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New Method of Simulation to Evaluate the Sensitivity to Oxidation of Lubricating Oils: An Aging Cell Coupled with Fourier Transform Infrared Spectroscopy

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This study presents a new method for evaluating the oxidation of lubricating oils. An aging cell adapted to a Fourier transform infrared (FT-IR) spectrometer allows the continuous and direct study of the oxidative aging of base oils. During the test, oxidation bands appeared in the spectra (carbonyl bands around 1730 cm^{-1}). The graphic representation of the carbonyl band modification—using a spectroscopic index—makes it possible to monitor the evolution of the lubricant composition. Comparing the oxidation constants, determined from the kinetic plots of several base oils, makes it possible to evaluate their relative sensitivity.

Index Headings: Oxidation stability; Lubricating oils; Fourier transform infrared spectroscopy; FT-IR spectroscopy; Aging cells; Simulation.

INTRODUCTION

A lubricant is a complex mixture of base oils and additives. The main purpose of lubricants is to lubricate the moving parts of a vehicle engine to reduce friction and wear and tear and increase the performance and the lifetime of the engine. The performance of a lubricant is increased by addition of additives such as pour-point depressants, antioxidants, dispersants, and detergents. New engine technologies lead to extreme heat stress, causing a deterioration of the properties of viscosity or the formation of deposits. The evolution of the lubricant's performance with time strongly depends on the resistance of the lubricant to oxidation.^{1–5}

Therefore, a higher stability towards oxidation is required. It is important for formulators to determine the long-term stability of a lubricant. They should be able to predict the results of engine tests using fast, simple, and cheap laboratory tests. Different tests can be used such as the iron catalyzed oxidation test (ICOT),⁶ the rotating bomb oxidation test (RBOT),⁷ pressure differential scanning calorimetry (DSC),⁸ or the thin-film oxygen uptake test (TFOUT).⁹ However, most of these tests are time consuming and do not give information about the chemical changes that may happen during these tests. Information is mainly obtained on the viscosity increases or the induction times or pressure differences.

Infrared spectrometry allows study of lubricant oxidation^{10–14} and an ASTM method has been built using peak area increase calculation (ASTM D7214-07).¹⁵ However, these methods require sample preparation and the thermal oxidation system is separate from the spectrometer. Therefore, it is desirable to develop a new oxidative test that allows a rapid evaluation of the stability of lubricating base oils and lubricants toward oxidation and a better understanding of their structural evolution over time. Thus, it should make it possible not only to compare the base oils according to their stability but also to discriminate between them according to their structural evolution.

The aim of this study is to develop a fast, continuous, and direct monitoring of the slow evolution of lubricant oxidation, using Fourier transform infrared spectroscopy (FT-IR). This paper presents a new oxidation test that comes up to these expectations: an aging cell coupled with FT-IR spectroscopy. The cell allows lubricating base oils to be oxidized under controlled atmosphere and temperature. FT-IR allows the qualitative and semi-quantitative analysis of the chemical composition of base oils. This method makes it possible to discover the functional and structural groups that account for the chemicals formed by aging, without destroying the oil's internal balance.

EXPERIMENTAL

Samples. The lubricating base oils used for this study were obtained from TOTAL Research Center, Solaize, France. They were selected from the different API groups in order to cover a wide range of applications.

“NS E” represents Group I basestocks, characterized by high sulfur and aromatic contents. “HT C” represents Group II basestocks. “HI J” and “HI+S1” represent Group III basestocks. “PAO” corresponds to the synthetic poly- α -olefin base oils of Group IV.

Infrared Spectroscopy. Fourier transform infrared spectra were measured on a Nicolet Protégé 460 spectrometer coupled with a Nicolet Nic-Plan infrared microscope fitted with a mercury cadmium telluride (MCT) detector cooled with liquid nitrogen. The standard analytical conditions were $15\times$ infrared

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FIG. 1. Schematic showing the principle of the aging cell.

objective, beam size of $100 \times 100 \mu\text{m}$. The spectra were acquired using Omnic 4.1. Nicolet software. Sixty-four (64) scans of symmetrical interferograms were averaged and the spectrum was calculated from 4000 to 650 cm^{-1} at 4 cm^{-1} spectral resolution.

