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THE COMPOSITIONAL CHANGES IN HIGH TEMPERATURE OXIDATION OF MINERAL AND SYNTHETIC LUBRICANTS

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ABSTRACT

The effects of temperature on chemical composition and the thermo-oxidation stabilities of mineral and synthetic lubricants was investigated using a modified version of the turbine oil oxidation test apparatus. The method involved simulation of those conditions encountered in internal combustion engines under normal operation and oxidation of the lubricant samples at various temperatures with an air flow of 1.0 litre per hour for 20 hours. The thermooxidation stability test as well as the compositional changes of the oil samples were assessed by measuring the Total Acid Number (TAN), the Total Oxidation Products (TOP) and the infra-red spectral changes of the oxidates at various temperatures ranging from very low to as high as 360°C. The results showed that all the samples possess high sensitivity to changes in temperature. The mineral oil showed the lowest thermooxidation stability and the highest oxidation and decomposition product content. The infra-red studies revealed that high temperature oxidation of the oil samples leads mainly to the formation of organic acids, peroxides and carbonyl compounds, especially in mineral oil. The parameters used in assessing the oil samples proved to be dependable means of predicting the stability and performance characteristics of lubricating oils under high temperature engine operation.

Key words: Thermo-oxidation stability, lubricants, compositional changes.

INTRODUCTION

Thermo-oxidation stability of lubricants is the most important factor which influences the performance characteristics of lube oil under the engine operating conditions. In internal combustion engine the crankcase oils are subjected to a vast array of hot-spot temperatures ranging from 90°C at the connecting rod cylinder to about 430°C at the piston crown (Gruse, 1967). Under this conditions lubricants undergo a combination of both thermal and oxidative decomposition leading to the breakdown of additives such as antioxidants (Korceth et al, 1980). Consequently, the oil stability falls and this eventually results in metallic rattling or engine knock. Thus, modern engine design imposes stringent requirements on the physicochemical characteristics of lube oils (McGee Ham, 1979) to ensure high performance under severe temperature regimes. However, at certain critical temperatures the performance capabilities of oil are lost considerably due to mechanochemical reactions between the oil molecules and the antioxidants. These reactions are responsible for the formation of volatile acid compounds and polymeric products deposited as sludge in valve trains (Jensen, 1986).

In modern tribology oil performance levels are defined by the engine dynometer tests, which measures the stability of base oil. One example of such tests is the sequence IIID test which measures the high temperature decomposition of engine oil (Rodgers et al, 1978). Recent study (Ofunne et al, 1989) has listed some of the problems besetting this test to include the multivariant nature of factors that affect oil degradation during service. Consequent up this set back a number of proprietory tests based on the simulation of the engine operating conditions have been developed. The test is simply designed to reproduce the engine oil performance in the laboratory (Johnson et al, 1987). By this method performance characteristics of lube oil have been measured by (Wellermet et al, 1978) with high degree of accuracy using standard Turbine Oil Test (TOOT) apparatus.

In this research a modified version of the open test tube type of oxidation apparatus was used to study some physicochemical characteristics of both mineral and synthetic lube oils and their mixed stock blend. The work was aim at isolating and quantifying sludge deposits and the volatile oil fragments formed at various temperatures. The type and the amount of these fragments were used to assess the compositional changes, hence the thermo-oxidation stability of these lubricants. The method evaluates the level of oil deterioration at selected temperatures based on sludge deposits of the oxidates, total acid number, total oxidation products and infrared characteristics of the oxidates. Taken together, these parameters have given a sharp picture of the compositional changes that take place at the molecular level when the lube oils are subjected to high temperatures at the engine operating conditions.

MATERIALS AND METHOD

Collection of Samples

Two commercially available grades of automotive

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oil used in the work were sourced locally. The SAE-20W50 Multigrade lube oil, representing the mineral oil blend was obtained from the Elf Petroleum (Nig) Ltd while the GT-10W40 Multigrade representing the synthetic base-stock, was obtained from Lenoil Petroleum and Petrochemicals (Nig) Ltd, all in Port-Harcourt Rivers State.

