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THERMAL, SPECTROSCOPIC AND RHEOLOGICAL STUDY OF MINERAL BASE LUBRICATING OILS

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Resumo – O processo de degradação térmica de óleos lubrificantes básicos minerais foi estudado neste trabalho em relação as suas propriedades térmicas, espectroscópicas e reológicas. Os óleos lubrificantes foram degradados em diferentes temperaturas variando de 150°C a 210°C, e sob diferentes tempos de degradação de 1 a 48 h. Após processo de degradação, os óleos foram caracterizados por fluorescência de raios-X, espectroscopia na região do infravermelho (IV) e ressonância magnética nuclear (RMN), propriedades reológicas e análise térmica (TG/DSC). As análises espectroscópicas determinaram os produtos das reações de oxidação. As análises TG/DSC indicaram uma diminuição nas temperaturas de início de decomposição. A diminuição nas temperaturas de degradação levou uma diminuição nas viscosidades dos óleos lubrificantes.

Palavras-Chave: óleo mineral básico; degradação; análise térmica

Abstract – The thermal degradation process of mineral base lubricating oils was studied in this work by means of their thermal, spectroscopic and rheological properties. The lubricating oils were degraded at temperatures varying from 150°C to 210°C, and for degradation times from 1 to 48 h. After the degradation, the oils were characterized by x-ray Fluorescence, infrared spectroscopy (IR) and nuclear magnetic resonance (NMR) spectroscopy, rheological properties and thermal analyses (TG/DSC). The spectroscopic analyses determined the oxidation reaction products. TG/DSC analyses pointed out to a diminishing of the onset decomposition temperature after the degradation. The decrease in the degradation temperature led to a decrease of the lubricant viscosity.

Keywords: mineral base lubricating oil, degradation, thermal analysis

1. Introduction

Formulation of an automotive lubricating oils is a complicated process. The modern engine lubricant is a carefully designed blend of base oils and performance enhancing additives, such as pour point depressants, antioxidants, dispersants and detergents (Souza, 2000; Pedersen and Ronningsen, 2003).

Regardless of the complexity, the lubricating oil formulator must assess the performance of the base oil and the additives, and finally balance the performance and the cost, prior to the full-scale engine testing of the oil. Because engine testing is an expensive process, a number of bench tests have been developed to screen out the lubricating oil throughout the formulation process (Perez, 2000). Many of these bench tests are time consuming, man-power intensive, empirical, show poor reproducibility, and require a large investment in specialized equipment and skilled operators, and may be advantageously replaced by conventional thermal analysis techniques (Keskin and Kok, 2001; Gamlin et al., 2002).

In this work, thermal, spectroscopic and rheological properties were determined after the thermal degradation of mineral base lubricating oils at different temperatures and for different degradation times.

2. Experimental

2.1 Oil Samples

Mineral base lubricating oils produced by Brazilian industries were used in this study. According to the manufacturer specifications, this mineral base lubricant is paraffinic, being used in the lubrication of automotive engines, working with gasoline, ethyl alcohol and natural gas. Their API classification is SJ group, with a typical analysis from the manufacturer of 0.87 g/mL density and 30W SAE viscosity.

The thermal degradation of the mineral base lubricating oils were assessed by means of heat treatments at 150, 170, 190 and 210 °C, using an apparatus similar to the ones used for distillation, with the oil samples being submitted to an air flow. The samples were withdrawn after degradation times that varied from 1 to 48 h. Thermal, spectroscopic and rheological properties were evaluated for the degraded and non degraded base lubricants.

2.2 Spectroscopic Measurements

Sulfur analyses were performed in an X-Ray fluorescence spectrometer by dispersive energy (EDX – 800, Shimadzu). Infrared spectroscopic measurements (MB Series, Bomem) were carried out using KBr pellets, at the 400 – 4000 cm^{-1} region. Proton nuclear magnetic resonance (^1H NMR – 300 MHz, Gemini) was used in the lubricating oil characterizations, at room temperature, using relaxation delay of 0.20 s, pulse of 5.0 degrees, acquisition time of 2.667 sec, width of 6000.0 Hz and 16 repetitions.

