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Thermoanalytical and Kinetic Study of Lubricating Lithium Greases

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Abstract: The study of thermoanalytical and kinetic properties of lubricating lithium greases is of great importance to understand its behavior when submitted to different temperatures and atmospheres and as those conditions affect its performance. In the present research, thermal analyses and infrared spectroscopy of lubricating greases were accomplished to the lithium base. The lubricating greases were submitted to Thermogravimetry (TG) and Differencial Scanning Calorimetry (DSC) analysis.

Key words: Lithium greases, stability, thermal analysis, TG, DSE, spectroscopy

INTRODUCTION

Lubricating grease can be defined as a solid to semi-solid material produced by the dispersion of a thickening agent in a liquid lubricant. The function of the grease is to keep that oil in contact with bearing surfaces (Nailen, 2002). Most of the thickening agents are derived of organic greases. The treatment of such greases with strong alkali, just as a composed of sodium, lithium or barium, produces a metallic salt of the wax acid-in chemical terms a soap-with the capacity to absorb and to retain liquid inside of a semi-solid matrix.

The applications of the lubricating greases have been growing aligned with the progresses of the technology. At the same time, it has been necessary to improve the acting of the greases for your varied applications. Being varied the soap, oil of addictive, is possible to produce different greases for a wide variety of applications (Czarny, 1995).

The quality control of lubricating oil is essential for preservation of the longevity and performance of industrial machines, automotives and equipment which depends on hydraulic fluids (Borin and Poppi, 2004). Lubricant grease degradation under operation conditions is a problem that involves meaningful economical losses. Oxidation is the primary agent of degradation and has given rise to many studies. Establishing a kinetic mechanism of reaction is difficult due to the complexity of these systems (Santos *et al*., 2004).

In the last years, thermoanalytic techniques have been enough used in the study of the thermal behavior of lubricating greases (Nailen, 2002; Czarny, 1995; Borin and Poppi, 2004). This research aims to study thermal stability of lithium base lubricating greases using different atmospheres through the Thermogravimetry (TG) and Differencial Scanning Calorimetry (DSC).

MATERIALS AND METHODS

Lithium base lubricating greases used in the lubrication of handles, cubes of wheels, pins and movable parts of equipments and machines and produced by Brazilian industries and obtained in the local trade were used in this study.

Thermogravimetric and differential scanning calorimetry curves used in the forecast of the thermal stability of the lithium greases were obtained in a simultaneous thermal analyzer of TA Instruments, model SDT-2670, in atmosphere of air and nitrogen in the reasons of heating of 10°C min^{-1}, in an interval of temperature of 25-700°C.

The theoretical basis for kinetic calculations by non-isothermal methods (integral and approximations) is obtained.

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$$g(\alpha) = \frac{A}{\phi}\int_0^T \exp\left(-\frac{E_a}{RT}\right) dT \qquad (1)$$

where: A is the frequency factor, T is the temperature, R is the gas constant, ϕ is the heating rate and E_a is the activation energy.

Among dynamic methods, differential, integral and approximation ones can be cited, whose studies were carried out in previous studies. In this research we have selected the following methods, representative of different categories and applied several equations to the thermal data: Coats-Redfern and Madhusudanan methods (Santos *et al*., 2002; Straszko *et al*., 2002; Santos *et al*., 2004). The kinetic parameters calculated were activation Energy (E_a) and frequency factor (A).

Coats and Redfern (Santos *et al*., 2004) developed an integral method that can be applied to TG/DTG data, assuming the different reaction orders. The order related to the most appropriate mechanism is presumed to lead to the best linear plot, from which the activation energy is determined. For $n \neq 1$, the equation used for analysis is:

$$\log\left[\frac{1-\ln(1-\alpha)^{1-n}}{T^2}\right] = \log\frac{AR}{\phi} - \frac{E_a}{2.303(RT)} \qquad (2)$$

An other integral method to evaluate a kinetic model was developed by Madhusudanan and others (Santos *et al*., 2005) for estimates the kinetic parameters from TG/DTG curves. The plot of the left side of equations versus the reciprocal of the absolute temperature gives linear curves. E_a and A can be calculated from the slope and intercept, respectively. For $n \neq 1$, the activation energy can be calculated from the following expression:

$$\ln\left[\frac{1-\ln(1-\alpha)}{T^{1.9206}(1-n)}\right] = \ln\frac{AR}{\phi R} + 0.02 - 1.9206\ln\frac{E_a}{R} - 0.12040\frac{E_a}{RT} \qquad (3)$$

RESULTS AND DISCUSSION

Infrared spectroscopy: Infrared spectra are shown in Fig. 1. The spectra showed peaks in the region of 3200-3700 cm^{-1}, related to the presence of OH groups. A strong peak was observed in 2800-3100 cm^{-1}, related to C-H bond in the CH_3 and CH_2 in aliphatic chains. Bands presented in the region between 1300 and 1600 cm^{-1} are characteristic of C = O groups (Silverstein and Webster, 2000). It can be due the presence of compounds as ketones, aldehydes or carboxylic acids.

