Journal of Thermal Analysis and Calorimetry, Vol. 55 (1999) 109-114

DEPENDENCE OF THERMAL STABILITY OF AN ENGINE LUBRICATING OIL ON USAGE PERIOD

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(Received October 23, 1997; in revised form March 27, 1998)

Abstract

Mineral oil type lubricating oils have an important role in reducing engine wear. But after some period, depending on the oil quality, oil replacement is needed since the oil loses its properties. In this paper, an engine oil was tested in a 1300 cc engine car and the change of the thermal stability of the collected portions of oil at different usage periods were experimented by TG/DTG and DSC techniques. Results show that, as usage period increases lubricating oil contains more of the light components that distill at low temperatures. The increase in the peak maximum temperature, T_{max}, of the DTG, as usage period increases, proposes that the molecular mass of the oil increase, which presumably changes the viscosity characteristics. Moreover as the usage period increases some residue type components, which only can be destroyed at very high temperatures, are produced in oil phase.

Keywords: differential scanning calorimeter, mineral oil, thermogravimetry

Introduction

Mineral-based lubricating oils used in car engines have an important role in reducing engine wear due to the movement of pistons by lubricating the moving parts. Thus durability of the oil becomes very important especially at high engine temperatures. But it is well known that after some period the oil loses its lubrication property. After that period if the oil is not changed with a fresh one, the extent of engine wears, particularly at heavy operating conditions and engine temperatures where the stability of oil towards high temperature changes.

The process of thermal degradation of engine lubricants proceeds by two mechanisms, namely oxidation and thermal decomposition. Engine lubricating mineral oils are very complex in nature because of the presence of a large variety of molecular types, and functional groups. This complex structure makes the oxidation reactions extremely complex and hard to understand. It is commonly accepted that oxidation proceeds via hydroperoxide radical mechanism. On the

1418–2874/99/ $ 5.00

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other hand thermal decomposition proceeds through C–C chain scission [1, 2]. As the degradation reactions proceed to higher conversion under the influence of increasing heat, oil insoluble products such as sludge, and residue type, oil insoluble products begin to appear. It is suggested that high molecular mass reaction products formed during degradation play a control role in oil insoluble product formation, affecting the lubricant life.

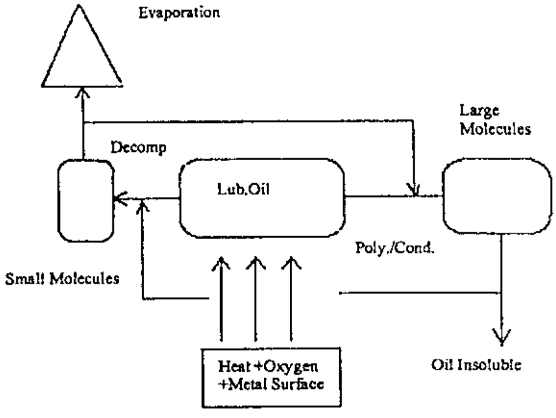

Fig. 1 Generalized degradation mechanism for engine lubricants

The generalized degradation mechanism for engine lubricants [3] is shown in Fig. 1. If oxygen is readily available in the fluid and in the engine system, which is normally not severe, molecules will begin to oxidize, because of lower activation energy requirement for oxidation. If there is a lack of oxygen in the system, thermal decomposition (pyrolysis) occurs. This reaction produces lighter reaction products, which are subject to volatilization easily, and heavy reaction products are formed via polymerization and condensation reactions. These heavy products usually constitute an insoluble fraction [4, 5] and decrease the life span of the mineral oil.

The lubricant circulating system of car engines are almost closed systems and the pumped oil circulated the hot surfaces and the effect of oxidation reactions can be expected to be at limited extent compared to thermal decomposition. And, thus, the time period during which the lubricant is exposed to hot surfaces should have an effect on the thermal stability of mineral oil. This stability, in turn, reflects the change in the composition and molecular structure of the used lubricating mineral oil. Determination of the thermal stability of a mineral oil during usage would provide a basis for mechanistic understanding and comparison, which could aid product development and consistency monitoring. Wesolowski [6] applied principal component analysis for thermal decomposition curves for the assessment of service performance of lubricating oils. The results indicate that principal component analysis greatly assisted the analysis of quality of lubricating oils by DTG.

