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OXIDATIVE STABILITY OF LUBRICANTS FOR DRY CIRCUIT SLIDING CONTACTS

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The thin film oxidation resistance of isoparaffin and two polyol esters synthetic lubricants was studied by high pressure differential scanning calorimetry. The oxidation induction time of each lubricant was measured by isothermally heating the sample in an oxygen environment. Arrhenius plots were constructed to predict the service life of the lubricant at low temperatures. The results indicate that polyol esters exhibit better oxidative stability than isoparaffins.

Lubricants in electronic computer applications involving dry-circuit, sliding contacts, are used to lower friction and reduce wear [1]. In addition, they have to inhibit corrosion and exhibit adequate resistance to oxidation and thermal decomposition. Unfortunately, the need for special lubricants is sometimes overlooked when modifying the connector material or utilizing such connectors in more severe environments with increased thermal exposure and more demanding systems operating conditions. Recent trends indicate that future electronic systems will operate in an environment with much higher temperature than the current systems. Therefore, understanding of the oxidative stability of lubricants at relatively high temperatures, 65–110°, is of great importance.

Clearly, one of the most important requirements of a lubricant is that its properties do not undergo appreciable changes during use. While some changes during operation result from contamination and evaporation most of them can be attributed to molecular changes resulting primarily from oxidation of the lubricant [2]. The exact composition of the oxidation by-products of lubricants independent of their class is unknown, because of the chemical complexity of the oils [3]. It is generally believed that the first reaction produts are organic peroxides, which are known to be corrosive to various metals [3]. During the oxidation process high molecular weight oil-insoluble polymers settle out of the oil as deposits and appear as varnish-like films [5–6]. Such reactions may be accelerated by the presence of certain active metal ions, heat or light. Therefore, antioxidants or stabilizers are

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used to prevent, or at least inhibit the deterioration of physical properties during the oxidation, thus improving the life expectancy of lubricants [7]. The antioxidants are effective until they are consumed in the oxidation process. Upon their depletion the oxidation reactions start to take over in an uncontrolled manner.

Walker and Tsang have used high pressure differential scanning calorimetry (HPDSC) to measure the oxidative stability of formulated, virgin and recycled lubricating oils [8]. Their study suggests that the onset of the oxidative process and the exothermic reactions during oxidation can be detected by differential scanning calorimetry (DSC). This method involves the rapid scanning of the sample's temperature to a preset value in an oxygen atmosphere and the measurement of the oxidation induction time. This time has been used as a measure of oxidative stability and it is defined as the duration of time to the onset of oxidative degradation as indicated by an exothermic reaction.

In this study, the oxidative stability of synthetic isoparaffins and polyol ester type lubricants is examined. These synthetic lubricating fluids have been used with top and side-entry, bifurcated contacts made of precious metal inlay. HPDSC in an isothermal or dynamic mode was used to measure the oxidative induction time and temperature to determine the ability of these fluids to resist oxidation and thermal decomposition.

Experimental

The samples investigated in this study were hydrocarbon based lubricant H–1, and two polyol esters E–1 and E–2. Both types of lubricants are commercially available. The oxidative stability and oxidation temperature were determined for each sample using a DuPont model 1090 thermal analyzer attached to a high pressure 910 DSC module. The DSC was calibrated with indium and lead standards. Sample weights of 1–2 mg were placed in hermetic aluminium pans with holes on top. Small weights were used to simulate the thin film conditions experienced in the actual connector coating process. Several isothermal and dynamic DSC scans were obtained for each lubricant at different isothermal temperatures keeping the O_2 pressure constant at 100 Psi and under different O_2 pressure, respectively. For all dynamic DSC scans the heating rate was 20 deg/min. The equilibration time necessary for obtaining the isothermal temperature ranged from 1.5–2 minutes and was not subtracted from the measured oxidation induction times. The DSC cell was purged with oxygen for five minutes at the beginning of each scan. The time needed to reach the extrapolated onset of the oxidation exotherm was used as the measure of the lubricant stability. The temperature where oxidation starts to take place is reported as the oxidation temperature.

Results and discussion

Figure 1 represents typical isothermal and dynamic DSC traces obtained from the polyol ester E–1. The induction time or the oxidative stability is deduced from the isothermal DSC scan while the oxidation temperature at a specified O_2 pressure is obtained from the dynamic DSC scan as shown in the figure.