The third oil sample used was a 1:1 mixture of the above two grades and is here refered to as the Mixed Stock Blend (MSB), The characteristics of the fully formulated mineral oil and its synthetic counterpart are given in tables 1 and 2 below.

Table 1: Typical characteristics of multigrade mineral oil (Lenoil Brochure, 1990)

SAE Classification-- -	SAE 20W50.
Appearance - -	Clear Amber.
Specific Gravity at 15°C -	0.89.
Viscosity Index (VI) -	130.00.
Kinetic Vis. @ 40°C (m^2/s) -	131.00
Total Acid Number $MgKOHg^{-1}$ -	0.44
Dynamic viscosity @ 40°C-	4500.00(max).
Pour Point (°C) - -	–12(max).
Total Base number $MgKOHg^{-1}$	6.30.
Zinc Content (wt%) -	0.13
Calcium content (wt%) -	0.04
Magnesium content (wt%) -	0.09.

All reagents used in this work which were either obtained from the University of Port-Harcourt chemical store or purchased from standard chemical departments, conformed with analytical grades.

EXPERIMENTAL PROCEDURE

The method used in measuring the compositional changes in high temperature oxidation of mineral oil and synthetic lubricants has been described elsewhere (Ofunne et al, 1989) but the modified version of the standard Turbine Oil Oxidation Tests (TOOT) apparatus was developed in our laboratory for the purpose of this work.. The procedure involves thermal oxidation of the oil samples using a thermostatically regulated heating mantle with a maximum heating capacity of 450°C.

The oxidation process was carried out in a three-necked flask (500cm^3) in which the oil sample

Table 2: Typical characteristics of multigrade synthetic base-stock (Lenoil Brochure, 1990).

SAE Classification -	SAE 20W50.
Appearance - -	Clear Amber.
Viscosity @ 40°C (cST) -	92.80.
Viscosity @ 100°C (cST) -	14.10.
Pour Point (°C) - -	–37.
Flash Point (°C) - -	232.00.
API Gravity - -	26.40.
Zinc Content (wt%) -	0.12
Total Base number $MgKOHg^{-1}$	8.00.

was heated at different temperature intervals from ambient to about 380°C with an airflow of 1.0 litre/hr. The temperature of oil was raised by 40°C after every 2 .5 hours and the oxidate sample withdrawn, quenched and stored in a fridge. The volatile oxidate were trapped in a second flask containing 200cm^3 of freshly prepared 0.1 MKOH solution. The volatiles were also withdrawn at every test temperature interval and preserved for analysis.

The oil sample were analysed for Total Acid Number (TAN), which was determined from a combination of oil soluble and volatile acidity. Also analysed for were sludge deposits (measured as n-heptane insolubles) and Total Oxidation Products (TOP). Infra red spectroscopy was also used as an additional tool to fully establish the physicochemical characteristics of the oxidates at the test temperatures.

RESULTS AND DISCUSSIONS:

The compositional changes in the high temperature oxidation of mineral oil and synthetic lube oils have been investigated. The evaluation of the changes was accomplished by carrying out the thermooxidation stability tests on the samples using a simple model or the modified version of Turbine Oil Oxidation Tests [TOOT] apparatus earlier mentioned in the procedure. The details of the results are given below.

