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THERMOANALYTICAL INVESTIGATION OF THE INTERACTION OF PHOSPHATE-BASED CUTTING FLUIDS WITH AN IRON SURFACE

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ABSTRACT

The interaction of two phosphate-based cutting fluids, the water based Anion 37 and the non-aqueous Nonion 100, with iron powder was investigated thermoanalytically. The atmosphere was air or nitrogen. For comparison, the thermochemical behaviour of the two cutting fluids in the presence of α-Al_2O_3 powder was also studied. In the presence of Fe a weight loss was detected in the region of 630–820°C and 670–830°C which was not found with α-Al_2O_3. This indicates the formation of a compound between Fe and the cutting fluids. Compound formation was also supported by the slowing down of the oxidation of Fe in the presence of the cutting fluids and by the smaller weight loss due to decomposition measured in the presence of Fe.

INTRODUCTION

Tribology is a rather young technical science dealing with the phenomena of friction, wear and lubrication. Several excellent reviews are available [1,2]. One most important aspect of current work done in the field of tribology involves studies of chemical reactions occurring under conditions of boundary lubrication. Such tribochemical reactions are initiated by the input of a mechanically induced temperature rise at points of contact between mating surfaces of, for example, tool and work-piece in a metal working operation [3]. Reactions occurring depend on the nature of additive chemistry in lubricants used, as well as on the chemical and mechanical characteristics of the surface material. Parameters of importance have been extensively studied using a great number of techniques [4,5].

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Additives in lubricants functioning as anti-weld reactants are usually called extreme pressure or anti-wear agents and may include chemicals of many different types. Typical additives involve organic molecules which have incorporated in their structure the elements phosphorus, sulphur or chlorine [6,7].

Most works to date have dealt with reaction mechanisms and performance of additives in mineral oil based lubricants. The present paper describes some preliminary experimental work aiming at studies of the thermochemistry of extreme pressure additives in water based synthetic lubricants using thermoanalytical technique.

Most work has been carried out on fluids containing sulphur in addition to phosphorus. Barcroft et al. [7] used the hot wire technique combined with SEM–EDX to study the decomposition of Zn thiophosphates. Amorphous deposits of the same type were obtained at 200–600 °C, not only on Fe, but also on non-interactive metals, such as Pt and Au. Faut and Wheeler [8] studied lubrication with TCP (tricresylphosphate) in air and in nitrogen. Above 200 °C a decrease of friction coefficient was observed at a characteristic temperature which, according to the authors, could be associable with phosphate formation on the Fe surface. However, for specimens preheated in an inert (nitrogen) atmosphere this effect did not show up.

DTA and DSC, using autoclave crucibles, have been employed [9–11], and for S-containing additives the DTA peak pattern could be correlated to their wear properties [11].

Oxidative degradation of phosphate esters was investigated by Cho and Claus [12]. Up to 250 °C they were found to be relatively unsusceptible to oxidation. Depending on the structure, the starting temperature for oxidation was 225–275 °C (cf. [7]).

In the present work, the possibility of using thermogravimetry for investigating the reaction of pure phosphate-based fluids with an Fe surface has been examined at atmospheric pressure (unlike the conditions in [9–11]). A comparative experimental scheme has been employed in order to gain more knowledge about the effect of substrate and of the atmosphere on the behaviour of the reaction products formed.

EXPERIMENTAL

The investigation involved comparative studies of the influence of substrate (“active”, Fe surface; “passive”, α-Al_2O_3 surface) and atmosphere (oxidizing, inert) on the thermal behaviour of two types of cutting fluids denoted Nonion 100 and Anion 37 (the first being a pure organic liquid and the second a 37% solution in water).

The measurements were made using a universal microthermobalance (Mettler TA1), capable of simultaneous recording of TG, DTG and DTA curves. The specimens, consisting of Fe (H_2-reduced quality) or α-Al_2O_3 powder (30–84 mg), mixed with the respective fluid (3–14 mg) were heated in open Pt (Al_2O_3) crucibles at a linear rate of 4–8°C/min to 500–1000°C. Blank tests were also made with Fe powder alone and Fe powder soaked with water instead of the cutting fluids. The characteristic parameters of the runs were the following: TGA–DTG–DTA ranges used; 10/100 mg (sensitivity: 0.05 mg)–20/50 mg min^{-1}–50/100 μV; temperature control, $\pm$ 1°C; reference substance, Al_2O_3; gases used, flowing air, nitrogen (oxygen content < 10 ppm); gas flow rate, 4.5 l h^{-1}.

X-ray diffractometry was used to identify the possible reaction products.

RESULTS AND DISCUSSION

The thermochemical characteristics of the fluids Anion 37 and Nonion 100 are summarized in Tables 1 and 2, respectively. The last column in the tables gives the total weight loss and the second one from the right shows how this weight loss is distributed relatively (i.e. total weight loss = 100%) among the different reaction steps.

