CORRELATION BETWEEN THE THERMAL STABILITY AND THE TRIBOLOGICAL PROPERTIES OF EP ADDITIVES

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Introduction

Extreme Pressure lubricating oil additives effective in wear reduction after rupture of the boundary lubricating layer may be of type organic compounds containing Cl, S or P.

In such cases of metallic contact temperature flashes of 300 to 1000°C occur without substantial raise of the average 150 to 250°C temperature of the surface [1—7].

Due to these temperature flashes, HCl or H_2S are split off from the molecules of the organic compounds containing Cl and S. These acids react with the metal surfaces and form a protective chemisorbed chloride or sulphide layer.

At very high loads, simultaneous application of additives containing chlorine and sulphur is suggested in order to form a sulphide protective layer after the rupture of the chloride layer at about 300 to 350°C.

These suggestions are not sufficiently supported by experiments carried out either by introduction of chlorine and hydrogen sulphide gas into frictional systems [1] or by tribological investigation of oils containing such additives without the study of chemical decomposition of the additives [3, 4].

EP additives containing P have scarcely been investigated, therefore their mode of action is practically not known.

In order to receive additional information concerning the mechanism of EP additives containing Cl, S and P results of tribological studies and data of thermal analysis have been compared.

Experimental methods

Thermal properties of the additives were measured by a derivatograph, tribological properties in a Shell four-ball apparatus [8—10]. The catalytic effect of the Pt-crucible was compensated by standardization of testing con-

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ditions. The weight of the samples was 500 mg, the heating rate 3°C/min. In order to reduce problems arising through evaporation, cylindric crucibles were used.

$AgNO_3$ was used for the detection of HCl, $CdSO_4$ for the detection of H_2S in the product gas stream. Residues of the samples were examined for P-content, using ammonium-molybdenate reagent.

Thermal decomposition of certain additives directly could not be studied by means of the derivatograph because of their volatility, as they evaporated before thermal decomposition. The rate of evaporation of such volatile additives was reduced by the addition of low vapour pressure residual oils. In this manner it was possible to retain these additives in the crucible at temperatures by 90 to 170 °C higher than the normal boiling point of the additive and thus the temperature of thermal decomposition could be attained.

The results of the studies of the following additives will be discussed: stearic acid (reference substance), 9,10-dichloro-stearic acid, chlorinated liquid normal paraffins containing 39% of chlorine, p-chloro-aniline-oleate, sulphurized oleic acid, sulphurized and chlorinated oleic acid, 2,4-dichloronitrobenzene, tri-n-butyl-phosphate, tri-n-octyl-phosphate, 2-etyhl-hexyl-phosphate and tri-n-octyl-phosphite. Kinetic calculations followed the method of FREEMAN and CARROL [11].

Results and discussion

In the majority of cases, thermal processes under increasing temperatures overlap. DTA curves are usually more characteristic than are DTG curves due to changes in the thermal characteristics of the processes. Therefore in the determination of characteristic temperature ranges of the processes data taken from the DTA curves had to be taken into account.

Results of the thermal analysis of stearic acid are shown as an example in Fig. 1. Six overlapping thermal processes can be distinguished under the given experimental conditions pertaining the most important to the temperature of 353°C.

Other processes are superimposed upon this endothermic process. Kinetic calculations could be carried out only on the basis of thermal processes occurring between 220 and 360°C. Results of these calculations are shown in Fig. 2.

The properties of the 9,10-dichloro-stearic-acid are greatly different from those of the stearic acid. The reaction order of four thermal processes occurring up to 370 °C is 1.0. Decrease of weight, up to this temperature, is 69% as opposed to 93% weight loss of stearic acid. Characteristic temperature ranges are the following ones: 140 to 240, 240 to 305, 305 to 330, 330 to 370°C.