2.3 Rheological Measurements

Rheological measurements (LV-DVII – Brookfield) were conducted at 25°C, at different shear rates, using a small sample adapter.

2.4 Thermal Analysis

Thermogravimetry (TG/DTG) and differential scanning calorimetry (DSC) analyses were performed in a simultaneous thermobalance (SDT-2960, TA Instruments), in air and nitrogen atmospheres, with a flow of 110 mL/min, using alumina crucibles, heating rates of 5, 10, 15 and 20°Cmin⁻¹, sample mass of 10.0 ± 0.5 mg, at a 25 – 620°C temperature range.

3. Results and Discussion

3.1 Spectroscopic analyses

According to X-ray fluorescence spectroscopy (XRF) data, non-degraded samples present 0.350 mass percent of sulfur. After a degradation at 210°C for 24 h, a decrease to 0.287% is observed, probably due to SO₂ formation. The samples degraded at 210°C for 36 h were polymerized.

On the other hand, infrared spectra presented a small difference, before and after the thermal treatment, indicating the occurrence of oxidation reactions (Figure 1).

Figure 1. Infrared spectra of mineral base lubricating oil

Thus, IR results indicate that lubricant degradation occurs by oxidation reactions, in agreement with the literature (Pavia et al., 1997), probably leading to the formation of carboxylic acids and ketones. It is noticed that these spectra indicate that the analyzed oils presented meaningful changes in the spectral regions of the groups O–H, C=O and C–O. This can be attributed to the stronger action of oxygen during the heating period for the degraded samples. The bands observed at 3415 and 1714 cm^{-1} suggest the presence of O–H alcohol groups and C=O carbonyl groups, respectively, for all the degraded samples. As for the bands found in all the samples at 1157 and 3600 cm^{-1} , they refer to the OH groups, originated from hydrogen bonds and free hydroxyl groups in monomers, respectively. Ketones, aldehydes, carboxylic acids and esters display a band at 1898 cm^{-1} , which originates from the axial deformation of the C=O bond, which is shown to be less intense in the non-degraded sample.

As for the C–H bands, no meaningful changes were observed between the degraded and non-degraded samples. The C–H deformation is characterized by the presence of bands at 1463 and 1377 cm^{-1} , which are representative of this group. The C–H stretch for the $-\text{CH}_2$ group appears at 2922 and 2850 cm^{-1} , and this latter band becomes more intense in the oils degraded at the highest temperatures, namely 190 and 210°C . The C–H asymmetric deformation bands for $-\text{CH}_2-$ and $-\text{CH}_3$ are noticed at 723 and 1377 cm^{-1} , respectively. The band at 1604 cm^{-1} probably indicates the aromatic C–C bond. The presence of a band at 2670 cm^{-1} in all the samples with the exception of the sample submitted to the highest degradation, 210°C for 24 h, refers to some sulfur compounds. The bands attributed to the C–C axial vibrations are weak and are noticed at the region between 1200 and 800 cm^{-1} . Bands between 800 and 1400 cm^{-1} presenting several peaks may represent the C–O bonds associated to a variety of oxygenated organic compounds. Some of these bands may be attributed to sulfonated compounds or to other sulfur-containing compounds, either produced upon the degradation or initially present in the lubricating oils (Santos et al., 2005; Pavia et al., 1997).

^1H NMR spectra of degraded and non-degraded mineral lubricant oils are shown in Figure 2. The spectra of the degraded lubricants show new peaks at 6.9 – 7.5 ppm , which can be attributed to protons in unsaturated ketones (Pavia et al., 1997; Silverstein and Webster, 2000).

Figure 2. ^1H NMR spectra of non-degraded and degraded mineral base oils

3.2 Rheological Behavior

Viscosity results are presented in Figure 3. It may be observed that all lubricants present an increase in viscosity, at the beginning of the degradation. This behavior is due to evaporative losses of lower boiling point and hence lower viscosity components.

