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THE EFFECT OF NATURAL ANTIOXIDANTS (FROM GROUNDNUT SHELL EXTRACTS) ON THE OXIDATION STABILITY OF LUBRICATING OIL

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ABSTRACT

The effect of Catechin-containing natural antioxidants, on the stability of lubricating oil has been assessed and evaluated. The base and the formulated oils samples were both subjected to the same reaction conditions designed to simulate a working crankcase engine environment. The kinematic viscosity, pH and the total acid number (TAN) were determined to assess the effectiveness of catechins (from groundnutshell extract) as an oil additive. The values of the kinematic viscosity for the formulated oil were much higher than the base oil, while the total acid number content for the base oil was found to be higher. Both the base oil and the formulated oil, showed similar pattern of deterioration as temperature of the reaction increased. However, the formulated oil proved to be more stable than the base oil due to the presence of the antioxidant.

KEYWORDS: Antioxidants, Lubricating oil, Viscosity, Acid Number, oxidation.

INTRODUCTION

Lubricating oil can be oxidized when exposed to air, particularly at elevated temperatures, and this has a very strong influence on the life of the oil. The rate of oxidation depends on the degree of refinement, temperature, presence of metal catalysts and other incorporated chemicals that serve as antioxidants. Antioxidants are those chemical substances that extend the induction period of oxidation process and thus help reduce destruction of the oil ingredients, (Kelly, 1968). The internal combustion engine is a model oxidator, since it contains a hydrocarbon motor oil with air under agitation at high temperatures. In addition, metals such as copper, lead, nickel, chromium and iron, used for the manufacture of the engines, are effective oxidation catalysts which increases the rate of oxidation. The oxidation process produces acidic bye-products within the lube oil which are corrosive, and can lead to the formation of sludge with an overall breakdown of viscosity characteristics. Antioxidants delay rancidity by binding the oxygen molecules and therefore make them unavailable to free radicals. They also function by reacting with initiating and propagating free radicals forming non-reactive substances that lay dormant within the substrate, (Jones, 1983; Gunsel *et al.,* 1988).

Several effective synthetic oxidation inhibitors (antioxidants) have been developed and used in the formulation of lubricating oils for automobiles and other engine applications. Typical of these antioxidants including sulphurized oil – soluble organic compounds, polysulphides and zinc dithiophosphates are burdened by economic and contamination problems, (Gould, 1968). It is preferred to maintain the sulphur content of the oil as low as possible. Natural antioxidants do exist but only a few of them are used as additives commercially for combating oxidation in oils, (Berab and Naga, 2006). Typical examples are tocopherols found in vegetable oil, ascorbic acid and quercetin found in red onion skins. Most of these natural antioxidants such as ascobic acid act as antioxidants by removing oxygen and also by reducing free radicals. Despite having good antioxidant activity , their usage is limited by both economic and technical factors. They are less stable at extreme temperatures and low pH, while some like locopherols are highly susceptible to oxidation because of their nature. Several antioxidants however, do exist in nature and occur mainly in food and vegetable substances, (Mitchell *et al.*, 2007). Catechins are polyphenolic antioxidant plant metabolites which belong to the family of flavan-3-ols (flavonoid) and are present in tea, groundnut shells, fruits and vegetables, (Stanbury *et al.,* 1950).

The increasing demand for quality and cheap lubricating oil has opened up a new research interest for cheap and available oil additives from natural sources., The main objective of this work is to investigate the effectiveness of crude extracts containing catechins as an antioxidant additive in lubricating oil formulation.

EXPERIMENTAL

Materials and methods

The base oil used was obtained from TOTAL Oil Blending Plant, Koko, Delta State. The groundnut shells were collected from the Omoku in Rivers State. The groundnut shell were collected and dried to lower the

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moisture content, after which they were washed in gasoline and sun-dried for about one week and were ground into powder with the aid of a milling machine. The antioxidant was extracted from the ground sample, and the solution concentrated and dried.