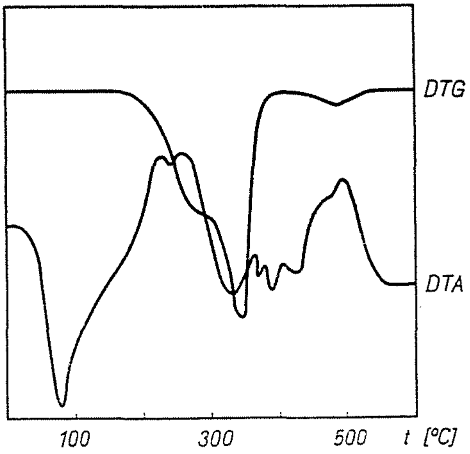

Fig. 1. DTG and DTA curves of stearic acid (Pt-crucible, sample 500 mg)

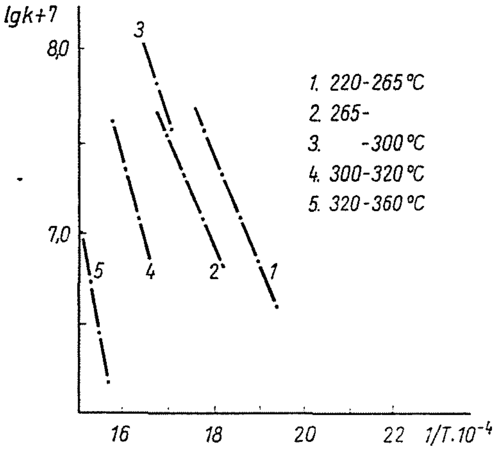

Fig. 2. lg K-1/T functions of stearic acid

HCl is formed mainly in the temperature range of 305 to 330°C, although this reaction starts already earlier and stops only in the range of 330 to 370°C. The modification of heating rate from 3 to 10°C/min did not change temperature values of HCl formation. HCl generation is therefore an accompanying process of several hydrocarbon decomposition processes and cannot be directly related to any separate thermal process.

HCl formation proved by thermal analysis is in accordance with hypotheses known from tribological literature and this supports the possibility of the formation of a chemisorbed chloride layer. In accordance with the above findings the welding load in the four-ball-machine increased from the value of 90 to 100 kp for the base oil to 180 kp, when 1% of 9,10-dichloro-stearic acid was dissolved in spindle oil.

In the course of the thermal analysis of the chlorinated n-paraffin containing 39% of chlorine, five thermal processes can be distinguished, the reaction order of which is 1.0.

HCl formation is very intensive between 310 and 335°C, but it starts already at a lower temperature and continues above 335°C. In respect of HCl formation, the chlorinated paraffin is very similar to the 9,10-dichloro-stearic acid.

Tests on the four-ball machine supported the findings of thermal analysis. The welding load was found to be 190 to 200 kp with a 1% additive solution in spindle oil, i.e. scarcely higher than with 9,10-dichloro-stearic acid. The higher chlorine content may account for the small difference.

The reaction order of the first four thermal processes during the thermal analysis of p-chloro-aniline-oleate is 1.0; while that of the fifth process is 0.75. No formation of HCl could be detected. This is in accordance with the fact that while in a paraffin chain the energy of the C—Cl bond of the chlorine substituents is about 80 kcal/mole, in an aromatic ring the energy of the C—Cl bond is about 50% higher. Thus the thermal decomposition products of this compound are molecules containing chlrorine in organic bond. No free HCl is present and accordingly the additive cannot display any EP effect. In accordance with thermal observations no chemisorption effect (i.e. increase of welding limit) could be detected in the four-ball apparatus, in spite of the fact that the additive contained chlorine. Thus under given experimental conditions no EP effect can be expected from monochloro-aromatic compounds. The change in the limit of abrasive wear is a consequence of physical adsorption processes, i.e. p-chloro-aniline oleate is no EP additive but an oiliness improver.

The lack of EP effect has been supported also by a study of 1-chloronaphthaline, which, in a 1% solution did not change the welding limit. Further, the behaviour of chlorine substituents on aromatic rings was studied. It is known that by increasing the number of substituents on an aromatic ring the C—Cl bond can be weakened to form HCl, 2,4-dichloro-nitrobenzene was chosen as a model.

The study of the thermal decomposition of 2,4-dichloro-nitrobenzene by a derivatograph operated under atmospheric conditions seemed to be difficult, the boiling point of this substance being lower than that of its decomposition.

