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RESEARCH ARTICLE

OXIDATION STABILITY INVESTIGATIONS OF SPINDLE BASE OILS USING SPECTRAL AND PHYSIO - CHEMICAL METHODS

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ABSTRACT

Group I base oils are low cost, availability is abundant and user's familiarity. Solvent neutral oils like SN 150, SN 500, SN70 and Spindle oils are belong to Group I. Generally Spindle oils are being used as low end applications like metal working fluids, transformer oils and power loom spindle oils. In this paper we selected HVI, LVI and SN 70 Group I base oils and their lubricating performance was analysed using NMR, physico-chemical and RPVOT measurements.

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INTRODUCTION

Conventional lubricants are formulated based on mineral oils derived from crude petroleum (Speight *et al.*, 1991). Mineral oil contains many classes of chemical components, including paraffins, naphthenes, aromatics, hetero-atom species, etc. Its compositions are pre-determined by the crude source (Adhvaryu *et al.*, 2000, Jayadas *et al.*, 2007). Low viscosity Group I base oils are generally not suitable for automotive engine oils. As these base oils have high Noack evaporation values. High Noack evaporation values leads to the lubricating oil top-up in automotive engine oils (Adhvaryu *et al.*, 2002, Shishkin *et al.*, 2006). As these Spindle oils have very high Noack evaporation values and hence used for manufacturing low end Industrial applications such as metal working fluids, transformer oils and power loom spindle oils. Mineral oils of such complex compositions are good for general-purpose lubrication, but are not optimized for any specific performance features. The major advantages for Group I mineral oils are their low cost, long history and user's familiarity.

Study Area

In this study, base oils such as LVI Spindle, HVI Spindle and SN 70 have been selected for physical and chemical characterization. The effect of sulphur on oxidation stability structural properties has been investigated on these three samples. The thermo-oxidative stability of these samples with anti-oxidant has also been assessed using RPVOT (Dunn Robert *et al.* 2005). The effect of heating with respect to kinematic viscosity has also been studied. In addition, chemical structure of these samples was obtained in terms of average structural parameters obtained using quantitative ¹H and ¹³C NMR experiments (Singh *et al.*, 1991, Sarpal *et al.*, 1997).

MATERIALS AND METHODS

Solvent processing is a viable technology for improving base oil performance using a fairly safe, recyclable solvent. Most base oil producers in the world today still use this process. Solvent refined base oils are commonly called Group I base oils which are characterized as those having less than 90% saturates (>10% aromatics) and / or more than 300 ppm sulfur. This LVI spindle, HVI spindle and SN70 base oils are manufactured through solvent processing technology (Kramer *et al.*, 1999).

Base oil Samples description

Spindle oils are being used in various machinery applications in most of the Industries. In this study low viscosity index spindle oils (LVI Spindle), high viscosity index spindle oils (HVI Spindle) and high viscosity oil (SN70) are selected for various physical and chemical properties to access the suitability for using automotive stroke industrial oils. The solvency factor differs from Low viscosity index spindle oils and High viscosity index spindle oil has been studied (Jain *et al.*, 2005, Barman 2002, Sharma *et al.*, 2008) The physio-chemical properties of the base oils and the general test results are presented in table 1.

Rotary pressure vessel oxidation tester (RPVOT) ASTM D 2272

Oxidation stability is one of the most important properties of lubricating base oil. The more resistant base oil is to oxidation, the fewer tendencies it has to form deposits, sludge, and corrosive byproducts in engine oil and industrial oil applications.

RPVOT measures the oxidation stability of oil. 50 +/- gm of sample was weighed in a glass container with copper wire as catalyst (55.6 gm) and add 10 ml of reagent water as per the method and kept in vessel. The sample was exposed to oxygen

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at moderate pressure and at a test temperature until the oxygen destroys the oxidation resistance of the oil.

HFRR (High Frequency Reciprocating Rig, ASTM D 6079) tests.

This experiments was carried out using a PC controlled DSC Q1000, TA Instruments. This equipment is ideal for Tg (glass transition), Tm and Cp (material heat capacity) measurements. The temperature range is 180-725°C and accuracy is 0.1°C and precision is 0.05°C. Weighed 3.0 mg of oil into new sample pan and sample was heated at a rate of 100°C/min maintained in oxygen pressure 3.5 MPa. The cell is held at a regulated temperature and pressure until an exothermic reaction occurs. The extrapolated onset time is measured and reported as the oxidation induction time for the base oil at the specified test temperature.