During the course of this study, oil samples used during different periods were collected and analyzed by TG/DTG and DSC. Changes in the thermal stability, which can reflect changes in the composition and shifts in main transition temperatures, were investigated.

Experimental

A SAE 20W/50-viscosity engine oil were tested in a 1300 cm^3 engine car with real road and loading conditions. Oil samples from the engine were collected at 1800, 2300 and 3600 km usage periods. The new oil sample as well as the used ones were experimented under pyrolysis conditions with DuPont 951 TG/DTG and 910 DSC equipment's. DSC monitors differential heat flow of the samples whereas TG/DTG has the capability of measuring the mass loss either as a function of temperature or time in a varied but controlled atmosphere. Prior to experiments DSC system was calibrated for temperature readings using indium as reference standard. The TG/DTG system was also calibrated for temperature readings with calcium oxalate monohydrate. It was also essential to calibrate the balance for buoyancy effects for the quantitative estimation of mass changes. The material chosen for the investigation of such effects was silver. The experimental procedure involves placing 10 mg of sample in a pan, setting the heating rate and flow rate of the purge gas (nitrogen), then commencing the experiment. All experiments were performed at a linear heating rate of 10°C min^{-1} over the temperature range 20–600°C with a nitrogen flow of 50 ml min^{-1}. In order to assess the reproducibility, experiments were performed twice.

Results and discussion

In this study, a commercial SAE 20W/50 engine lubricating oil was collected after 1800, 2300 and 3600 km when the engine oil is changed with the unused one. The oil samples as well as the unused one was tested with TG/DTG and DSC techniques under nitrogen atmosphere. Mass loss curves of the oils with respect to temperature is shown in Fig. 2. In this plot, it is seen that at lower temperatures, till the major mass loss starts, the unused lubricating oil is more stable and shows almost no mass loss. But the used oils start to loose mass from low temperatures. This indicates that at lower temperatures, unused oil is more stable towards heat effect. This fact may be explained as the presence of lighter, readily vaporizable components in the used oil. These compounds are probably produced from the larger molecules during the heating cycles of the engine and retained in the oil phase. Some oxidation of the lubricant in the engine may also accelerate this process. Since oxidation has a lower activation energy requirement, oxidative decomposition accelerates the decomposition rate, breaking the lubricant molecules into smaller molecules which have lower boiling temperatures, which makes the lubricant unstable at lower temperatures.