The evaporation rate was therefore reduced by dissolving the compound in heavy residual oil. In this way the decomposition temperature could be attained. As an example for this method the DTG and DTA curves of the pure additive and a mixture are shown in Figs 3 and 4. Contrary to the pure substance, HCl formation could be demonstrated in the mixture. This formation of HCl, however, occurs in a wider temperature range (274 to 410°C)

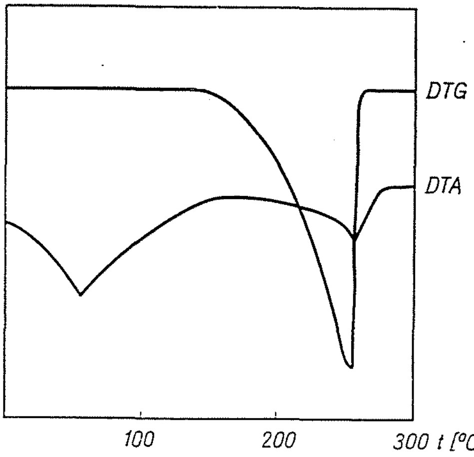

Fig. 3. DTG and DTA curves of 2,4-dichloro-nitrobenzene

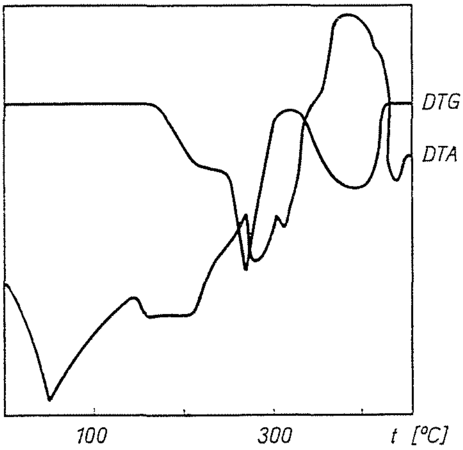

Fig. 4. DTG and DTA curves of a mixture of 2,4-dichloro-nitrobenzene in residual oil solution

than in the case of aliphatic compounds, and also the temperature range of maximum formation rate is higher (370 to 400°C). In accordance with the HCl formation demonstrated, 2,4-dichloro-nitrobenzene proved to be an active EP additive, the welding load being 190 kp in a 1.0% solution.

Results of four-ball tests with chlorinated additives are summarized in Fig. 5.

The DTA and DTG curves of sulphurized oleic acid are similar to the corresponding curves of the 9,10-dichloro-stearic-acid and the chlorinated paraffin. Formation of H_2S may be observed already at 195°C, contrary to the relatively higher formation temperature of HCl.

The intensity of H_2S formation, verified by a $CdSO_4$ solution, reached a maximum at 330°C, consequently the rate of CdS formation is approximately proportional to the 300°C peak of the DTA curve.

It can be ascertained that also the formation of H_2S is accompanied by several processes, as in the quoted wide temperature interval at least two thermal processes may be registered.

According to the opinion of Bowden and Tabor [1], H_2S displays its anti-wear effect up to about 600°C.

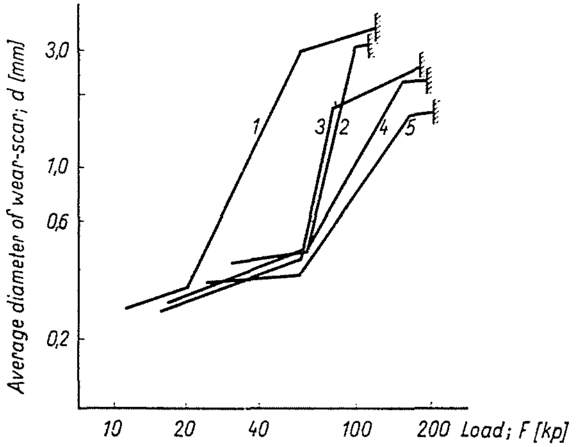

Fig. 5. Four-ball tests of EP-additives containing chlorine (1%). 1. Base oil; 2. p-Cl-aniline oleate; 3. 9,10-dichloro-stearic acid; 4. chlorinated paraffin wax (39% Cl); 5. 2,4-dichloronitrobenzene

According to measurements, H_2S formation starts at 195°C and it is already intensive at 260°C, it has therefore to show up an EP effect in load ranges characterized by these lower temperatures. Our four-ball test results agree with those of thermal analysis. (See later, Fig. 7.)