A 2-mL test specimen of sample is placed in the test reservoir of an HFRR and adjusted to either of the standard temperatures (25 or 60°C). The preferred test temperature is 60°C, except where there may be concerns about loss of sample because of its volatility or degradation of the sample because of the temperature. When the sample temperature has stabilized, a vibrator arm holding a non rotating steel ball and loaded with a 200-g mass is lowered until it contacts a test disk completely submerged in the sample. The ball is caused to rub against the disk with a 1-mm stroke at a frequency of 50 Hz for 75 min. The ball is removed from the vibrator arm and cleaned. The dimensions of the major and minor axes of the wear scar are measured under 1003 magnification and recorded.

Kinematic viscosity (ASTM D 445)

Viscosity is a measure of the resistance of a fluid which is being deformed by either stress or tensile stress. Kinematic viscosity measurement was carried out using the equipment CAV 2000 Automatic viscometer. The bath temperature was controlled to an accuracy of +/- 0.01°C at 40° or 100°C. Kinematic viscosity is expressed in centistokes (cSt) and it is normally determined 40°C and 100°C. These two values can then be used to determine the viscosity Index (VI).The sample was taken in auto sampler and it is sucked. After 20 minutes or as per the specified time as per design of the equipment, the measurement was taken (time in seconds) and the constant of particular viscometer was taken for calculation. Viscosity – temperature characteristic of base oil is an important parameter for lubricant formulation and is represented by viscosity Index (VI).

Sulphur and Nitrogen (ASTM D 5762)

Nitrogen & Sulphur were analysed using TN 3000 nitrogen analyser manufactured by Thermo Electron Corporation. 250 mL diluted sample was injected into the sample tube along with pure oxygen carrier gas and the furnace was heated up to the temperature of 925+/- 25°C. Measure the chemiluminescence and it was converted to calibration curve. The nitrogen & sulphur content was measured for all the samples and given in table 1.

Evaporation method (ASTM D 5800)

This test was measured in Automated Noack Evaporation loss tester, ISL model NCK2 5G. 65 gm of sample weighed into the crucible and screw the cover using the clamp and spanner. The sample was kept assembly into the heating block at 250°C. Adjust the heating control on the heating block to

maintain the temperature approximately 5°C below the test temperature. The evaporated vapour sucked in pressure differential of 20 +/- 0.2 mm vacuum. After an hour the crucible was taken out from heating block and kept in water bath for 30 minutes. The crucible was removed from water bath and removed adhering alloy and weigh nearest to 0.01g. The difference in weight is evaporation loss and the same procedure was followed for all samples.

Auto Pour point and Auto Flash point (ASTM D97& D92)

The pour point of a petroleum specimen is an index of the lowest temperature of its utility for certain applications. The pour point of a liquid is the lowest temperature at which it becomes semi solid and loses its flow characteristics. In crude oil a high pour point is generally associated with a high paraffinic content. The flash point is one measure of the tendency of the test specimen to form a flammable mixture with air under controlled laboratory conditions. It is only one of a number of properties that should be considered in assessing the overall flammability hazard of a material.

RESULTS AND DISCUSSION

Structural interpretation of samples by ¹H and ¹³C NMR

Quantitative estimation of the carbon content by ¹³C NMR was done using an inverse gated decoupling sequence and was considered quite adequate in the present situation. This has resulted in the accurate estimation of various carbon types without any assumptions on chemical shifts (Gillet *et al.*, 1981, Begon *et al.*, 2003). The area covered under a specific peak was translated to its relative concentration corresponding to a particular carbon type. The assignment of peaks to specific carbon types was based on earlier studies (Kramer *et al.*, 1999, Adhvaryu *et al.*, 2000). The inverse gated ¹³C NMR spectra resulted in well separated peaks with no overlaps between adjacent peaks. The carbon atoms are first divided into saturate (5-60 ppm) and aromatic (100-160 ppm). In the analysed samples, there are no signals observed in the aromatic region due to severely hydro treated based oils. Hence these samples do not contain any aromatic carbon. The naphthenic hydrocarbons appear as a broad hump in the paraffin region (24-60 ppm) and can be digitally removed by using spline baseline spectral correction for estimation of normal paraffin (C_{np}) and isoparaffin (C_{ip}) carbons.