The Aging Cell: Design and Development. The aging test was run in an aging cell developed in our laboratory to study the structural evolution of fluid fossil organic material¹⁶ during aging. This aging test corresponds to a thin layer test. The cell was fitted in the motorized stage of the microscope so that it under-regulated thermo-oxidizing conditions.

The aging cell consisted of a metallic body heated by two heating cartridges (Fig. 1). These two cartridges were connected to a regulator (WATLOW 988), itself connected to

FIG. 2. NaCl window allowing the study of fluid materials.

FIG. 3. FT-IR spectra of HI+S1 base oil before and after oxidation between 2000 and 650 cm^{-1} .

a temperature probe fitted in the center of the cell. A heated gas flow was flushed through the cell. The gas heating block was connected to a second regulator (WATLOW 988). The system was equipped with a by-pass to select the gas. Analyses could be performed either under oxidant gas (Synthetic air (80% N_2 , 20% O_2) Air liquide, 99% purity) or under neutral gas (argon, Air liquide, 99% purity), allowing the thermal effect to be distinguished from the oxidative effect during simulated aging. The cell is always maintained at atmospheric pressure thanks to the gas outlet.

The sample was supported by a NaCl window ($13 \times 2 \text{ mm}$). Two 1 mm deep cavities were created in this NaCl window. The bigger cavity (diameter, 5 mm) was to contain the sample, the smaller one (diameter, 0.5 mm) did not contain any sample (Fig. 2). Thus, it was possible to collect a background spectrum at any time.

The window was fitted at the bottom of the cell. A removable upper NaCl window ($30 \text{ mm} \times 2 \text{ mm}$) was fixed by some screws during analysis. The cell was fixed on a Teflon stand, itself fitted in the motorized stage of the microscope. Using a Teflon stand reduces the diffusion of heat to the motorized stage so that its movement is not affected.

Continuous Collection of Spectra Within the Heating Cell. Six milligrams (6 mg) of oil were placed in the 5 mm diameter cavity of the NaCl window and heated from 25°C up to a chosen temperature under argon at $11^\circ\text{C min}^{-1}$ for around 15 min. Then, the heating was maintained at the chosen temperature under synthetic air during the rest of the experiment. Spectra were collected every 15 min during the oxidation process.

The more the temperature increases the more the oil becomes fluid and the more it spreads. The gas flow should be sufficient to ensure either an oxidizing atmosphere or a neutral atmosphere but should not sweep away the oil. Thus, the non-oxidizing conditions in the first fifteen minutes are reached thanks to an argon gas flow of 80 mL min^{-1} . The optimum air flow was found to be equal to 50 mL min^{-1} .

Figure 3 shows typical FT-IR spectra before and after

FIG. 4. Spectra of HI+S1 at different times of oxidation at 170 °C between 2000 and 650 cm^{-1} .

oxidation of the HI+S1 base oil between 2000 and 650 cm^{-1} . In addition to bands at 1460 and 1375 cm^{-1} , attributed to the bending vibration of the CH_2 and CH_3 groups existing in “fresh oil”, the FT-IR spectra obtained during the aging show absorption bands relative to carbonyl species corresponding to the oxidation products. These bands correspond to the $\nu_{\text{C=O}}$ stretching mode from 1850 to 1685 cm^{-1} (acids, ketones, esters, anhydrides, and lactones) and to the $\nu_{\text{C=O}}$ stretching mode from 1300 to 850 cm^{-1} . Assignments were made according to the works of Coates and Setti.¹⁷

The oil aging was followed by calculating a spectroscopic index named the carbonyl index. This index was calculated from the band areas measured from valley to valley.^{18–21} The band areas were considered rather than the band heights in order to obtain a finer index. The following areas were defined (Fig. 3):