If H_2S were really effective only in the temperature range of 600°C, there would be, in the case of a lubricating oil containing only sulphurized oleic acid, a temperature gap of about 400 to 450°C between the rupture of the adsorptive layer of the oil and the formation of the chemisorption layer, because according to Cameron the film rupture temperature of the adsorbed layer is about 150 to 200°C [2], and therefore, before a sulphide layer could form, welding would occur. According to this theory, only combined additives containing chlorine and sulphur could furnish appropriate safety in the whole load range. Actually sulphurized stearic acid alone gave practically the same results as 9,10-dichloro-stearic-acid or chlorinated paraffin. These results can easily be interpreted by the findings of thermal analysis. H_2S formation starts at a substantially lower temperature than formerly supposed and therefore the chemisorbed EP-active layer may form immediately after the rupture of the adsorbed layer.

On the DTG curve of the oleic acid derivative containing sulphur and chlorine (Fig. 6) an exothermal double peak is noticed which may be observed also during the decomposition of compounds containing only chlorine or only sulphur. Among these, especially the second is very sensitive to any change of experimental conditions. Contrary to the samples mentioned so far, the appearence of an endothermal peak at 215°C is remarkable (Fig. 6). The properties of this substance are otherwise similar to the analogous stearic acid derivatives from the point of view of H_2S and HCl formation.

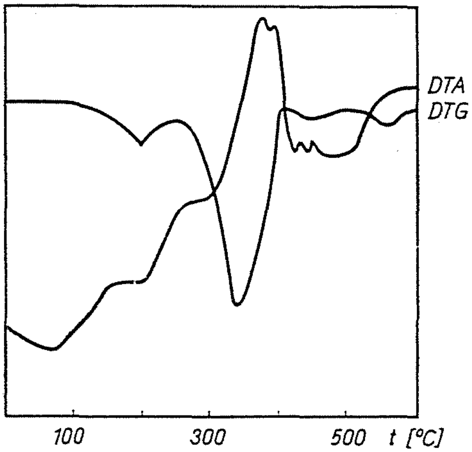

Fig. 6. DTG and DTA curves of both chlorinated and sulphurized oleic acid (CdS precipitate appearing at 230°C, AgCl at 280°C. Maximum rate of precipitation at 310 to 330°C)

In this case, too, the wear curves in the zones of low and medium loads can easily be interpreted by data of thermal measurements, but it cannot be explained why this system shows an essentially higher load capacity (320 kp) than the individual compounds (Fig. 7).

Contrary to the opinions known from literature, according to which HCl and H_2S exert their wear-reducing effect at different load conditions (corresponding temperatures: 300 and 600°C, respectively), it could be shown that they are effective in the same load range. If both of them are present simultaneously a synergic effect is produced. A physicochemical explanation of this fact is hoped to be derived from future tests.

According to literature, in case of additives containing chlorine the reaction causing the EP effect ceases at about 300 to 350°C, and the protective layer is broken through.

According to our experiments, however, the formation of HCl is not finished. In this state the chemisorbed layer may be supposed not to be mechanically stable enough and to be sheared off, a fresh metal surface being again exposed to HCl. Thereby the surface will be subject to corrosive wear.

Such cases are known to us from lubrication practice and these may therefore be well interpreted by data of thermal analysis.

According to new tendencies in the formulation of EP-lubricating oil, phosphorus compounds are incorporated instead of additives containing chlorine. The mode of action of additives containing phosphorus is practically unknown, therefore also some compounds of this type, such as alkyl-phosphates and alkyl-phosphites were investigated.

Thermal processes occurring below 200°C were different for phosphorus compounds of different types. In the case of tri-n-octyl-phosphite and tri-n-butyl-phosphate (Fig. 8) large quantities of decomposition products evaporated probably due to the splitting off of alkyl chains.

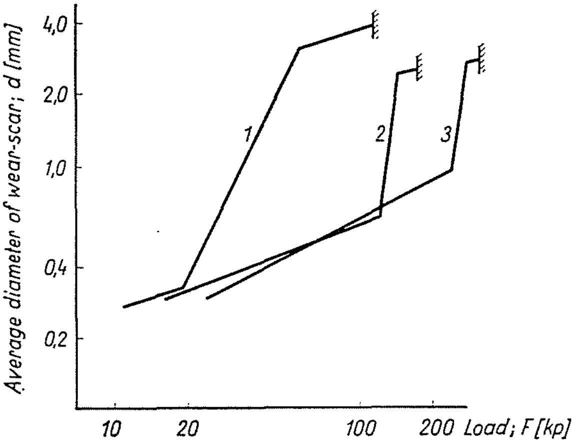

Fig. 7. Four-ball tests of EP additives containing sulphur (1%). 1. Base oil; 2. sulphurized oleic acid; 3. additive containing S and Cl