Thermal analysis: TG and DTG curves of the samples analyzed under different atmospheres are presented in Fig. 2 and 3. The oxidation process of the lubricating greases can be verified when analyzed in atmosphere of air, because It is had significant variations in the amount

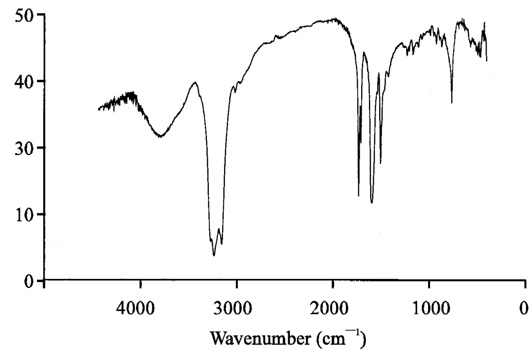

Fig. 1: Infrared spectra of lubricating lithium grease

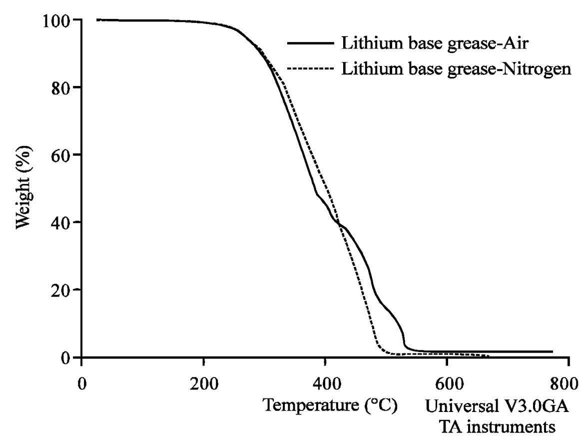

Fig. 2: TG curves of lithium base grease at 10°C min^{-1} in atmospheres of air and nitrogen

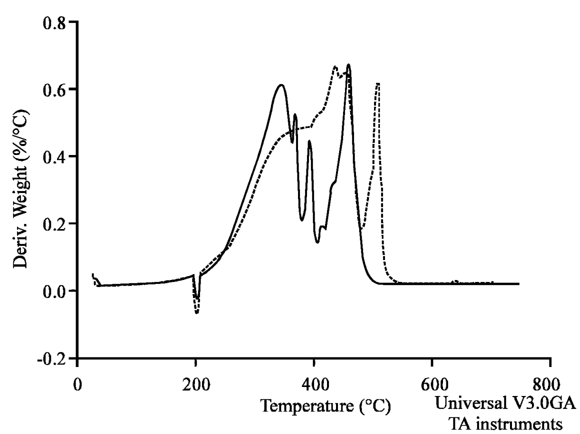

Fig. 3: DTG curves of lithium base grease at 10°C min^{-1} in atmospheres of air and nitrogen

of events associated to the thermal decomposition of the samples. In spite of the variations in the amounts of events, it is verified that the thermal stability do not depends of the atmosphere, because the process begins to 210°C. In nitrogen the decomposition reaction of the grease happens in an only step, varying of 210-500°C, with loss of mass of 98%.

In air atmosphere, the existence of five steps is verified among 210-520°C. The first step (210-350°C) that corresponds to the evaporation of the most volatile components and products of low molecular weight possesses a loss of mass of 45.3%. Second (350-375°C) and third (375-400°C) steps that correspond to the first degradation possess losses of mass of 6.8 and 7.0%, respectively. Fourth step (400-470°C) corresponds to the oxidation under high temperatures and possesses a loss of mass of 24.7%. While the fifth step (480-520°C) that corresponds to the decomposition of high molecular weight compounds possesses a loss of mass of 13.1%.

DSC results show that, in air atmosphere, four exothermic peaks appear in the temperatures of 344.3, 368.2, 391.6 and 504.9°C at heating rate of 10°C min^{-1} (Fig. 4) with initial temperature of 317.9°C. At heating hate of 15°C min^{-1}, Fig. 5 shows four exothermic peaks in the temperatures of 353.1, 419.3, 451.5 and 519.4°C. In atmosphere of nitrogen, there is the appearance of only one exothermic peak in 203.0°C at heating hate of 10°C min^{-1} and one exothermic peak in 201.2°C at heating rate of 15°C min^{-1}, confirming the decomposition in one step as showed in the TG curves (Fig. 2).

The existence of the exothermic peaks can be related to the oxidation processes. That peaks are related to reaction between lithium base grease and oxygen of the air atmosphere, with formation of new compounds like showed infrared spectra.