Table 1 Physiochemical properties of base oils

Tests	LVI Spindle	HVI Spindle	SN 70
KV@40°C,cSt	15.81	11.85	14.27
KV@100°C,cSt	3.35	2.94	3.37
VI	70	101	108
KV @100°C , cSt (after heating the oil @200°C for 2 hrs	3.518	3.00	3.485
Pour Point,°C	Minus 6	Minus 6	Minus 21
Flash Point,°C	194	188	218
Sulphur, %	1.125	0.614	0.026
Nitrogen, %	0.043	0.004	Traces
Aniline Point, °C	76.8	90.1	102.4
RPVOT, Min	87	46	45
RPVOT, Min(with 0.2% anti oxidant)	115	118	114
HFRR	375	416	416
Noack evaporation	49.5	53.9	38.3

Then naphthenic (C_n) carbons can be calculated from the difference of saturate carbons (C_{sat}) and combined C_{np} and C_{ip}. Actually this procedure eliminates overestimation of total paraffin and under estimation of naphthenic carbons.

(Adhvaryu *et al.*, 2000, Sharma *et al.*, 2007). The data (table 2) illustrates that the relative distribution of carbon using ¹³C NMR inverses gated decoupling. Generally, VI is largely dependent on the amount of C_{ip} and to a certain extent on C_n in the base oils. Hence high C_{ip} and C_n percent with result in high VI. The high viscosity index value and low average chain length value of SN70 shows that SN70 has better oxidation stability than that of LVI and HVI Spindle oils.

Table 2 Structural parameter values of analyzed samples

Structural parameter	LVI Spindle	HVI Spindle	SN 70
VI	70	101	108
Cn	18.88	11.12	25.90
Cp	64.44	88.87	71.09
Cip	46.56	66.82	49.56
ACL(Average chain Length)	12.54	14.59	12.0
API Group type	I	I	I

This concludes SN70 is higher oxidation stability and more suitability to use as an automotive engine oils/ industrial oils. Considering the values of paraffinic and iso-paraffinic carbons of the tested samples, higher values of Cp and Cip values of HVI spindle oil appears to be the suitability of engine oil characters. However the high viscosity index (108) value and lesser contribution of sulphur value (0.026%) indicated that Relationship between base oil structure and thermo oxidative properties.

Table 3 Thermo oxidation data for LVI Spindle, HVI Spindle &SN70

Tests	LVI Spindle	HVI Spindle	SN70
RPVOT, minutes	87	46	45
RPVOT, min (with 0.2% Antioxidant)	115	118	114
Sulphur, % wt	1.125	0.614	0.026

Table 4 Kinematic viscosity values with various temperatures

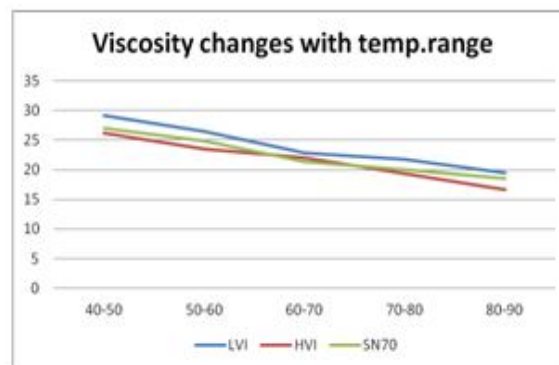
Tests	LVI	HVI	SN70
KV@40°C	15.81	11.85	14.27
KV@50°C	11.20	8.74	10.41
KV@60°C	8.23	6.68	7.82
KV@70°C	6.35	5.21	6.15
KV@80°C	4.97	4.20	4.92
KV@90°C	4.00	3.50	4.01
KV@100°C	3.35	2.94	3.37
% Decrease from 40°C to 100°C	78.81	75.19	76.38
VI	70	101	108
KV@100°C(after heating at 200°C for 2 hrs)	3.52	3.00	3.49
% increase	5.07	2.04	3.57

Table 5 Percentage of decreasing viscosities Vs Temperature Range

Temp. Range	LVI	HVI	SN70
40-50	29.15	26.24	27.05
50-60	26.52	23.57	24.88
60-70	22.84	22.01	21.36
70-80	21.73	19.39	20.00
80-90	19.52	16.67	18.49

The sample was measured for oxidation with operating temperature at 150°C, with oxygen charge is 90 psi (620 kPa)

and the oil is rotated at 100 rpm at a 30° angle until the recorded oxygen pressure in the chamber falls rapidly to the end of the test. The oxidation stability of the samples was recorded in table 3. SN70 base oil is more suitable base oil than the LVI and HVI spindle oils.