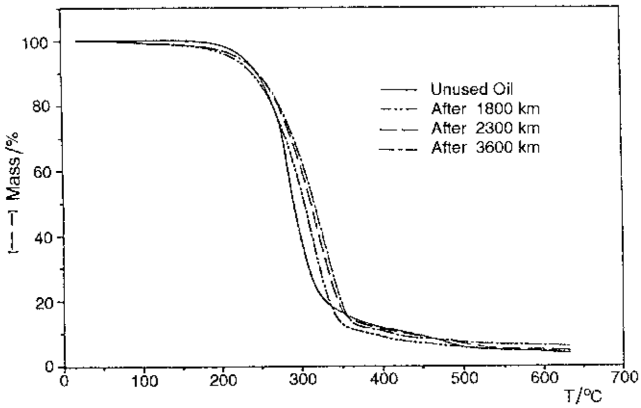

Fig. 2 TG curves of the unused and used engine lubricating oils

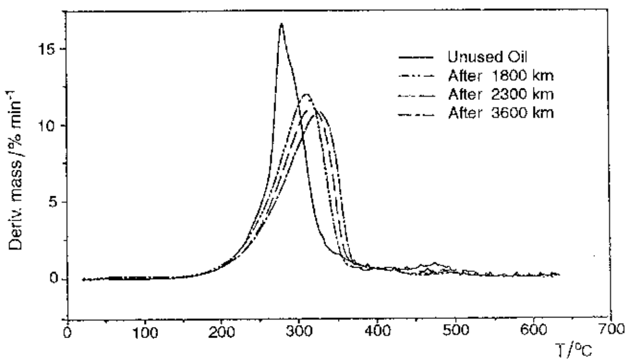

Fig. 3 DTG curves of the unused and used engine lubricating oils

As the reaction sequence proceeds in TG under nitrogen atmosphere, the region of main vaporization is reached. In Fig. 2, this region is between 260–370°C. The unused oil in this main decomposition region shows faster mass loss, the used oil shows slower mass loss as usage period increases. This may be due to the fact that the unused oil contains undegraded large molecules, which are prone to break and vaporize in this temperature interval. But as the usage period in engine increases, these large molecules loses some of their chains and lower molecular mass components is produced whose effect is seen as evaporation. Since large molecules lose their mostly unstable and degradable bonds they become more resistant towards thermal effect. So in main vaporization region, as usage period of engine oil increases, mass loss rate decreases. DTG curves

(Fig. 3) supports this discussion. In this plot the mass loss rate of unused oil is more rapid (a steeper curve) and maximum decomposition rate occurs at lower temperatures. As usage period increases the maximum mass loss rate decreases and the temperature at which maximum decomposition occur shifts to higher temperatures. This is due to the existence of more stable and strong molecules in the used oils. The temperatures at which the maximum decomposition rate occurs and the value of this rate are given in Table 1. The increase in the T_{max} with the usage period, also an indication of increase in the molecular mass of the oil as explained by Kopsch [7]. The increase in vaporization onset temperature given in Table 1 can also be due to the increase in molecular weight of the oil.

Table 1 Vaporization onset temperature and T_{max} values (°C)

Sample	$T_{vapori. onset}$/°C	T_{max}/°C	Mass loss/% min^{-1}
Unused oil	205	282.4	16.54
1800 km	220	312.5	11.97
2300 km	230	321.4	11.03
3600 km	238	328.1	10.78

DSC analysis (Fig. 4) of the lubricating oils also shows the change of structure of molecules as usage period increases. In this analysis between 400–600°C range, behavior of oils towards heat shows a starting hump as usage period increases. This region is where the pyrolysis decomposition of large and strong molecules (cracking) occurs. In this region the behavior of unused oil is placid, with no definite reaction humps. This is an indication of most of the unused oil molecules are lost in vaporization and there is not much molecules to be cracked. But as usage increases, a humping trace starts to develop. This hump development is the cracking of large molecules formed during the working period of the

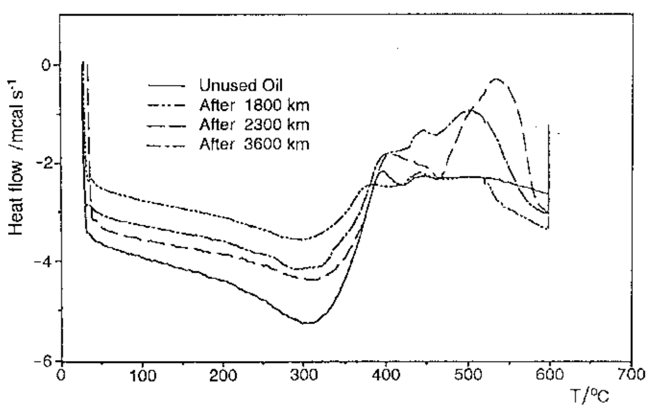

Fig. 4 DSC curves of the unused and used engine lubricating oils

oil. Since aromatic structures are more prone to cracking reaction, it can be concluded that there is an increase in the polymerization/condensation reactions with increasing working hours of the oil. This reaction also increases the molecular mass of the oil as concluded from TG/DTG curves. This is a direct evidence of the molecular change, thus the stability of molecular structure, of the oil with usage period.

Conclusions

TG/DTG and DSC are useful techniques to study the change of thermal stability and molecular change of lubricating oils during usage. In this study, it was concluded that the oil used in engines at different periods are unstable at low temperatures due to the increased amount of lower molecular mass components because of the combined effects of oxidation in the engine and heating effects during working times. But at higher temperatures, the rate of mass loss is slower as usage period increases. This is due to the stabilizing of large molecules, as unstable bonds have been broken away during the working period in the engine and the molecular mass of the oil increases. Also possible aromatization is observed in DSC experiments in long term used oils, as inferred from the behavior of DSC curve in cracking region. Such a study may particularly be important during the engine lubricating oil production and when the change of oil properties towards thermal effect at high engine temperatures and heavy operating conditions are under consideration.

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