cyclic hydrocarbons.

4. Conclusion

- This paper evaluate the quality of base oils using standard test procedures (flash point, viscosity, sludge content and carbon residue), and compared the data obtained from these procedures to the data from GC analysis. Oxidized base oil designated B3 is characterized by the having high viscosity, carbon residue, sludge content, flash point and total acid number, while base oil B2 has medium values of these characteristics, but base oil B1 is characterized by having high evaporation loss and low values of total acid number. The results obtained from determining the total acid number indicates that the thermal stability of base oils decrease with increase the heavy ends. In general, total acid number increased with increasing oxidation time.
- The paraffinic hydrocarbons represent the lowest percentages in lubricating oil samples compared with the aromatic and naphthenic hydrocarbons. Most composition of studied lubricating oils is unresolved complex mixture including poly aromatic and poly cyclic hydrocarbons.

Heavy oil has the lowest percentages of paraffinic hydrocarbons compared with the other light and middle lubricating oils which decrease with increasing interval times of oxidation. The area of UCM increases with increasing oxidation times for the studied lubricating oils and this area increases in the order, light, middle and heavy ones.

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