Sulphur containing base oils is viewed as desirable since they inhibit hydrocarbon autocatalytic oxidation through free-radical chain termination pathways. RPVOT values of LVI spindle shows higher than that of HVI and SN70 due to presence of high sulphur in LVI spindle. However, the RPVOT value increases while adding 0.2% of antioxidant (Dunn Robert *et al.* 2005) in HVI and SN70 shows three times increase (300%) where as LVI shows only 40% increase. The tremendous increase in kinematic viscosity of HVI Spindle and SN70 are due to the presence of more paraffinic carbons.

Table 5a Viscosity changes after heating 2 hrs at 50°C

Temperature.	LVI	HVI	SN70
KV @ 40°C	15.81	11.85	14.27
KV@t40 after 2hrs at 50°C	15.89	11.88	14.29
Difference	0.08	0.03	0.02
% change	0.5	0.25	0.14

In plain base oil the presence of sulphur influences the oxidation stability. The oxidation stability is also influenced by (DBPC- 2,6 di tertiary-butyl para cresol) antioxidant. It can be concluded that the oxidation stability of the base oils are well influenced by the addition of antioxidant (Jose Carlos Oliveira Santos *et al.* 2004). The oxidation stability (in terms of RPVOT) increased in three times due to the addition of 0.2% antioxidant in HVI Spindle and SN70 base oils. However the tremendous enhancement of oxidation stability of HVI spindles oils is not only due to the addition of 0.2% antioxidant but also due to the presence of 0.614 % of sulphur whereas the enhancement of oxidation stability in SN 70 is wholly responsible for the addition of 0.2% antioxidant. Hence the SN70 is more suitable engine oil / industrial oil than that of LVI and HVI spindle oils. This is a useful tool for selecting suitable base oil for automotive / industrial lubricants.

Relationship of kinematic viscosity with temperature

The kinematic viscosity were measured on LVI, HVI and SN70 samples at various temperature viz., 50°C, 60°C, 70°C and 80°C and the values are given in table 4.

It may be noted that the viscosities are decreasing with respect to increase of temperature from 40°C up to 100°C. The percentage decrease is almost same in LVI, HVI and SN70.

The percentage change of viscosity with respect to temperature (table 5) is almost same during 60 to 70°C. In these temperature ranges all the samples showed same percentage of decreasing viscosity values. This shows that this temperature range is the suitable working temperature for a particular application.

All the samples were under gone for the testing of oxidation. Samples were taken into a beaker and heating up to 50°C and kept for 2 hrs and measured their kinematic viscosity at 40°C and the results were given in table 5a. The lesser magnitude of difference in viscosity values and the % change in viscosity values shows that SN70 base oil has better oxidation stability.

The High Frequency Reciprocating Rig (HFRR) tests are reciprocating friction and wear test system which provides a fast assessment of the performance of lubricants. It is particularly suitable for wear testing for boundary friction measurements of oils. The samples were undergone for testing of HFRR and results were given in table 6.

Table 6 Lubricity tests (HFRR)

Tests	LVI	HVI	SN70
HFRR, mm	375	416	416

The HFRR test shows that HVI & SN70 are excellent performance in boundary lubrication than the LVI oil. Based on the results the blender can choose suitable base oils for industrial purpose.

Noack evaporation study

Generally, more evaporation values are less stable or less evaporation values shown more stable behavior. The Noack evaporation value of SN70 is lesser than that of LVI & HVI. This reveals that SN70 base oils are more stable than that of LVI & HVI.

Table 7 Noack Evaporation Results

Tests	LVI	HVI	SN70
Noack Evaporation loss %wt	49.5	53.9	38.3

CONCLUSION

The suitability of base oils were derived from the results of physio-chemical, thermal and NMR spectral data of some group I based oils. The Cp, Cn and Cip type carbons percent contribution were derived from NMR measurements and the results were shown that the SN 70 base oil is more suitable for industrial applications.

- VI is largely depends on Cip values and certain extent of Cn.
- A decrease in average chain length among the oils increases the viscosity index.
- Oxidations of base oils are depend upon the presence of iso paraffinic carbon and percentage of sulphur.
- Addition of antioxidant (DBPC- 2,6 di tertiary-butyl para cresol) remarkably enhanced the oxidation stability of all the tested base oils.

- The viscosity study shows that 60-70°C temperature range is the ideal temperature range for any industrial applications.

Finally, the current investigation focused on the point that all the base oils can be used for industrial applications where the operating temperature is about 60°C to 70°C. LVI spindle oil is useful for water based Metal working Fluid. The other base oils HVI & SN70 can be used for Neat cutting application and Hydraulic applications.

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