- A₁: from 1850 to 1685 cm^{-1} (multiple C=O bands)
- A₂: from 1502 to 1419 cm^{-1} (bands at 1467 and 1450 cm^{-1})
- A₃: from 1396 to 1369 cm^{-1} (band at 1378 cm^{-1})

The carbonyl index is given by the following equation:

$$I_{\text{C=O}} = A_1 / (A_1 + A_2 + A_3) \quad (1)$$

Bulk Oxidation Tests. Two bulk oxidation tests were used. The first one was adapted from the iron catalyzed oxidation test (ICOT) for this study (modified ICOT). The protocol of the ICOT, used in the oil industry, is described by Faure et al.²² and Obiols.²³ Twenty-seven grams (27 g) of base oil were oxidized in test tubes placed in a thermo-regulated bath (170 °C) for 72 h. Each test tube was equipped with an air gas inlet and an oxidized gas outlet. The air flow was 10 L h⁻¹. This modified ICOT was performed without catalyst. A sample of 20 μL was taken every hour and analyzed by FT-IR microscopy, as previously described. The fresh base oil and the final oxidized base oil after 72 h of oxidation were

FIG. 5. Evolution of the carbonyl index ($I_{\text{C=O}}$) versus time for HI+S1 heated to 170 °C in the aging cell.

recovered and placed in an automatic viscosimeter. The ratio between the initial viscosity (V_i) and the final viscosity (V_f) gives the kinematic viscosity increase (KVI):

$$KVI = [(V_f - V_i) / V_i] \times 100 \quad (2)$$

The second test (laboratory oxidation test, LOT), carried out on 250 g of oil, used a laboratory apparatus consisting of a 500 mL three-necked flask, a right condenser, a thermo-controlled heating bath (160 °C), a controlled flow of synthetic air for bubbling (50 mL min⁻¹) and a septum to take a 1 mL sample every hour. Oil is agitated by a magnetic stirrer. Each sample was analyzed by FT-IR microscopy.

The flows used in each test allow optimal oxygen diffusion (at least at the beginning of each test).

RESULTS AND DISCUSSION

Choice of Experimental Conditions. The use of the carbonyl index eliminates the constraints due to the sample thickness and thus to the spectrum intensity. Then, it is possible to compare the different tests on the same scale. Figure 4 shows a set of spectra collected during the oxidation of HI+S1 in the heating cell at 170 °C. The carbonyl index was calculated after the integration of all the spectra and its evolution was graphically represented as a function of the oxidation time (i.e., a kinetic plot) (Fig. 5).

The kinetic plot starts with an induction period, and then the oxidation itself starts. The exponential evolution is representative of the oxidation up to a maximum called the plateau. Then the oxidation stops. The kinetic plot could be interpreted according to five constants: (1) Induction time (It): time corresponding to the beginning of the oxidation process; (2) Slope: representative of the rate of the oxidation reaction; (3) Half life time (Hlt): time necessary to reach 50% of the plateau height; (4) Plateau onset time (Pot): time corresponding to the end of the oxidation; and (5) Plateau height (Ph): maximum oxidation rate.

Common tests usually oxidize oils at high temperatures^{6–9,24} (160–180 °C). This aging cell should be able to oxidize oil rapidly whatever the oil. Five temperatures were thus tested with HI+S1: 140, 150, 160, 170, and 180 °C, as shown in Fig. 6. The oxidation constants obtained from these five kinetic plots are given in Table I. The temperatures of 140 and 150 °C were dismissed because the induction times (238.6 min and

FIG. 6. Kinetic plots of HI+S1 at 140, 150, 160, 170, and 180 °C.

TABLE I. Oxidation constants of HI+S1 heated to 140, 150, 160, 170, and 180 °C.^a

Temperature (°C)	It	Slope	Hlt	Pot	Ph	Ft
140	238.6	0.0014	No	No	No	615
150	86.5	0.0028	242.0	357.2	0.79	515
160	55.3	0.0055	132.5	194.8	0.81	330
170	32.0	0.0079	81.2	131.8	0.80	240
180	19.8	0.0097	67.6	103.6	0.82	165

^a It = induction time; Hlt = half-life time; Pot = plateau onset time; Ph = plateau height; Ft = final time. No = not observed. Each time is expressed in min.

