Evaluation of the Thermooxidation Stabilities of Additive-free Automotive Crankcase Lube Oils

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--ABSTRACT--
The incorporation of additives as fortifiers in lube oils is meant to enhance their performance characteristics during normal engine operations. In this study the thermooxidation stabilities of two commercially available grades of automotive crankcase oils namely, SAE-28W50 and SAE-10W40 and their mixed stock blend have been evaluated to determine their additive-free stability status, which can be used as baseline in crankcase lubricant formulation. The assay on the crankcase basestocks was carried out by simulating the high temperature conditions encountered in the spark ignition internal combustion engines under normal operation. To obtain the base oil samples the two commercial grades of the oils were stripped of their additive components using chromatographic columns stacked with Florisel (100-200) and Silica Gel (90-230) mesh arranged in alternate positions. The recovered basestocks were treated in a modified version of the Turbine Oil Oxidation Test (TOOT) apparatus developed in our laboratory. The tests were carried out by thermally oxidizing the base oils with a steady air flow rate of 1.0l/hr at a given test temperature for 2.5hrs. The temperature was raised by 40^0C after every 2.5hrs till a maximum temperature of 380^0C was attained. A blend of of 1:1 mixture of the basestocks was also treated under same test conditions. The thermooxidation stabilities of the basestocks were evaluated based on standard parameters namely, the Total Acid Number (TAN) and the Total Oxidation Products (TOP,) Infrared spectroscopy was also used to evaluate the molecular changes in the degraded basestocks .The results showed that the synthetic basestock was thermooxidatively most unstable, followed closely by the mixed stock blend; while the mineral basestock was the least unstable at all temperatures ranging from 100^0 up to 380^OC.Thereforeon on quality consideration, it can be deduced that the knowledge of thermooxidation stability status of the basestocks can be used as a guide for formulating lubricants with high performance characteristics for the spark ignition internal combustion engines.

KEY WORDS: Crankcase basestocks, Thermooxidation, Stability status, Performance characteristics

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I   INTRODUCTION

The performance characteristics of lubricating oils used in the spark ignition internal combustion engines depend largely on their thermal and oxidation stabilities. The more stable the oil the greater the tendency to reduce friction between two surfaces in relative motion. In an automotive crankcase engines friction constitutes a great deal of nuisance which can result in engine damage. [1] has described friction and wears as the major tribological problems which have remained an object of great concern even before the invention of wheels. One of the ways in which friction affects the automotive engine is through the production of heat. [2] noted that hot‑spot temperatures in automotive engines can be in the range of 90°C at the connecting rod cylinder to about 380°C at the piston crown. Under this condition the engine without a lube-oil with high stability is bound to be adversely affected if not completely damaged. This explains why well formulated lubricant is required to absorb the heat generated by frictional interactions between surfaces in relative motion. Formation of lube-oil for effective surface separation [3] therefore requires a careful combination of materials with high thermal and thermoxidative stabilities. Thus, the modern engine design imposes stringent requirements on the physiolochemical characteristics of the automotive crankcase lube oils [4]. However, the choice of lubricant is usually detected by the prevailing temperature at the surface of the engine components [5].

Another important requirement for lube oil formulation is the choice of additives such as antioxidants (example hindered phenol) to prevent lube oil deterioration associated with oxygen attack on the base fluid. The antioxidants function by interacting with the hydroperoxide radicals to form inactive compounds thereby preventing the formation of varnish and sludge [6]. Other additives incorporated as fortifiers including viscosity improvers which are long-chain high molecular weight polymers such as styrene-butadene co-polymer and

polymethacrylate, both of which function by counteracting the temperature effect on the hydrocarbon matrix [7] of the base oil. Beyond the enhanced stability from the vast array of additives, lubricant as defined by the engine dynometer tests is fundamentally a measure of the stability of base oil (additives free component). [8] used sequence IIID test to evaluate the high temperature degradation of engine base oils. [9] used Turbine Oil Oxidation Test (TOOT) apparatus to study the stability of various grades of oil formulation. In this work a modified version of the Turbine Oil Oxidation Test apparatus was used to evaluate the stabilities of base oils used in formulating two of the most commercially available types of multigrade crankcase lubricants, namely Mineral Oil and Synthetic Oil, both rated by the Society of American Engineers as SAE-20W50 and SAE-10W20 respectively. Based on the observable physiochemical changes that occurred during thermoxidative decomposition of the base oils the manufacturers will be in a better position to know the quality as well as the quantity of the additives required for the lube oil formulation in order to achieve optimum performance.