As can immediately be seen, the total weight loss is systematically lower for Anion 37 in nitrogen than in air. This is mostly due to the experimental performance of the measurements in nitrogen. Each measurement was preceded by double evacuation of the system. Anion 37 contains appreciable

TABLE 1

Thermoanalytical data for Anion 37

Al_2O_3:fluid	Fe:fluid	Atmosphere	DTA	DTG (°C)	Temperature interval (°C)	Weight loss (rel. %)	Total weight loss (%)
1:0.54	–	Air	Endo	40	40–160	64.5	68.4
			Exo	160	160–450	35.5	
1:0.70	–	Nitrogen	–	40	25–160	19.0	27.8
				160	160–250	25.8	
				250	250–420	55.2	
–	1:0.18	Air	Endo	40	25–180	72.6	60.7
			Exo	180	180–310	27.4	
–	1:0.18	Nitrogen	Endo	30	25–160	50.7	47.5
				160	160–270	13.4	
				270	270–410	32.8	
				630	630–820	3.0	

TABLE 2

Thermoanalytical data for Nonion 100

Al_2O_3 : fluid	Fe:fluid	Atmosphere	DTA	DTG (°C)	Temperature interval (°C)	Weight loss (rel. %)	Total weight loss (%)
1:0.20	–	Air	Endo	95	40–160	24.3	86.6
			Exo	160	160–250	59.7	
				250	250–400	16.0	
1:0.63	–	Nitrogen	Endo	110	70–240	65.3	87.6
				240	240–285	32.7	
					285–370	2.0	
–	1:0.17	Air	Endo	80(140)	80–250	76.7	80.4
			Exo	250	250–290	23.3	
–	1:0.16	Nitrogen	Endo	140	50–250	80.7	84.3
				250	250–290	16.7	
				670	670–830	2.6	

amounts of water (63%), some of which is lost due to vaporization during evacuation.

Figure 1 shows a thermogram for the fluid Anion 37 soaked up in the inert α-Al_2O_3 powder and tested in air (6°C min^{-1}) to 1000°C.

Basically, two major reaction steps can be discerned. The first (endothermal), in the range 40–160°C (Table 1), seems to involve a number of consecutive reaction steps (DTG), the main ones probably being associated with the volatilization of water and the organic component of the fluid. The second one above 160°C displays a higher rate (in proportion to the amount

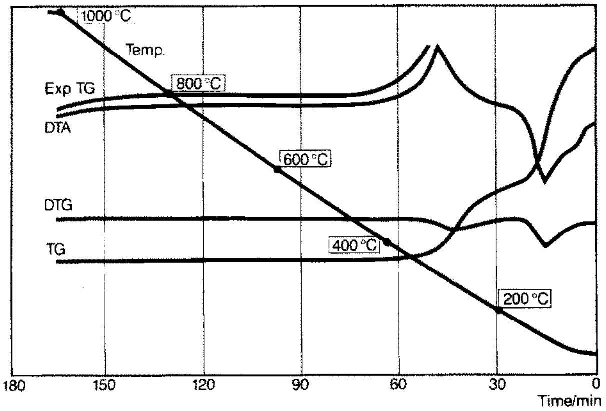

Fig. 1. Thermogram for the fluid Anion 37 on Al_2O_3 powder heated in air (6°C min^{-1}) to 1000°C.

of material left after the H_2O evaporation) and can be supposed to correspond to the decomposition of the organic component.

In air, this step is markedly exothermic (DTA), indicating a combustion process. The reaction, however, occurs within a broad temperature range (160–450 °C). This suggests that the combustion process does not necessarily involve the organic compound itself, but rather the volatile products of decomposition. In the N_2 atmosphere the decomposition above 160 °C occurs in at least two steps—the total mass loss, however, is about the same, regardless of atmosphere (35.5% of 68.4%, 81% of 27.8%, respectively, Table 1).

When heating the Anion 37 fluid mixed with Fe powder, the first reaction step (volatilization) is observed within the same temperature range, as in the case of Al_2O_3 powder. The reaction above 180 °C in air is exothermic as before, but takes place within a more narrow temperature range, and the total mass loss is significantly lower (Table 1) than in the case of the inert Al_2O_3 powder substrate. This indicates that a reaction occurs between Fe and the cutting fluid during its decomposition. In a N_2 atmosphere a somewhat lower mass loss is also obtained, above 160 °C. The most significant difference, however, is manifested by a separate mass-loss step at 630–820 °C, which has no counterpart in the case of the inert Al_2O_3 substrate. The occurrence of this step clearly indicates that Fe has reacted with the Anion 37 fluid (presumably within the temperature region of its decomposition) forming reaction products which decompose only at relatively high temperatures (630–820 °C).

Oxidation of Fe powder in the presence of Anion 37 starts (as detected by TGA) at about 310 °C. Reference measurements with only Fe powder, or Fe powder where H_2O was added instead of Anion 37, showed the Fe powder to have already started oxidation at 170–180 °C. This is still another indication that a protective layer of reaction product is formed on the iron surface.