The graph in fig.1 shows the changes in total acid number with temperature. Between 140 and 220°C mineral oil showed little or no changes in acidity, until about 300°C where the acidity increased almost exponentially. Whereas synthetic oil showed no appreciable increase in acidity even at high temperature regime. However, the mixed stock blend came between the two extremes. The sharp increase in soluble acidity of the mineral oil can be attributed to the formation of

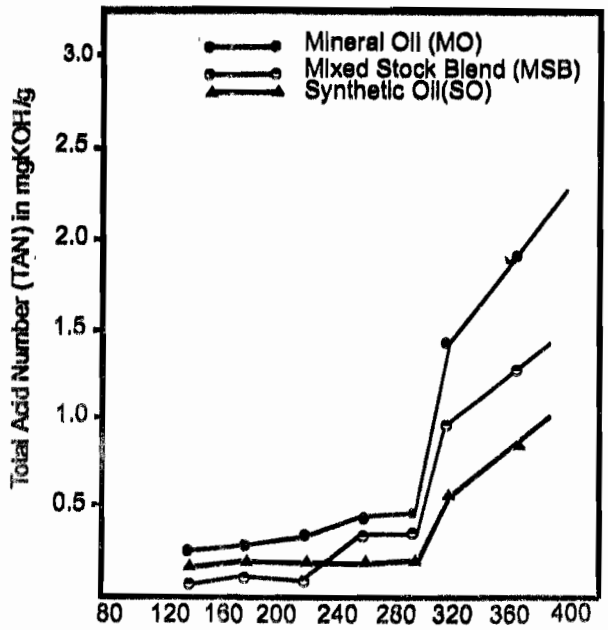

Fig. 1: Variation in total Acid Number With Temperature (°C)

the oxidation products which may include peroxides carboxylic acids and carbonyl compounds. Synthetic oil on the other hand showed a high degree of high temperature stability probably due to the type of hydrocarbons used in formulating its base stock coupled with the action of the high temperature resistant additives incorporated in it . At much higher temperatures the rate of autooxidation reations leading to the formation of more oxygenated products such as alcohols and hydroperoxides. However the dicernable regime of acidity changes for the three samples are consistent with those demarcated in the study of jet oil [Hazlett,1980].