II   EXPERIMENTAL

2.1   Materials and Method
The crankcase oils (mineral oil and synthetic oil) were sourced from the then ELF Petroleum Company of Nigeria and LENOIL Petroleum and Petrochemicals (Nig) Ltd respectively. The base oils of the two samples were recovered from the blended formulations by stripping them of their additives. This was achieved by the use of stacked column beds of Florisil (100-200) and silica gel (70-230) mesh arranged in alternate position. All then reagents used conformed to the analytical grades. The recovered base oils (mineral base and synthetic base) were subjected to thermo-oxidative degradation using a modified version of the standard Turbine Oil Oxidation Test (TOOT) apparatus. The samples were heated from ambient to 100°C and kept at this temperature with an airflow rate of 1.0L/hr for 2.5hours. The temperature was raised by 40°C after every 2.5hours till the maximum test temperature of 380°C was attained. A 1:1 blend of the two basestocks was also subjected to the thermooxidation stability test under the same conditions. The heating was thermostatically regulated to allow the withdrawal of the oxidized samples (oxidates) at appropriate intervals. The volatile or the gaseous products of thermoxidative degradation were at various temperature regimes trapped in freshly prepared 0.1 Molar solution of KOH and preserved for analysis.

2.2   Analytical Procedure
The analysis of the samples were carried out in accordance with the world class standard of American society for Test and materials (ASTM) method-D664 [10]. The total Acid Number (TAN) was determined a combination of oil soluble and volatile acid. It is generally believed that increase in TAN is either an indication of contamination with acidic combustion products or the results of oil oxidation [11, 12, 13].

2.3   Determination of the Oil Soluble Acidity
About 3.0g of the oxidate placed in 1.25cm^3 of 100: 99:1 Toluene/ Isopropanal/water mixture was titrated potentiometrically with 0.1M isopropanotic KOH using Kent Electronic Instrument model EIF 7050 potentiometer, with a combined glass/Calomel electrode (PYE Unicam Ingold No.44852). The volume of KOH required to titrate the oxidate (sample) to zero millivolt potential was taken as the end point of the titration. A blank determination was run by titrating 125cm^3 of the solvent mixture with KOH solution; and the soluble acidity of the oil sample was calculated using the formula: S_A (mgKOH/g) = $\dfrac{(V_a - Vb) \ x \ M \ x \ 56.1}{W}$

where V_a =   Volume of isopropanolic KOH required to titrate the
                                   sample to zero millivolt potential.
          M   =   Molarity of Isopropanolic KOH solution
          W   =   Weight of the oxidate sample in grams
          V_b =   Volume corresponding to V_a for blank titration.

2.4   Determination of the Oil Volatile Acidity
1.0cm^3 of the trapped volatile product was diluted to 10cm^3 and titrated with 0.01MHcl, using phenolphthalein indicator. The acidity of the volatiles was so determined from the formula:

V_A (mgKOH/g)   = $M/10 - (HV_x/V_y) \ 56$
  where   M   =   Molarity of KOH solution in the trap flask
          H   =   Molarity of HCL solution
          V_X =   Volume of HCL required to neutralize the sample
          V_Y =   Volume of the sample

Based on the results obtained, the Total Acid Number (TAN) of the degraded samples which is the quantity of the base expressed in milligrams of KOH required   to neutralize all the acidic constituents present in one gramme of the sample to the end point to approximately pH of 11 was determined by summing up results of both soluble acidity and volatile acidity.

2.5   Measurement of the Sludge Deposits

$1.0cm^3$ of the degraded samples were weighed into a $10cm^3$ cone-shaped centrifuge tube. $7.0cm^3$ of normal heptane (n-heptane) was added to each tube and stirred vigorously until homogenous . The mixtures were centrifuged at the maximum speed of MSE minor 35 centrifuge for 30 minutes. The oil solution was decanted and the weight of the deposits determined as heptane insolubles using the following scheme:

	S	=	(A-B)/Wx100%
where	A	=	Weight of dried insolubles and the centrifuge tube
	B	=	Weight of clean dry centrifuge tube
	W	=	Weight of degraded samples

From the foregoing, the Total Oxidation Products (TOP) was evaluated by summing up the volatile Acidity, soluble Acidity and sludge Deposit of the degraded oil samples, as given by the formula:

$$TOP (\%) = S + 180(V_A + S_A)/56$$

where	V_A	=	Volatile Acidity in mgKOH/g
	S_A	=	Soluble Acidity in mgKOH/g
	S	=	Total sludge (% insoluble)
	180	=	The assumed molecular weight of the base oil