The reactions of the cutting fluid Nonion 100 have been examined in the water-free state.

Initiation of the first mass-loss step (Table 2) for Nonion 100 dissipated in the Al_2O_3 powder substrate could be observed at about 100 °C in both air and nitrogen atmospheres alike. Similarly to Anion 37, the process is endothermal and presumably corresponds to volatilization (evaporation).

The second (decomposition) step is then very sensitive to atmosphere. In air this (exothermal) step starts at 160 °C, compared to 240 °C in nitrogen—the oxidative degradation seems to increase the decomposition rate of the compound. Similarly to Anion 37, the decomposition is terminated at a higher temperature in the presence of oxygen. The total mass loss, however, is approximately the same, regardless of atmosphere.

Figure 2 shows the thermogram obtained on heating Nonion 100 and Fe powder in nitrogen atmosphere. The decompositional step is seen to occur

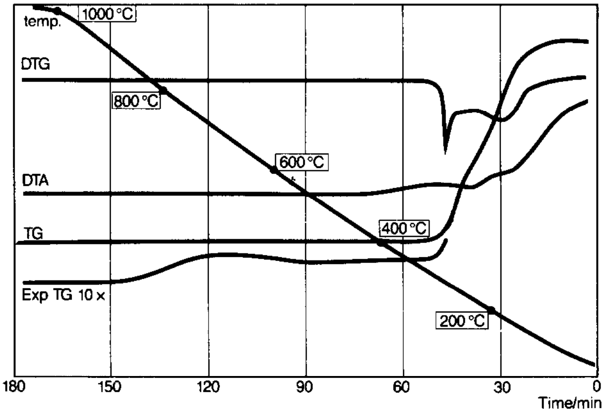

Fig. 2. Thermogram for the fluid Nonion 100 on Fe powder heated in nitrogen (6 °C min^{-1}) to 1000 °C.

within a much narrower temperature range (250–290 °C) than is the case for the inert Al_2O_3 powder substrate. The same pattern exists in air and, also, the mass loss is lower (Table 2). As in the former case, this seems to imply that the cutting fluid Nonion 100 reacts with Fe during the decomposition stage. Similarly to Anion 37, a separate small decomposition step (but within a narrower temperature range, 670–830 °C) is obtained in the inert atmosphere. This, again, indicating the formation of a reaction product stable up to a relatively high temperature. In order to ascertain whether the formation of this reaction product is related to the presence of oxygen a Nonion 100–Fe mix, as above, was first run in air up to 285 ° C. Then the system was evacuated and filled with nitrogen. The same type of mass loss (at 680 ° C) was again observed. When heating in air, this relatively small effect would be disguised by the large mass gain due to Fe oxidation.

This reaction (which has to occur before the Fe surface is covered by an oxide layer) is thus not confined to the inert atmosphere.

The initiation of the Fe surface oxidation (as measured by TG) was delayed to 280–290 °C in mixtures with Nonion 100 and Anion 37, compared to those to which H_2O only was added (about 180 °C). If a well-adhering layer of reaction products formed in the course of the reaction of the fluids with the Fe surface then an increased thickness of this layer should at least qualitatively lead to a decreased oxidation rate in the initial stage of oxidation.

The data in Fig. 3, showing a plot of mean oxidation rate of Fe powder at 300–400 °C against the amount of fluid (Nonion 100) added to a constant amount of Fe, seem to support this idea. As apparent in Fig. 3, an indirect proportionality exists between the oxidation rate and the amount of fluid added within the given region. This can be interpreted in terms of decreased

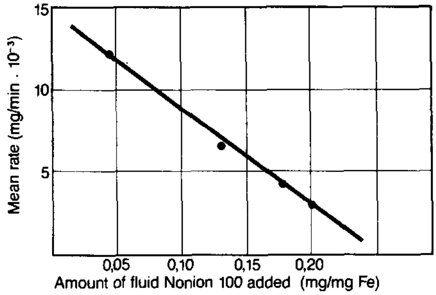

Fig. 3. Mean rate of oxidation of Fe powder in the temperature interval 300–400°C as a function of the amount of Nonion 100 fluid added.

diffusion gradient of oxygen through an increasingly thicker layer of reaction product, leading to a decreased rate of oxidation.

In all cases, X-ray diffraction measurements did not indicate the presence of any crystalline phase. This may be due either to the reaction products forming too thin a layer on the iron surface to be detectable or to their amorphous or microcrystalline nature.

CONCLUSION

The above thermoanalytical work, using a comparative experimental scheme (active–inert substrate, oxidizing–inert atmosphere), has given clear indications that phosphate-based cutting fluids react with the Fe-surface to give reaction products stable up to high temperatures—a precondition for boundary layer operating lubrication at high-cutting speed.

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