Figures 2, 3 and 4 show the oxidative stability of the lubricants under study at several isothermal temperatures. It is noted that polyol ester based lubricants

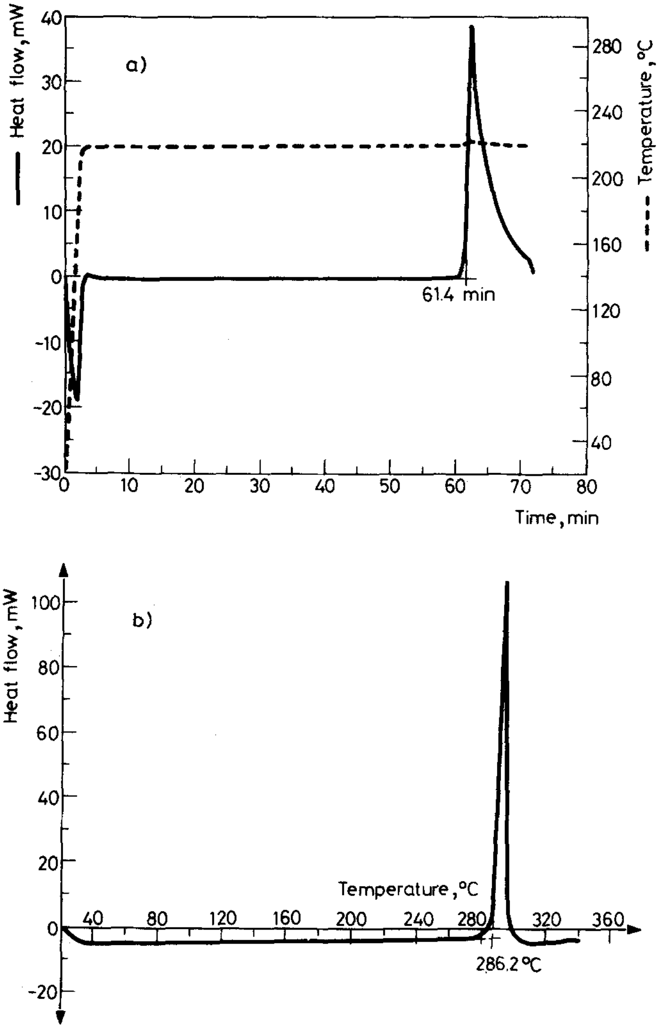

Fig. 1 Typical HPDSC a) isothermal and b) dynamic scans obtained for E–1 lubricant

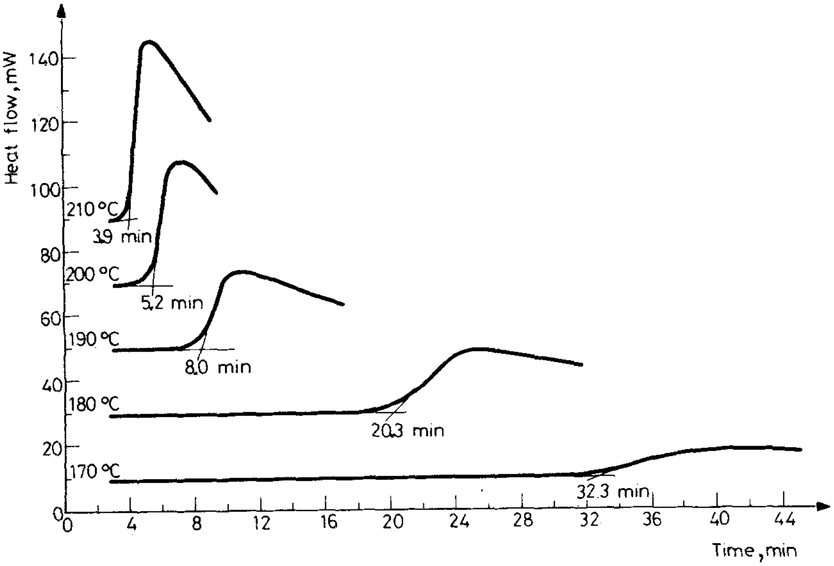

Fig. 2 Isothermal HPDSC scans obtained for H-1 lubricant at different temperatures and 100 psig oxygen pressure