III   RESULTS AND DISCUSSION

3.1   Thermooxidation Stability Based on TAN

The results for the first stability parameter obtained from the analysed samples are presented in table 1. These show the variation in the oil soluble acidity in mgKOH/g of the degraded samples. The oil soluble acidity ranges from 0.03 to 1.25 at T_{max} (380°C) for SAE-20W50 basestock while the value for SAE-10W40 basestock ranges from 0.05 to 1.85 at T_{max} (380°C).The observable difference between the two values at T_{max} indicates that SAE-20W 50 basestock is more thermally stable than SAE-10W 40 with the oil soluble acidity as high as 1.85 at T_{max} .In the same vein the results of the second stability parameter, namely the oil volatile acidity obtained from the analysed samples are shown in table 2. Again the mineral basestock (SAE-20W50) gives the oil volatile acidity increasing from 0.021 at T_{min} (100°C) to 1.081 at T_{max} while its synthetic counterpart (SAE-10W40) gives the oil volatile acidity ranging from 0.012 at T_{min} to 1.314 at $T_{max.}$

Table 1
Oil soluble Acidity in mgKOH/g

Temp. (°C)	100	140	180	220	260	300	340	380
SAE-20W50	0.00	0.03	0.05	0.06	0.18	0.65	0.85	1.25
1:1BLEND	0.00	0.03	0.06	0.09	0.25	0.90	1.45	1.60
SAE-10W40	0.00	0.05	0.07	0.15	0.26	1.35	1.70	1.85

Table 2
Oil Volatile Acidity in mgKOH/g

Temp. (°C)	100	140	180	220	260	300	340	380
SAE-20W50	0.00	0.01	0.02	0.01	0.25	0.50	0.85	1.65
1:1 BLEND	0.00	0.02	0.01	0.02	0.30	0.60	1.15	1.85
SAE-10W40	0.00	0.01	0.02	0.02	0.30	0.60	1.25	1.90

Using the above data (Table 1) a graph of variation in the Total Acid Number (TAN) with Temperature was plotted (fig.1) shown below:
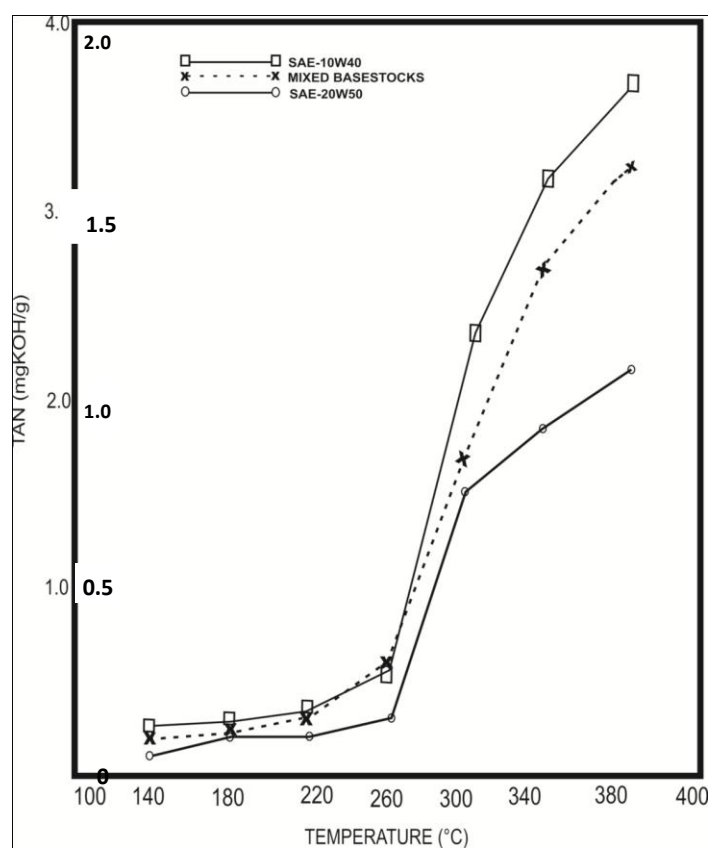

Fig. 1: Variation of Total Acid Number (TAN) with Temperature

The graph depicts a rise in TAN with temperature. Worthy of note is an exponential increase in the Total Acid Number at $260^{O}C$ for both basestock, with SAE10W40 being more affected at that temperature than the SAE20W50. This is a clear indicator that the former has lower thermooxidation stability than the latter and will require more antioxidant and other stabilizers to enhance performance characteristics during high temperature engine operation.The four temperature regimes demarcated on the graph starting from the induction period between $100^{O}C$ and $220^{O}C$; the onset of thermooxidative degradation between $220^{O}C$ and $260^{O}C$; the rapid degradation regime with exponential rise in TAN between $260^{O}C$ and $340^{O}C$; and the last regime between $340^{O}C$ and $380^{O}C$ marketing complete degradation of the bascoils, are consistent with the results obtained by [14] in the study of thermooxidation stability of jet oils.