Figure 3. Viscosity variation as a function of time and temperature

For the samples degraded at 150 °C, after this first increase, the viscosity remains constant, indicating that no further degradation occurs. After the initial increase in viscosity values, samples degraded at 170 and 190 °C present a viscosity decrease. According to literature data (Pavia et al., 1997), from NMR and infrared spectra, oxidation products are formed after the degradation, leading to the formation of hydrogen bonding and dipole-dipole interaction, respectively. As a consequence, higher intermolecular forces are formed, increasing the lubricant viscosity. On the other hand, oxidation products are observed in all samples after degradation.

The polymerization reaction was observed, what of course leads to a viscosity increase. When the molecular weight of the polymer achieves a too high value, the material may become insoluble, leading to its precipitation. This degradation mechanism was observed by Kauffman et al. (2000), in aircraft turbine engine oils. The viscosity variation, as well as other rheological aspects, may be related to the polymerization followed by precipitation of these products. This precipitation is very deleterious, as these products are harmful to machines.

3.3 Thermal Analyses

Oxidation reactions, leading to decomposition, are confirmed by thermogravimetry in different atmospheres. Different decomposition profiles are observed at different atmospheres, for the same lubricant, at the same heating rate of 10°Cmin⁻¹, as indicated in Figure 4.

Figure 4. TG curves of the non-degraded mineral base lubricating oils in different: (a) atmospheres; (b) heating rates.

TG results in air atmosphere present three stages: the first one (173 – 351°C) is probably due to the elimination of low molecular weight products, followed by hydrocarbon degradation. This stage is the most important one to determine the thermal stability of the base lubricants. The second mass loss stage (405 – 431°C), as well as the third one (458 – 548°C), are related to decomposition of hydrocarbons of higher molecular weight.

TG results in nitrogen atmosphere present two stages: the first one (171 – 390°C) is probably due to the elimination of low molecular weight products, followed by hydrocarbon degradation and the second mass loss stage (390 – 500°C) is related to decomposition of hydrocarbons of higher molecular weight.

This result corroborates the TG data in an air atmosphere, indicating the occurrence of an oxidation reaction between the lubricant constituents and the oxygen present in the air atmosphere. This reaction may lead to the formation of compounds such as carboxylic acids and ketones, indicated by infrared and NMR spectra. Oxidation may also lead to a polymerization reaction, with formation of higher molecular weight products.

The Table 1 contains the thermogravimetric data of the base mineral lubricating oils. It may be observed that, for short degradation times, the higher the thermal degradation temperature, the lower the onset decomposition temperature, indicating that the samples became less stable.

Table 1. TG/DTG data of mineral base lubricating oils

Conditions	1 st stage			2 nd stage			3 rd stage		
	T _i (°C)	T _p (°C)	Δm (%)	T _i (°C)	T _p (°C)	Δm (%)	T _i (°C)	T _p (°C)	Δm (%)
5°C/min – Air	161	297	85.5	342	398	6.4	450	493	8.5
10°C/min – Air	173	318	90.2	407	422	1.7	458	516	9.0
10°C/min – N ₂	179	331	94.5	396	435	4.9	—	—	—
15°C/min – Air	181	329	86.5	456	537	12.5	—	—	—
20°C/min – Air	188	346	90.8	437	543	9.1	—	—	—

T_i = Initial Temperature; T_p = Peak Temperature; Δm = Mass Loss

DSC curves (Figure 5), in air atmosphere, indicate two highly exothermic peaks, with temperatures of 320 and 519°C and a degradation onset temperature of 212°C. In nitrogen atmosphere, two endothermic peaks are observed at 333 and 440°C. These results indicate the occurrence of oxidation reactions. According to Lehrle et al. (2002), evaporation occurs below 250°C.

Figure 5. DSC curves of non-degraded mineral base lubricants under different (a) atmospheres and (b) heating rates

The Table 2 contains the calorimetric data of the base mineral lubricating oils. Transitions are probably related to oxidation and combustion processes. It may also be observed that the increase in degradation time leads to an enlargement and consequently, an increase in the area of the thermal decomposition peaks.