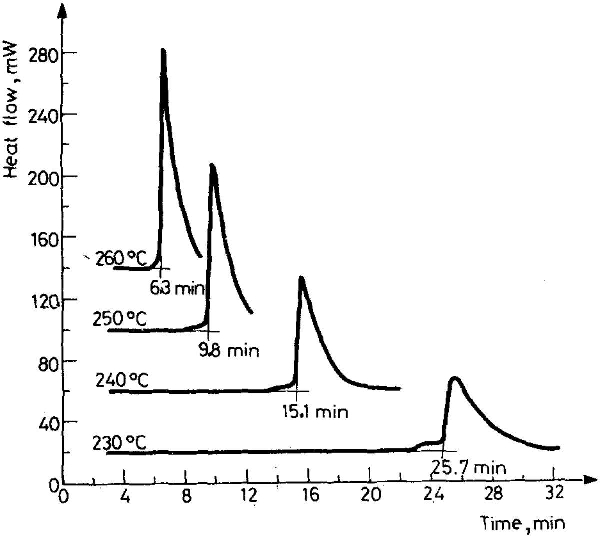

Fig. 3 Isothermal HPDSC scans obtained for E-1 lubricant at different temperatures and 100 psig oxygen pressure

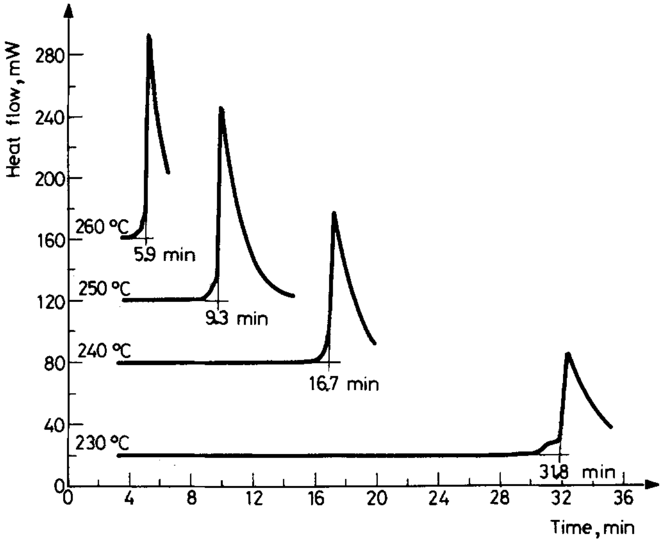

Fig. 4 Isothermal HPDSC scans obtained for E-2 lubricant at different temperatures and 100 psig oxygen pressure

exhibit a better thermal stability than hydrocarbon based ones at the same O_2 pressure. This could be attributed to the differences in formulation i.e. the types of base stock as well as antioxidants used in each lubricant. Notice that there is not significant differences between the two lubricants which are polyol ester based oils. The isoparaffin H–1 used in this study is uninhibited type lubricant.

The above results can be plotted to reflect the dependence of the induction time on the isothermal temperature as shown in Fig. 5. Figure 5 indicates that the induction time exhibit an exponential dependence on temperature. The relationship can be described by

$$t_{\mathrm{ind}}(T) = t_{\mathrm{ind}}(T_{\mathrm{ox}}) \exp\left[E_a/R(1/T - 1/T_{\mathrm{ox}})\right]$$

t_{ind} is the induction time and it represents the life expectancy of the lubricant at temperature T. t_{ind} is obtained from the DSC isothermal scan at temperature T. T_{ox} is the oxidation temperature as obtained from the dynamic DSC scan at a preset oxygen pressure. E_a is the activation energy for the oxidation process and it is calculated from the slope of the line in Fig. 5. The induction time at the T_{ox}, $t_{\mathrm{ind}}(T_{\mathrm{ox}})$ is deduced from the interception obtained from the Arrhenius plot. The simplicity of determining the oxidation temperature from a dynamic DSC scan and $t_{\mathrm{ind}}(T_{\mathrm{ox}})$ from the interception of the Arrhenius plot makes this choice of parameters attractive. Although T_{ox} would depend on the heating rate, the predicted life time deduced from the above equation would not. Notice that any change in the value of