3.2   Thermooxidation Stability Based on TOP
The second parameter used in evaluating the thermooxidation stability of the base oils is the total oxidation products (TOP). This was computed from the formula earlier stated as heptanes in soluble and incorporated in the values obtained from the soluble and volatile acidity tests. The TOP - temperature graph below further shows that SAE-10W40 basestock is more prone to thermooxidation decomposition than the SAE-20W50 basestock especially at temperatures above $300^{O}C$. The exponential rise in degradation products namely, sludge deposit, volatiles and oxidates at higher temperature regimes is in agreement with the results obtained by [9] in the study of the compositional changes in high temperature oxidation of mineral and synthetic lubricants.
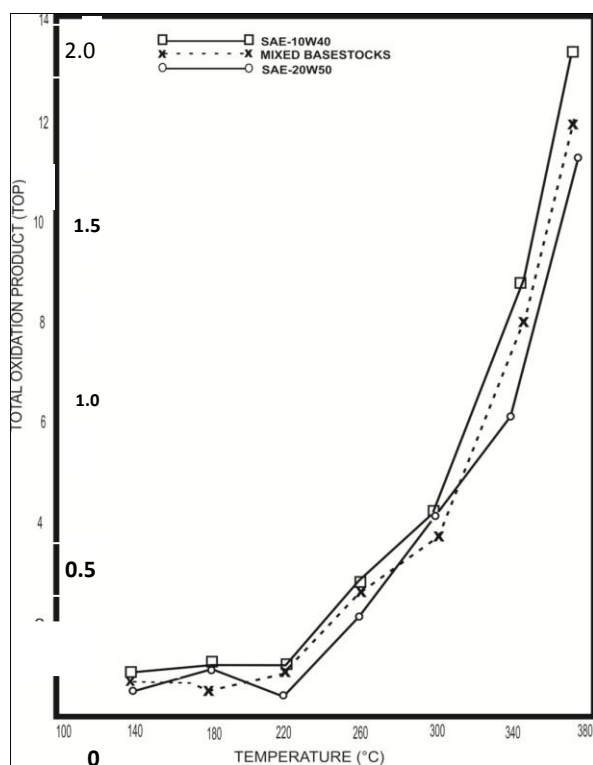
Fig. 2: Variation of Total Oxidation Products (TOP) with Temperature