Table 2. DSC data of mineral base lubricating oils

Conditions	1 st stage			2 nd stage			3 rd stage		
	T _i (°C)	T _p (°C)	ΔH (J/g)	T _i (°C)	T _p (°C)	ΔH (J/g)	T _i (°C)	T _p (°C)	ΔH (J/g)
5°C/min – Air	212	303	2236	381	385	18.6	444	494	734.4
10°C/min – Air	212	321	2809	425	519	1474	—	—	—
10°C/min – N ₂	253	334	173	399	440	41.7	—	—	—
15°C/min – Air	230	329	2686	467	541	937	—	—	—
20°C/min – Air	233	345	3041	461	549	1075	—	—	—

T_i = Initial temperature; T_p = Peak temperature; ΔH = Decomposition enthalpy

4. Conclusions

The thermal, spectroscopic and rheological results indicate that thermal treatment leads to a degradation of mineral base lubricating oil samples, being observed an increase in the viscosity. These characteristics may be due to oxidation processes, with the formation of high molecular weight products, which become insoluble. Fluorescence, infrared and NMR results indicate oxidation reactions.

Thermogravimetric curves indicate the thermal stability of lubricating oils below 161 °C. Thermogravimetric curves in air present three decomposition stages, whereas in a nitrogen atmosphere, only two decomposition stages are observed. DSC analyses in air atmosphere, indicate two highly exothermic peaks, related to hydrocarbon oxidation and combustion processes, while in nitrogen atmosphere, only two endothermic decomposition stages are observed.

The results obtained in this work for the selected mineral base lubricating oil samples provide convincing evidence that the simultaneous utilization of TG/DTG/DSC is an easy measurement technique of the lubricant degradation.

5. References

- BOWMAN, W. F., STACHOWIAK, G. W. Application of sealed capsule differential scanning calorimetry - Part II: assessing the performance of antioxidants and base oils. *Lubr. Eng.*, v. 55, n. 5, p. 22-29, 1999.
- GANLIM, C. D., DUTTA, N. K., ROY CHOUDHURY, N., KEHOE, D., MATISONS, J. Evaluation of kinetic parameters of thermal oxidative decomposition of base oils by conventional, isothermal and modulated TGA, and pressure DSC. *Thermochim. Acta*, v. 392, p. 357-369, 2002.
- KAUFFMAN, R.E., FENG, A. S., KARASEK, K. R. Degradation mechanism of turbine engine oils. *Tribol. T.*, v. 43, n. 4, p. 677-702, 2000.
- KOK, M. V., KESKIN, C. Comparative combustion kinetics for in situ combustion process. *Thermochim. Acta*, v. 369, p. 143-147, 2001.
- LEHRLE, R. S., DUNCAN, R., Liu, Y., PARSONS, I. W., ROLLINSON, M., LAMB, G., BARR, D. Mass spectrometric methods for assessing the thermal stability of liquid polymers and oils: study of some liquid polyisobutylenes used in the production of crankcase oil additives. *J. Anal. Appl. Pyrol.*, v. 64, n. 2, p. 207-227, 2002.
- PAVIA, D. L., LAMPMAN, G. M., KRIZ, G. S. Introduction to Spectroscopy. New York: Harcourt Brace College Publishers. 1997. 510p.
- PEDERSEN, K. S., RONNINGSEN, H. P. Influence of wax inhibitors on wax appearance temperature, pour point, and viscosity of waxy crude oils. *Energ. Fuel.*, v. 17, n. 2, p. 321-328, 2003.
- PEREZ, J. M. Oxidative properties of lubricants using thermal analysis. *Thermochim. Acta*, v. 357, p. 47-56, 2000.
- SANTOS, J. C. O., SOUZA, A. G., SANTOS, I. M. G., SOBRINHO, E. V., CONCEIÇÃO, M. M. Thermodynamic and kinetic parameters on thermal degradation of automotive mineral lubricant oils determined using thermogravimetry. *J. Therm. Anal. Cal.*, v. 79, n. 2, p. 461-467, 2005.
- SILVERSTEIN, R. M., WEBSTER, F. X. Identificação Espectrométrica de Compostos Orgânicos. Tradução de AGUIAR, P. F. 6ª edição. Rio de Janeiro: LTC Editora, 2000, 460p.
- SOUZA, M. S. M. Métodos analíticos para lubrificantes e isolantes. *Quím. Derivados*, v. 382, p. 20-28, 2000.