TABLE II. Oxidation constants of HI+S1 and HI J heated to 160 and 170 °C.

		It	Slope	Hlt	Pot	Ph	Ft
160 °C	HI+S1	55.3	0.0055	194.8	132.5	0.81	330
	HI J	72.0	0.0051	203.6	130.1	0.79	No ^a
170 °C	HI+S1	32.0	0.0079	81.2	131.8	0.80	240
	HI J	42.9	0.0074	84.1	127.4	0.79	No ^a

^a No = not observed. Each time is expressed in min.

TABLE III. Repeatability of the test on HI+S1 heated to 170 °C.

	It (min)	Slope	Hlt (min)	Pot (min)	Ph
Test 1	32.8	0.0074	85.3	127.2	0.83
Test 2	31.3	0.0079	81.3	131.8	0.79
Test 3	30.0	0.0073	80.6	129.6	0.85
Test 4	31.5	0.0074	89.5	137.1	0.83
Test 5	32.6	0.0079	81.1	131.8	0.80
Test 6	33.5	0.0075	82.6	123.2	0.83
Mean	32.0	0.0076	83.4	130.1	0.82
Standard deviation	1.2	0.0002	3.1	4.3	0.02
Coefficient of variance (%)	3.6	3.2	3.8	3.3	2.5

86.5 min, respectively) were too long. On the contrary, at 180 °C the induction time was too short (19.8 min) and the slope was too steep. This can lead to errors in the classification of base oils according to their sensitivity to oxidation. Therefore, this temperature was also dismissed. In order to choose between 160 and 170 °C, the results obtained for HI+S1 were compared with those obtained for HI J. They are given in Table II. HI+S1 was the most sensitive to oxidation. The difference between the induction times of the two oils was ≈17 min at 160 °C and ≈10 min at 170 °C. The difference between their slopes was nearly the same for both temperatures. Therefore, the discrimination between the two oils was better at 160 °C but took more time. Finally, 170 °C is the most suitable temperature. It makes it possible to observe complete kinetics (up to the plateau height) and to obtain the five required oxidation constants.

To evaluate the repeatability of the method, the test was carried out six times by the same experimenter on HI+S1 at 170 °C. Table III summarizes the oxidation constants of each kinetic plot, their means, and their standard deviations. The coefficient of variance (CV), defined by the following equation (Eq. 3), is a repeatability evaluation tool:

$$CV\% = (\text{Standard deviation}/\text{Mean}) \times 100 \quad (3)$$

None of the CVs given in Table III exceeded 3.8%; therefore, the test can be considered repeatable and was in accordance with other tests.⁸

Comparison with the Modified Iron Catalyzed Oxidation Test. The samples NS E, HT C, HI J, and PAO were oxidized using both the modified ICOT (a bulk oxidation test) and the heating aging cell (a thin layer test). Graphical and numerical results are shown in Fig. 7 and Table IV. Base oil can be considered resistant to oxidation if its induction time, its half-life time, and its plateau onset time are high and if its slope is weak and its plateau height is low. The HT C base oil has the lowest times—in particular the lowest induction time (≈38.6 min)—and the highest plateau height. The induction times and

FIG. 7. Kinetic plots of NS E, HT C, HC J, and PAO at 170 °C.

the slopes of PAO and NS E are similar, but the plateau height of NS E is lower than that of PAO. HI J is intermediate between HT C and PAO/NS E. Therefore, according to each constant, orders of sensitivity to oxidation are proposed in Table V. The base oils are classified from the most sensitive to the least sensitive and a global order of sensitivity is proposed as follows:

$$\text{HT C} > \text{HI J} > \text{PAO} > \text{NS E}$$

This order is in accordance with the characteristics of the base oils. Actually, group II base oils are more sensitive to oxidation than group III base oils, themselves more sensitive than group IV base oils.²⁵ The result obtained for group I base oils is due to their content of sulfur and aromatic compounds, which are natural antioxidants.²⁶