3.3   Infrared Spectroscopy of the Degraded Oil Samples
The use of infrared spectroscopy as a veritable tool in detecting the oxidation products in used oils by [15] added a new dimension to the evaluation of the thermo-oxidation stability of base oils. Beyond this is the application of computer-aided infrared spectrophotometry to measure the total oxidation products in used oils by integrated area   calculation [16]. In this work infrared spectroscopic analysis was also used to evaluate the extent of base oil degradation at the maximum test temperature (Tmax) of 380°C. The spectra (figures 3 and 4) were obtained for the three basestock samples subjected to the thermo-oxidative degradation for a total of fifteen (15) hours at temperatures ranging from ambient through 380°C.
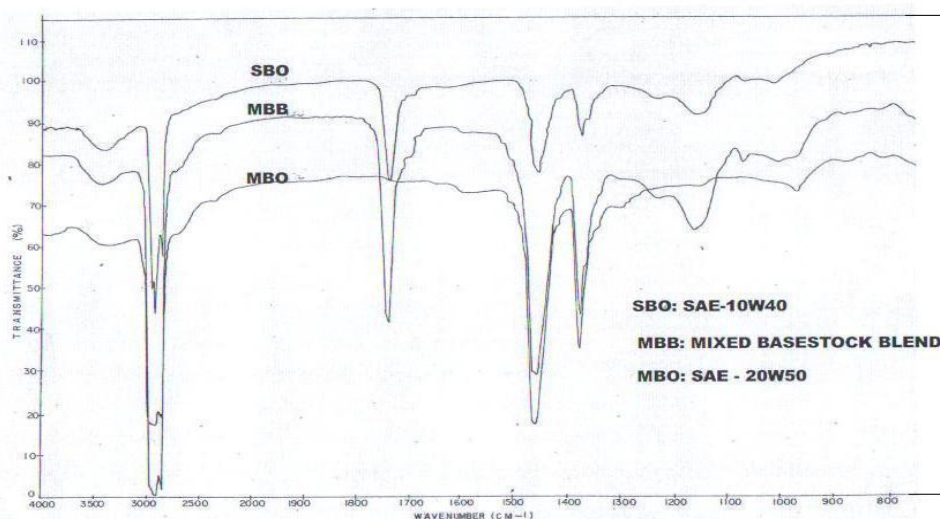
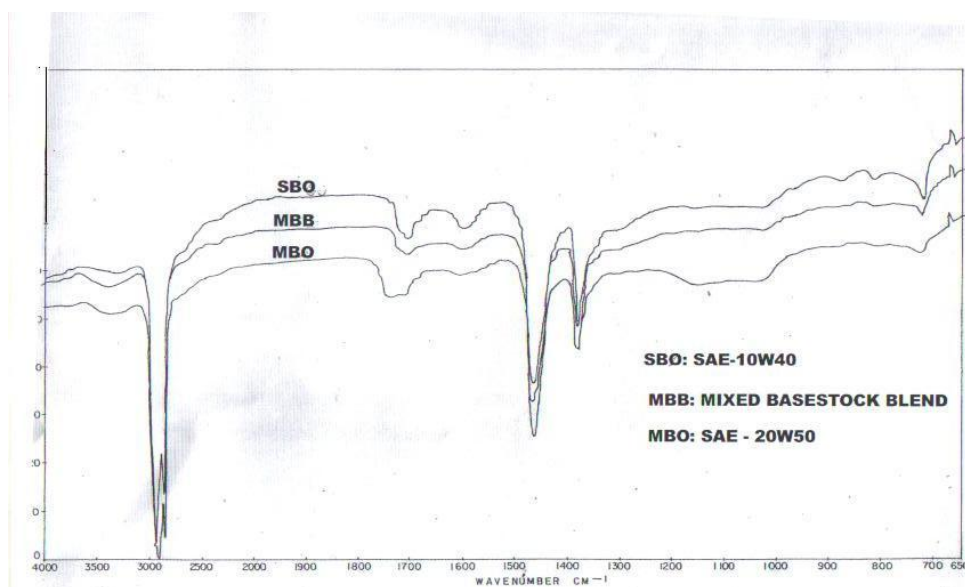FIG. 3 INFRARED SPECTRA OF THE BASE OIL SAMPLES AT AMBIENT TEMPERATURE

FIG.4 INFRARED SPECTRA OF THE BASE OIL OXIDATES AT 380°C AFTER 15 HOURS.

The absorption bands of interest in this analysis are those between 1800cm^{-1} and 1700cm^{3} where aldehyde, ketone, carboxylic acid and ester derived functional groups show their vibrational frequencies [15]. The presence of these species in the base oils as indicated in the spectra of the basestocks at ambient temperature, are basically due to trace quantity of additives which could still be found in the base oils after recovery processes [16]. However, near total disappearance of peaks (fig. 4) indicates that the species have been converted to volatile materials and sludge rich in polymeric materials [9] after 15 hours of heating the base oils to a temperature of 380^{0}C. This is a measure of the extent of degradation in the base oils. The spectra depicts synthetic base as the most thermooxidatively unstable basestock. This is closely followed by the mixed blend basestock, then the mineral oil, as the least unstable basestock. However, the spectrum of the 1:1 mixed basestock blend lies between the two extremes, showing that at the molecular level there was no chemical interactions between the two basestocks that could have either boosted or suppressed the thermoooxidative degradation of the blended basestock at the test temperatures.

CONCLUSION

The results of this work broadly indicate that the base oils have low thermooxidation stabilities even at a simulated temperature as low as 260^0C, especially when the stabilities are evaluated based on the total oxidation products. . What this means is that the base oils are not ideal for use as crankcase oils even if the engines were designed to operate a little below the normal operational temperature of above 300^0C. Because at the temperature of 260^0C and above almost all the basestocks would have lost their stabilities and performance characteristics as depicted by the exponential increase in both volatile acidity and sludge deposits at that temperature regime. This is the critical temperature for the stabilities of the crankcase basestocks tested in this work. In other words without additives such as anti-oxidants and stabilizers these lubricating base oils cannot be used in any automotive crankcase engine operating at temperature above 260^0C without compromising the safety the engine. In particular the results from the two basestocks studied indicate that the multigrade basestock SAE10W40 (synthetic basestock) is more prone to thermoxidative degradation than its multigrade SAE-20W50 (mineral basestock) counterpart at almost all   temperature regimes, and will therefore require more antioxidants and other stabilizers during formulation. Based on the results of the thermooxidation stability tests which can serve as baseline stability status for the additive-free oils, the manufacturers will be in a better position to know the quality as well as the quantity of the additives required for the crankcase oil formulation in order to achieve their optimum performance characteristics.

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