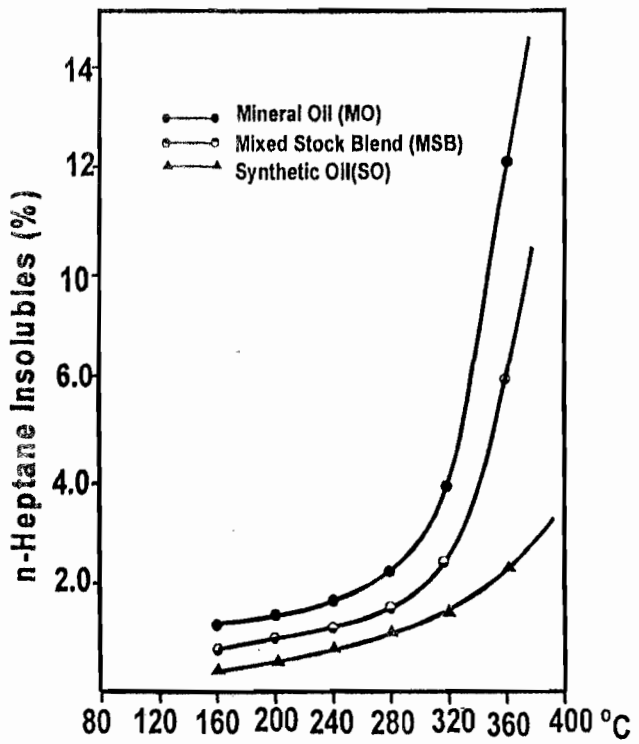

Fig. 2: Sludge Deposition Profile of the Oxidates

The sludge deposits of the oxidates measured as the per centage of the materials insoluble in normal heptane comprised all high molecular weight [HMW] polymeric products otherwise known as resins. These products resulted from the high temperature thermooxidative degradation of the oil molecules and their additives. The results of the sludge deposits obtained for the oil samples were plotted as a function of temperature [fig.2]. The profile shows that at low temperatures between 120°C and 180°C only very little sludge was formed. It was particularly observed that no sludge was formed from the fully formulated synthetic oil and the mixed stock blend , while only a very small amount of sludge was observed for mineral oil. However , between 180°C and 260°C, there was a gradual sludge formation by all the samples with mineral oil as the most susceptible to temperature increase while synthetic is the least. Above 260°C the increase sludge formation became exponential for the mineral oil without a corresponding increase for the synthetic oil . However a slight increase was also observed for the synthetic blend at 300°C . The low sludge level in the synthetic oil could be due to the fact that at very high temperature the synthetic oil sludge decomposes into smaller fragments which are collected as volatiles. Another factor that may have contributed to low sludge content in synthetic lube is the high concentration of the dispersants [Asseff,1975]. The activities of dispersants according to Asseff could hinder the settling of the sludges as they are being formed. The difference in sludge formation between the samples can be explained at molecular level by the compositional structure and steric factors [Ofunne et al, 1990]. The synthetic oil generally contains more substituted aromatic and naphthanic hydrocarbons which are resonance stabilized even at relatively high temperatures. While mineral oils are richer in aliphatic hydrocarbons which are quite vulnerable to high temperature reactions such as polymerization.

Fig. 3 depicts variations in the total oxidation products which include all the products irrespective of their chemical origins, that were formed as a result of oxidative degradation of the oil samples. These products give a clear indication of the total conversion of the hydrocarbons and the overall extent of oxidation that occurred at various test temperatures. The total oxidation products of the oil were thus obtained by summing up all the oxidation products based on the tested parameters. These comprised the volatile acidity, the oil soluble acidity and the sludge contents, all of which were measured in accordance with the Institute of Petroleum Standard for analysis and testing (IP,1980).

The graph also shows a slow formation of oxidation products between 140°C and 220°C. But at higher temperatures ranging from 260°C and above, the total oxidation products increased significantly with the mineral oil giving the highest value of the total oxidation products. The pattern observed here is similar to that of sludge formation earlier discussed. This observation

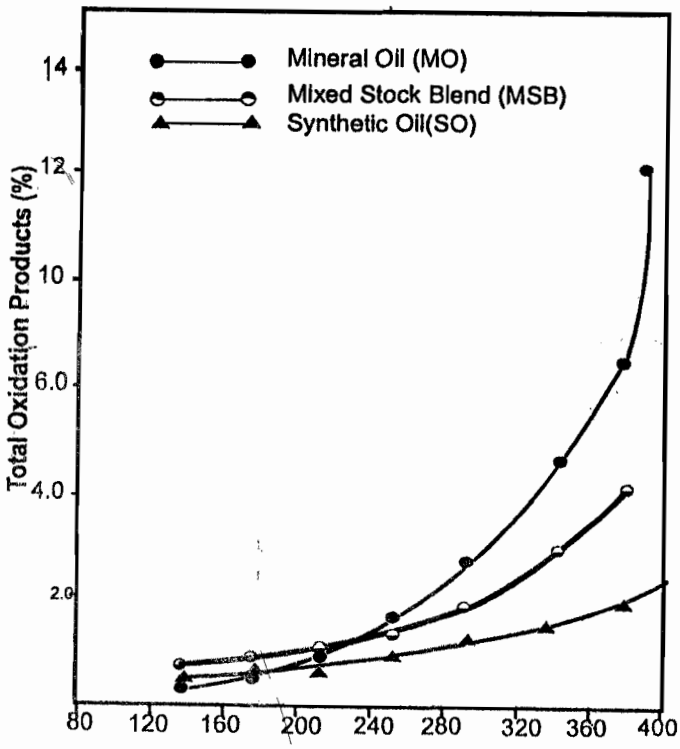

Fig. 3: Variation in the Total Oxidation Products with Temperature (°C)

suggests that the thermoxidation stability is mainly a function the structural composition of the hydrocarbons present in the oil. As earlier noted in the sludge formation profile study, the aromatic based oils are more heat resistant than the parafinic based oil. In all cases the mixed stock blend shows thermoxidation stability which lies midway between that of mineral oil and synthetic lube. However, at the highest test temperature, the MSB tends to lose stability a little close to that of mineral oil. This may be due to sudden changes in the hydrocarbon matrix which parafinic fraction of the mixture experiences at high temperature regimes.