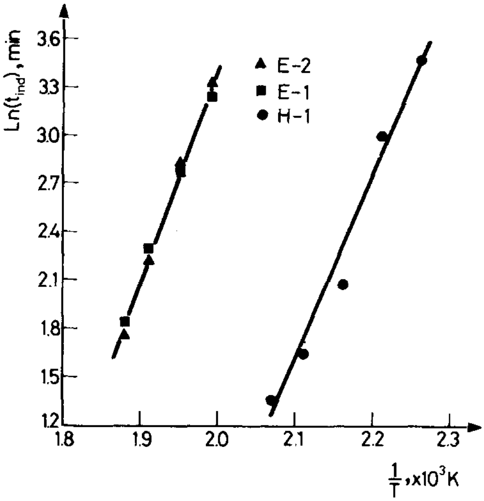

Fig. 5 An Arrhenius plot of the induction time versus reciprocal temperature

$t_{ind}(T_{ox})$ because the $t_{ind}(T_{ox}) * \exp[-E_a/RT_{ox}]$ should be constant and equal to the interception obtained from the Arrhenius plot.

The oxidation temperature and its dependence on the O_2 pressure can be deduced from the dynamic DSC scans obtained at several O_2 pressures. Figure 6 shows a typical set of dynamic DSC scans obtained for the isoparaffin based lubricant. It is

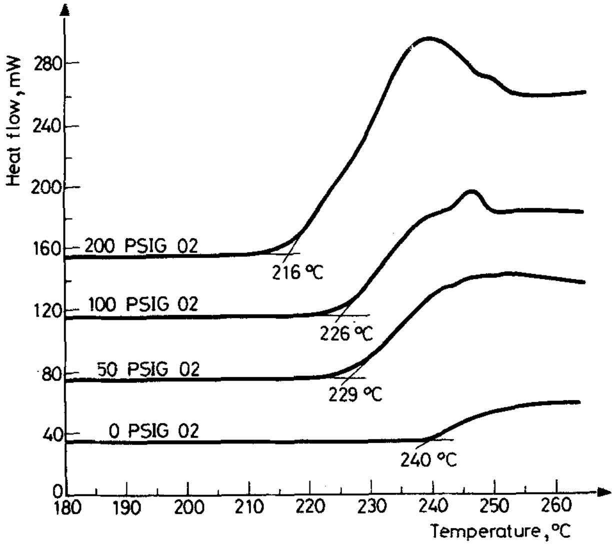

Fig. 6 Dynamic HPDSC scans obtained for H-1 lubricant at different oxygen pressures

noted that the oxidation temperature decreases as the O_2 pressure increases. Furthermore, it is observed that the oxidation process is highly exothermic and the shape of the exotherm changes with oxygen pressure. Higher oxygen pressures produce a better definition of the exothermic peak where as the peaks at ambient pressures tend to be very broad.

Table 1 Results obtained from Fig. 5 and dynamic DSC scans at 100 psi oxygen pressure

Lubricant type	T_{ox}, °C	E_a, kJ/mol	$t_{ind}(T_{ox})$
H-1	226	97	1.6
E-1	283	114	2.0
E-2	283	112	2.0

Table 1 summarizes the results obtained from Fig. 5 and the DSC dynamic scans at 100 Psi oxygen pressure. Notice that the activation energy and induction time at T_{ox} for the hydrocarbon and polyol ester based lubricants are different, however, they are approximately identical for the polyol ester based lubricants. These findings support the fact that polyol ester type oils are less susceptible to free radical attack than hydrocarbon based oils.

Figure 7 shows a plot of the oxidation temperature as a function of O_2 pressure for the different lubricants studied here. All lubricants exhibit a linear relationship

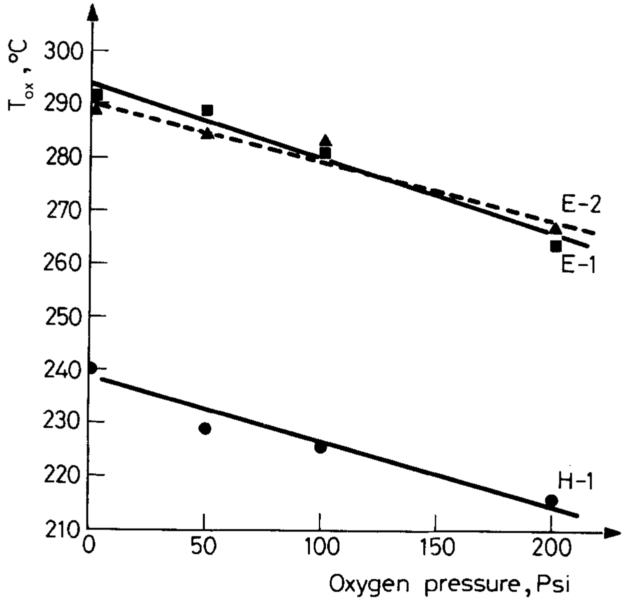

Fig. 7 A plot of the oxidation temperature as a function of the oxygen pressure for the lubricants studied here