Extraction of the antioxidant

The Soxholet extraction technique was used to extract the antioxidants from the groundnut sample, in compliance with the procedure of Association of Official Analytical Chemists (AOAC) while employing acetone as the extraction solvent. The solvent-extract solution was first concentrated in a water bath to a semi-solid matter, and later sun-dried to dryness. Detailed extraction procedure and the property characterization were given elsewhere (Stanbury *et al,* 1950).

Formulation of the base oil and Catechin-containing extracts

Approximately 0.1g of the crude extract was dissolved completely in about 1ml of acetone in a 250 ml beaker after which 100ml of the base oil was added and mixed thoroughly. This was prepared into five (5) different samples for the reactions and analysis. The raw base oil was similarly prepared and used as standard. Each sample was heated with constant stirring, at different temperatures ranging from 40 to 240^0 C for a time period of 2 hours.

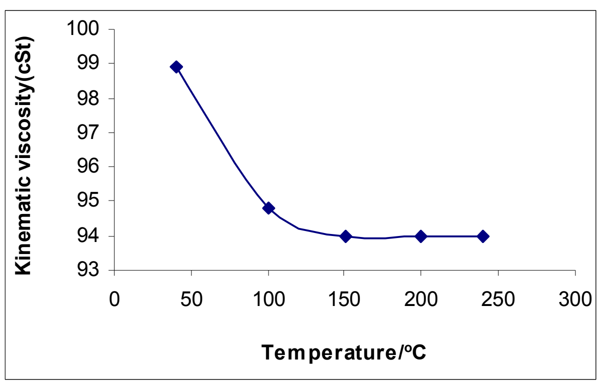
Analysis

The kinematic viscosity of each oil sample was measured at 40^{o}C and 100^{o}C, following the standard method stipulated by ASTM D88, using viscometer SETA KV – 8. The total acid number (TAN) of the oil samples were measured in accordance with ASTM D974 - 01. Each of the oil samples was dissolved in a mixture of titration solvent containing a small amount of water, isopropyl alcohol and toluene, and the resulting single phase solution titrated at room temperature with standard ethanolic potassium hydroxide solution to the end point using P-naphtholbenzein solution as an indicator.

RESULTS AND DISCUSSION

Figures 1 and 2 show the graphs of kinematic viscosity measured at 40^{o}C and 100^{o}C as a function of reaction temperature. The graphs showed a general decrease in the kinematic viscosity of the two oil samples as temperature increases. However, the kinematic viscosity of the base oil without the antioxidant is seen to be much lower than the formulated lube oil at a temperatures 100^{o}C. The kinematic viscosity of the formulated oil showed relatively higher values due to the effect of the antioxidants.

The kinematic viscosity of the formulated oil was found to be more improved and better than the unformulated base oil. After heating up to about 240^{0}C, the antioxidants still showed some level of positive effect in stabilizing the lube oil.



- **Figure 1: Kinematic viscosity of Base oil measured at 40^{o}C, as a function of reaction temperature**

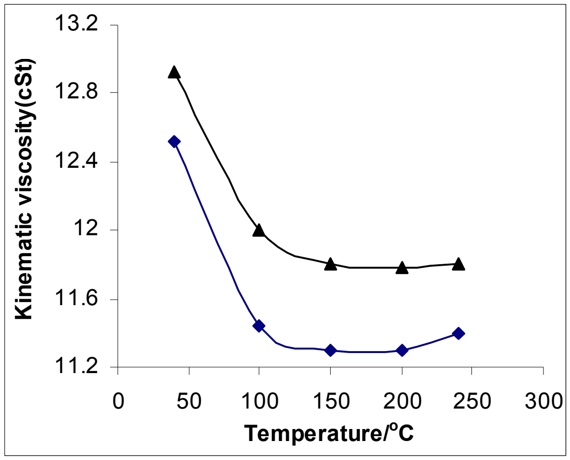


Figure 2: Kinematic viscosity measured at 100°C, as a function of reaction temperature ◆ Base oil ▲ formulated oil

Table 1 shows the result of kinematic viscosity, and the total acid number of the formulated and the base oils. These results clearly showed that the kinematic viscosity of the formulated oil is higher than the base oil at these temperatures.