Infrared spectroscopy has been used to detect the presence of oxidation products in used oil samples (Barcelo et al, 1969) . The use of computer aided infrared spectroscopy to measure the total oxidation products by integrated area calculations has proved quite successful in the recent time (Wooten, et al 1984). In this work infrared studies were also used to confirm the extent of oxidation of oil samples at various temperatures ranging from ambient up to 380°C.

Fig. 4 shows the changes in the spectra for the three samples. Fig. 4a, b and c represent the spectra for mineral oil, mixed stock blend and synthetic oil respectively. The spectra obtained were used to study the molecular conditions of the oil samples at different thermoxidation levels. The absorption peaks of interest are those due to oxidation products at different vibrational frequencies of $3500cm^{-1}$ - $3400cm^{-1}$, $3000cm^{-1}$ - $2900cm^{-1}$, $1800cm^{-1}$ - $1700cm^{-1}$ and $1000cm^{-1}$ - $900cm^{-1}$. The absorptions between $3500cm^{-1}$ - $3400cm^{-1}$ indicate the presence of alcohols or organic acid in the oil samples. But any absorption in this region by the samples at low temperatures may be due to hydroxyl groups present in phenolic additives, since there could be no reaction leading to the formation of alcohols at those temperatures. Absorption in this region diminishes slowly with increase in temperature showing that hydroxyl groups are being lost due to interaction with other functional groups during oxidation. At about 260°C the synthetic oil gave a more prominent peak suggesting the formation of alcoholic species as primary oxidation products. Above this temperature regime the peak diminishes indicating the gradual disappearance of alcohols as a component of volatile products. Absorptions between $1800cm^{-1}$ - $1700cm^{-1}$ are due to formation of carbonyl species. The absorption intensity increased as the rate of thermooxidative degradation reaction increased steadily with rise in temperature. However the mixed stock blend gave no noticeable band up to 260°C. This may be due to interactions between the additive blends in the mixture which might result in the carbonyl band interference. At 300°C the mixed stock gave a small absorption peak with increased intensity at 340°C. Above this temperature all the samples showed either diminished or broad peaks, indicating the involvement of carbonyls in high temperature processes such as polymerization and other complex reactions leading to the formation of high molecular weight products. This observation agrees with the reports by Klaus et al (1980), that the main reactions at the later stage oil deterioration involve adol-type condensation resulting in the formation of high molecular weight resinous products. It must be noted however that

Table 3: Physicochemical characteristics of oxidates at 380°C after 15 hrs test period.

Oil Sample	Soluble acidity MgKOH/g	volatile acidity mgKOH/g	Pentane Insoluble W+%	Colour of the oxidates
Mineral Oil (MO)	0.946	0.896	14.52	Dark Brown & Waxy
Mixed Stock Blend (MSB)	0.890	0.716	10.84	Brown & Waxy
Synthetic Oil (S)	0.831	0.715	6.45	Dark Brown