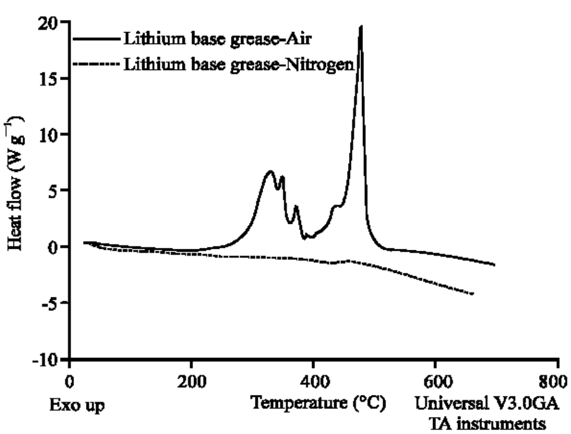

Fig. 4: DSC curves of lithium base grease at 10°C min^{-1} in atmospheres of air and nitrogen

Table 1 presents calorimetric data to lithum base lubricant studied at diffirent reasons of heating (10 and 15°C min^{-1}) in air atmosphere.

Table 2 presents calorimetric data to lithium base lubricant studied at different reasons of heating (10 and 15°C min^{-1}) in atmosphere of nitrogen.

Kinetic analysis: Table 3 shows kinetic parameters (activation energy and frequency factor) and statistic parameters (correlation coefficient and standard deviation) of the first thermal decomposition step of the lubricating lithium grease, using Coats-Redfern and Madhusudanan methods.

It is observe that in atmosphere of nitrogen the activation energy is higher than in air atmosphere. This fact confirm that in nitrogen atmosphere greases present more stability than in air atmosphere, in that occur oxidative reactions with oxygen in the air.

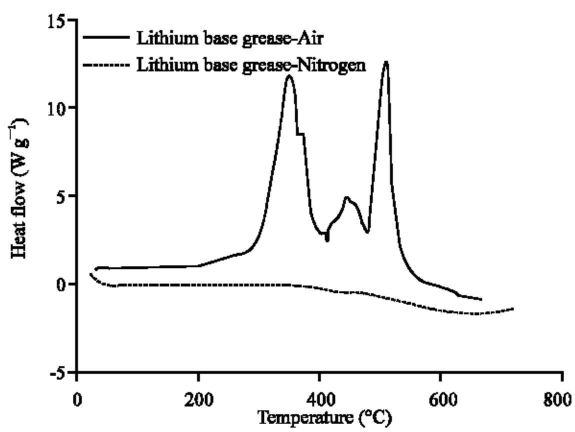

Fig. 5: DSC curves of lithium base grease at 15°C min^{-1} in atmospheres of air and nitrogen

Table 1: Calorimetric data to lithium base lubricant in different reasons of heating

	Air atmosphere			
	T_{peak} (°C)		ΔH* (J g^{-1})	
Steps	10°C min^{-1}	15°C min^{-1}	10°C min^{-1}	15°Cmin^{-1}
1	344.3	353.1	421.2	713.0
2	368.2	419.3	78.06	6.8
3	391.6	451.5	122.90	22.9
4	504.9	519.4	3565.0	1002.0

*ΔH corresponds to the enthalpy

Table 2: Calorimetric data to lithium base lubricant in different reasons of heating

	Nitrogen atmosphere			
	T_{peak} (°C)		ΔH* (J g^{-1})	
Steps	10°C min^{-1}	15°C min^{-1}	10°C min^{-1}	15°C min^{-}
1	203.0	201.2	3.177	2.123

*ΔH corresponds to the enthalpy

Table 3: Influence of heating rate on the kinetic parameters

	Heating rate (°C min^{-1})			
	Coats-Redfern		Madhusudanan	
Parameters	10-air	15-air	10-air	15-air
E_a/KJ mol^{-1}	72.47	75.26	72.77	76.94
A s^{-1}	$5.063{\cdot}10^3$	$1.10{\cdot}10^4$	$5.98{\cdot}10^3$	$1.77{\cdot}10^4$
r	0.9997	0.9998	0.9997	0.9999
sd	0.0074	0.0052	0.0175	0.0052

CONCLUSION

Thermal and oxidative stability of lubricating lithium greases has been studied. Infrared spectroscopy showed the presence of OH and C = O groups, related to compounds as ketones, aldehydes or carboxylic acids. Thermogravimetric curves showed that, in atmosphere of nitrogen, the decomposition of the lithium grease occurs in only a stage. The appearance of new decomposition stages when the grease is exposed to the atmosphere of air it confirms that, in that case, there is reaction of the components of the grease. Calorimetric evaluation indicates that, in atmosphere of synthetic air, appear four exothermic picks, probably related to the oxidation of the grease. Kinetic parameters confirm lower stability of the lubricating greases in air atmosphere, probably due oxidation reactions.

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