Figure 3 depicts the total acid number as a function of temperature. The result shows a general increase in the total acid number for both the formulated and the base oil, which increases with increase in temperature of the reaction. However, the formulated oil had a lower acid content than the base oil. The observation above suggests that an acid-forming process may have occurred but the effect was less pronounced with the formulated oil. The nature of these increase further suggest that both the base and formulated oils have similar pattern of oxidation. Increase in oil acidity is said to be related to sludge formation, which is due to secondary polymerization reactions, initiated by peroxide formation and decomposition, (Klaus *et al.,*1983). Oil oxidation at elevated temperatures normally leads to the formation of acidic components which are responsible for the sludge deposition metal corrosion and fatigue, (Korcek *et al.,*1980). It also causes additive depletion, loss of dispersancy and viscosity changes, (Johnson *et al.,* 1987). However, the experiment was kept within the automobile crankcase engine operating conditions and also below the melting point of the catechins, in order to avoid thermal breakdown of the this antioxidants or the hydrocarbon component of the lubricating oil. A decrease in viscosity at elevated temperatures has been attributed mainly to thermal cracking of the oil hydrocarbons, which starts above 260°C, when the oil breaks down to smaller molecules, (Ofunne et al., 1990). The maximum temperature of 230°C used in this study is well below 260°C where thermal cracking is said to be important. Similar studies by Gunsel et al, (1988), on the issue of deposit formation in mineral oil-based lubricants, showed that deposits were formed from an aldol-type condensation of carbonyl compounds in a stage –wise manner. It was therefore believed that deposits that are polymeric in nature were responsible for oil degradation and aging phenomenon seen at elevated temperatures. In this study we have taken steps to investigate the effect of time on the aging process of the lubricating oil samples. Figure 4 depicts the total acid number as a function of time of reaction. The total acid number for both the formulated and the base oil, showed a similar pattern of increase with time, and this observation is thought to be due to more oxidation which produce acids from higher molecular weight carbonyl compounds.

Table 1: The Properties of the base and formulated lubricating oil

Temp (°C)	K.V. at 40°C		K.V. at 100°C		Total Acid Number	
	Base oil	**Formulated oil**	**Base oil**	**Formulated oil**	**Base oil**	**Formulated oil**
40	98.89	-	12.52	12.92	0.015	0.015
100	94.8	96.25	11.44	12	0.095	0.067
150	94	98.44	11.3	11.8	0.12	0.08
200	94	-	11.3	11.78	0.15	0.096
230	94	-	11.4	11.8	0.27	0.12

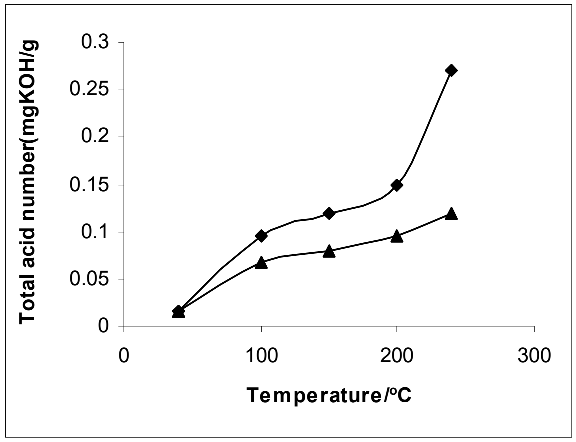


Figure 3: The Total Acid Number TAN (KOH/mg) as a function of reaction temperature ◆ Base oil ▲ formulated oil