with nearly identical slopes except that the hydrocarbon based lubricant exhibits lower oxidation temperature than polyol ester ones. The decrease in oxidation temperature with increasing oxygen pressure could be attributed to the increase in the average kinetic energy of the oxygen molecule due to the increase in the number of molecules at the high energy tail of the Boltzman distribution. This increase in the average kinetic energy would lead to higher rate of collision resulting in an increase in the rate of oxidation and a decrease in the oxidation temperature. Also, this increase in the average kinetic energy could lead to an increase in the gas diffusivity thus increasing the bulk degradation and again resulting in a decrease in the oxidation temperature.

Although the above studies revealed that both types of lubricants exhibit thermal stability at temperatures higher than 170°, oxidative reactions may occur with appreciable rates at temperatures of 65–110°. In reality, the metal corrosion products produced during the oxidative processes may act as catalysts to speed up the oxidation reaction. These products also appear to promote the production of oil-insoluble species and varnish-like film which can completely insulate the contact and as a result induce contact resistance failures. In this sense, the thermal stability of the lubricant is also affected by the environment.

Visual examination of the oil samples after the DSC analysis indicated that the lubricants degraded forming dark colored films with increased viscosity and a varnish-like appearance. This process involves both degradation and polymerization of the lubricants at the test temperatures.

Conclusions

HPDSC has been a very useful technique for the study of lubricant oxidation. The method can be used as a comparative technique for screening lubricants applicable in dry circuit sliding contacts. Results obtained using this method demonstrate that the polyol esters based lubricants E–1 and E–2 offer higher oxidation resistance compared to the synthetic isoparaffins. Further studies related to the oxidative breakdown of such lubricants can be useful in the compounding and optimization of the lubricant base stocks and their additive packages.

An understanding of the kinetics of the reaction mechanism is needed in order to predict the behaviour of such lubricants in the actual working environments. In fact, the ability of these fluids to inhibit corrosion under steady state and accelerated thermal cycling environments is presently under study.

References

1 R. V. Steenstrup, V. M. Fiacco and L. K. Schultz, Proceedings of the Twenty–Eighth Annual Holm Conference on Electrical Contacts, 1982 p 59–68.

2 J. P. Coates and L. C. Setti, ASLE Trans., 29 (3) (1985) 394.

3 J. R. Barcelo and C. Otero, J. Inst. Pet., 50 (1964) 15.

4 A. Zeman, R. Stuwe and K. Koch, Thermochim. Acta, 80 (1984) 1.

5 E. Dimiroff, J. V. Moffitt and R. D. Quillian, ASME Trans., J. Lubr. Techn., (1969) 406.

6 D. T. Rogers, W. W., Rice and F. L. Jonach, SAE Trans., 64 (1956) 782.

7 J. F. Ford, J. Inst. Pet., 54 (1967) 198.

8 J. A. WAlker and W. Tsang, Nat. Bur. Stand. (U.S.), Spec. Publ., 584 (1980) 271.

Zusammenfassung — Mittels Hochdruck-Differential-Scanning-Kalorimetrie wurde die Dünnschicht-Oxydationswiderstandsfestigkeit von Isoparaffin- und zwei synthetischen Polyolesterschmiermitteln untersucht. Die Oxydationsinduktionszeit jedes Schmiermittels wurde durch isothermes Erhitzen der Probe in Sauerstoff gemessen. Zur Vorhersage der Lebensdauer der Schmiermittel bei niedrigen Temperaturen wurden die entsprechenden Arrhenius-Diagramme erstellt. Die Ergebnisse zeigen, dass Polyolester über eine bessere oxydative Stabilität verfügen als Isoparaffine.

Резюме — Методом дифференциальной сканирующей калориметрии высокого давления изучена устойчивость к окислению тонких пленок изопарафина и двух сложных эфиров полиспирта, как синтетических смазок. Индукционное время окисления каждой смазки было измерено путем изотермического нагрева образца в атмосфере кислорода. Для установления срока службы каждой смазки при низких температурах были построены аррениусовские графики. Результаты показали, что сложные эфиры полиспиртов более устойчивы и окислению, чем изопарафины.