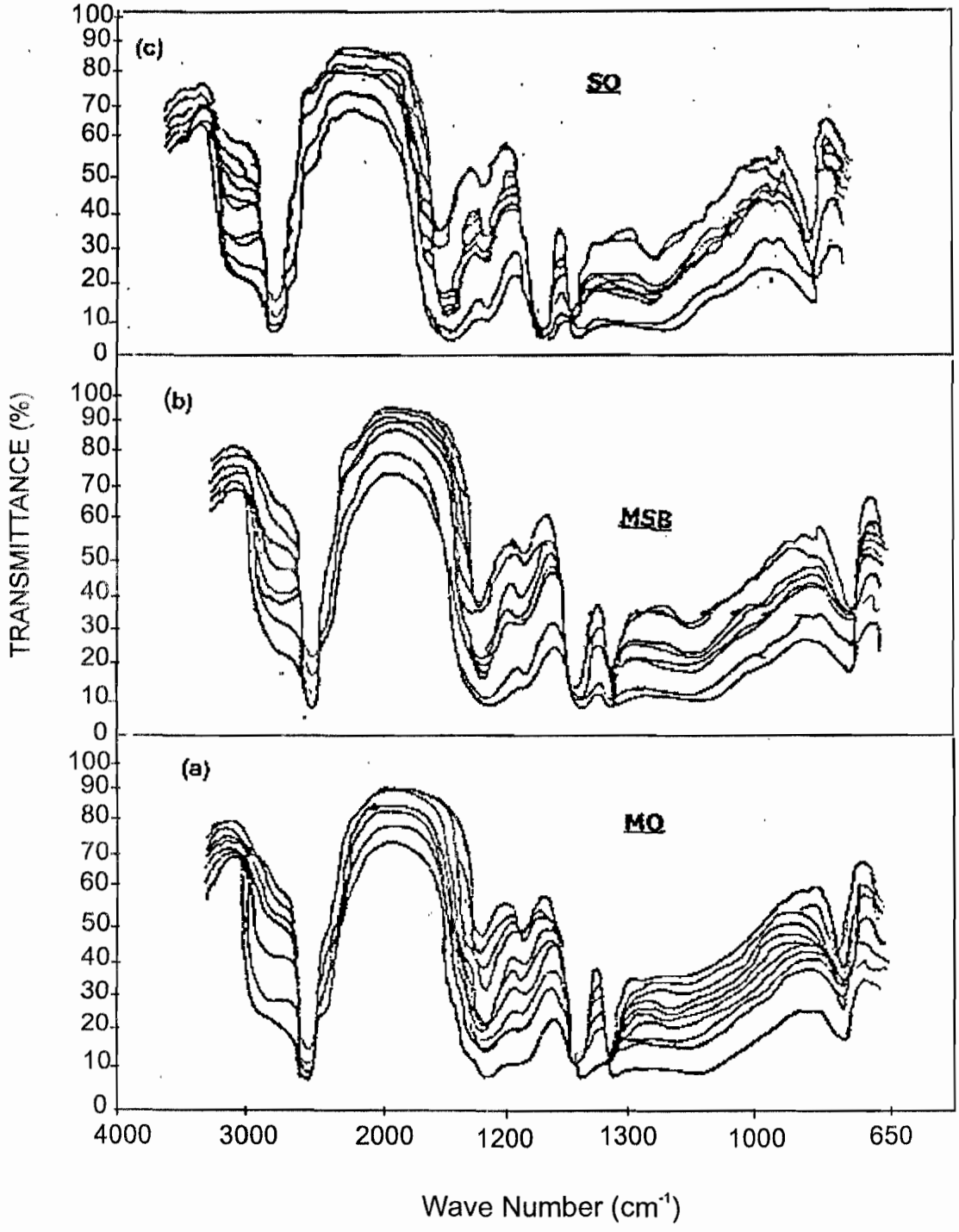

Fig. 4: The infrared Spectra of the Oil Samples Between 180° and 380°C

the formation of various carbonyl compounds such as Ketone absorbing at 1750cm^{-1}, conjugated ketones (1675cm^{-1}), aldehydes (1725cm^{-1}), organic acids (1710cm^{-1}), carboxylates (1610 - 1550cm^{-1}), esters (1745 - 1725cm^{-1}) are all influenced by temperature and chemical composition of the lubricants.

CONCLUSION

The results of the investigation indicate that the mineral oil has the lowest thermal oxidation stability, probably due to high concentration of parafinnic hydrocarbon which are known to be more thermally unstable than the naphthemic and aromatic species which of course form the bulk of hydrocarbons in synthetic oil. Based on these findings synthetic lubricants have been recommended for high temperature operations in internal combustion engines. However, a 1:1 mixture of the two grades can also be used to save cost since the pure synthetic lube oils are generally more expensive than the mineral lubes.

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