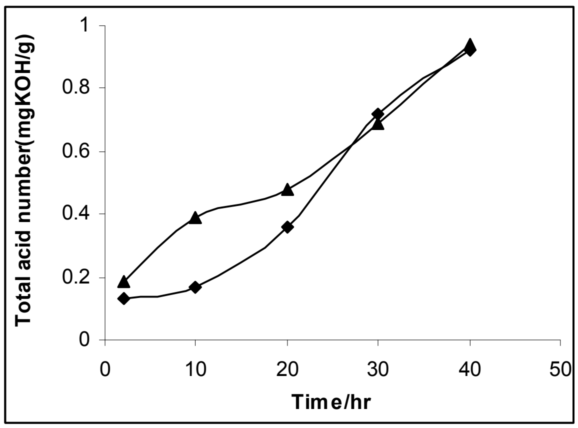


Figure 4: The Total Acid Number TAN (KOH/mg) as a function of time of reaction ◆ Base oil ▲ formulated oil

CONCLUSION

The summary of the results obtained in this study is shown in table1, and it clearly demonstrates that the oxidation process is more pronounced with the base oil without the antioxidants. Both the base oil and the formulated oil, showed similar pattern of deterioration as temperature and the reaction time are increased. However, the formulated oil proved to be more stable than the base oil due to the presence of the antioxidants. It could therefore be concluded that the groundnut shell extracts a catchin-containing natural antioxidant, is effective as a lube oil additive.

REFERENCES

ASTM (1989), Petroleum Products and Lubricants, vol.05.01, An Annual Book of ASTM Standard, American Society For Testing and Materials, Philadelphia, USA.

Berab, D.L and Naga, A., 2006. “Studies on a natural antioxidant for stabilization of edible oil and comparison with synthetic antioxidants”. J. Food Engr. 74 (4) 404.

Gould, R. K., 1968., Selecting the lubricant under various conditions. Handbook on General lubrication Engr. Practice. Academic Press Inc. NY 161.

Gunsel, S., Klaus, E. E. and Duda, J., 1988. “High temperature deposition characteristics of mineral oil and synthetic lubricant base stock”. Lubr. Engr. 44, 703.

Johnson M. D., Korcek S. and Zinbo M., 1987. High-temperature antioxidant capabilities of base oils and base oil additive mixtures, *Industr. Engng Chem. Prod. Res. Dev.,* 26, *1754-1757*

Jones W. R., 1983. Thermal and oxidative stabilities of liquid lubricants, *Tribology in the 80’s, NASA Conference Publication,* 2300.

Kelly, G. E., 1968. Refining and manufacturing of Petroleum Lubricants. Handbook on General Lubrication Engr. Practice, Academic Press Inc. NY 13.13

Klaus E. E., Cho L.,andDang H., 1983. Adaptation of Penn State microoxidation test for the evaluation of automotive lubricants, *SAE Paper No 801362, SAE SP 90 473,* 980

Korcek S., Jonhson M. D., Jensen R. K., and Zinbo M., 1980. Determination of the high-temperature antioxidant capability of lubricants and lubricant components, *Industr. Engng Chem. Prod. Res. Dev.,* 19. 621-627.

Mitchell, A. E., Hong, R. B., Koh, E., Barrett, D.E. Denison, R. F. and Kaffka, S., 2007. “Ten-Year comparison of the influence of organic and conventional crop management practices of flavonoids in tomatoes”. J. Agric. Food Chem.55 (15) 6154 – 6159.

Ofunne, G. C., Maduako, A. U. and Ojinnaka, C. M., 1990. “ High temperature oxidation stability of automotive crankcase oils and their base oils”. Tribology Intl. vol. 23, No. 6, 407 – 412.

Stanbury, M. F., Field, G. T. and Guthrie, J. D., 1950. The tannin and related pigments in the red skins (testa) of peanut kernels”. J.Am. Oil Chem.Soc. *27,* 317