Table IV shows ICOT results for these base oils. ICOT gives an idea of the oxidation sensitivity through the kinematic viscosity increase. The base oils are classified from the most sensitive to the least sensitive as follows:

$$\text{HT C} > \text{PAO} > \text{HI J} > \text{NS E}$$

In comparison with the previous order, PAO and HI J are inverted, but the order found with ICOT is similar to the one found by using the plateau height (Table V). This can be

TABLE IV. Oxidation constants of all the base oils.^a

	It (min)	Slope	Hlt (min)	Pot (min)	Ph	KVI (%)
NS E	58.4	0.0079	96.2	134.4	0.69	16.0
HT C	34.7	0.0101	74.1	104.1	0.82	3206.9
HC J	42.9	0.0074	84.1	127.4	0.79	2002.7
PAO	58.2	0.0086	103.1	147.0	0.79	2700.1

^a KVI (%) = kinematic viscosity increase in percent obtained after the modified ICOT.

explained by the fact that ICOT is a technique that makes it possible to measure the final residue after 72 h of oxidation.

Index Validity. The modified ICOT was performed on HI+S1 at 160 °C to confirm the oxidation constants obtained by the thin layer test carried out with the aging cell (HI+S1, 160 °C). The carbonyl index was calculated from the spectrum of each sample taken every hour. The kinetic plots are shown in Fig. 8. The oxidation constants are as follows: It = 52.8 min, Slope = 0.0361, Hlt = 600 min (10 h), Pot = 18 h, and Ph = 0.612. The comparison of the kinetic plots obtained with the modified ICOT and with the aging cell shows that the induction times are very similar whatever the oxidized volume: 55.3 min for the oxidation by the aging cell and 52.8 min for the oxidation by the modified ICOT.

To confirm this result, a bulk oxidation test by LOT was carried out on 250 g of HI+S1 at 140 °C. The kinetic plot is compared to the one obtained with the aging cell (HI+S1, 140 °C) (Fig. 9). The induction times are similar: 232.9 min with the cell and 230.3 min with the LOT. The slopes obtained are very different. This means that the ratio of oxygenated compounds formed is not proportional to the quantity of oil. The propagation of the peroxy radicals^{27,28} may be more difficult if the quantity of oil is significant.

The induction time is an oxidation constant non-sensitive to the quantity of oil. Therefore, this constant can be used as an internal reference because it can be transposable from a bulk

TABLE V. Classification of the base oils according to their sensitivity to oxidation based on their oxidation parameters.

	Most sensitive	>	>	Least sensitive
Induction time	HT C	HC J	PAO	NSE
Slope	HTC	HC J	NSE	PAO
Half-life time	HT C	HC J	NSE	PAO
Plateau onset time	HT C	HC J	NSE	PAO
Plateau height	HT C	PAO	HC J	NSE

FIG. 8. Kinetic plots of HI+S1 at 160 °C obtained by the aging cell and with the modified ICOT.

FIG. 9. Kinetic plots of HI+S1 at 140 °C obtained by the aging cell and with the LOT.

oxidation test to the thin layer test using the aging cell whatever the temperature.

CONCLUSION

The aging cell allows the discrimination between base oils. Moreover, an FT-IR analysis of the oxidation products in each phase (induction, exponential, and terminal phase) is possible. This study has demonstrated that the induction time is an intrinsic characteristic of oil. Moreover, the classification obtained according to the plateau height (results obtained using the aging cell) is the same as the one obtained according

to the viscosity increase (modified ICOT results). Therefore, the information obtained using the aging cell is in accordance with the information obtained using other techniques, and they are even obtained more rapidly and from smaller sample quantities. Therefore, this new method should be an interesting alternative to the usual oxidation tests.

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