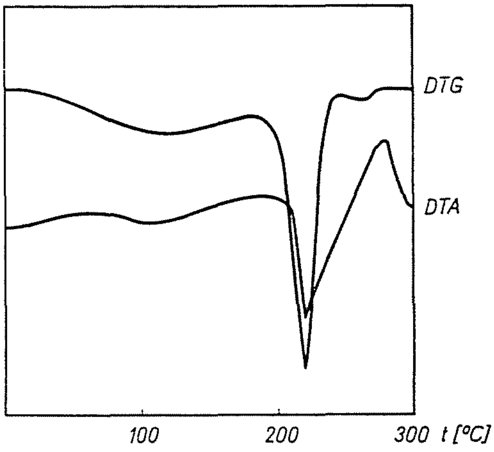

Fig. 8. DTG and DTA curves of tri-n-butyl-phosphate

Contrary to this behaviour, the weight loss observed in the course of thermal decomposition of tri-n-octyl-phosphate and di-2-ethyl-hexyl-phosphate is low, and is probably due to the evaporation of impurities, including traces of water (Fig. 9). The characteristic kinetic data of this process are seen in Table 1.

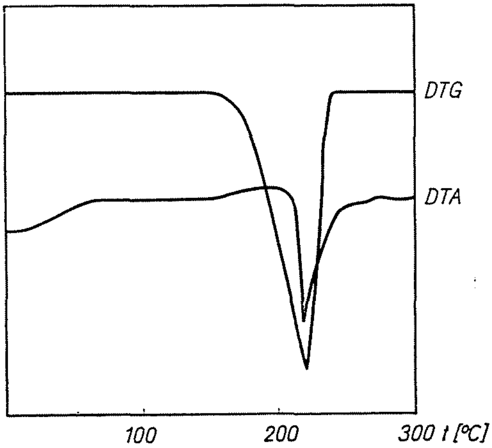

Fig. 9. DTG and DTA curves of di-2-ethyl-hexyl-phosphate

Table 1

Kinetic data of reactions below 200 °C in the course of thermal decomposition of EP-additives containing phosphorus

Substance	Temperature range, °C	Weight loss, %		E
tri-n-butyl-phosphate	40—180	26	1	12.8
tri-n-octyl-phosphate	40—205	16	—	—
tri-n-octyl-phosphite	70—200	53	1	10.6
di-2-ethyl-hexyl-phosphate	50—180	1	—	—

The most characteristic thermal decomposition process of the investigated phosphorus compounds takes place between 190 to 210°C, and is registrated in form of a highly endothermic peak.

No kinetic evaluation of these processes is possible due to the very high rate of decomposition.

The characteristic temperature data of the four compounds for a heating rate of 3°/min and 500 mg samples are shown in Table 2.

Investigating the DTA curve of tri-n-butyl-phosphate, an exothermic reaction without weight loss may be registered at 285°C. This peak seems to be

Table 2

Characteristic temperature ranges of endothermic decomposition of EP-additives containing phosphorus

Substance	Temperature range, °C	Temperature of DTG peak maximum, °C
tri-n-butyl-phosphate	190—245	221
tri-n-octyl-phosphate	250—290	258
tri-n-octyl-phosphite	210—250	238
di-2-ethyl-hexyl-phosphate	200—240	210

due to the polymerization of meta-phosphoric acid to compounds of the type $(PO_3)_n$. [12]

Stoichiometric calculations based on the DTG and TG curves as well as the qualitative analysis of the residue using ammonium-molybdenate indicate that after heating to 350°C the contents of the crucible is reduced mainly to coke and phosphoric acids. The presence of phosphoric acids indicates that additives containing phosphorus may act by developing a phosphate layer on the rubbing surfaces.

Results of four-ball tests with the additives containing phosphorus are shown in Fig. 10. These curves indicate that octyl (and ethyl-hexyl) derivatives do not improve the EP-behaviour of the oils (i.e. welding limits remain unchanged) while they reduce the diameter of the wear-scar at loads below 70 kp. These additives may be regarded to be oiliness improvers. Butyl derivatives improve antiwear properties as well as welding limits.

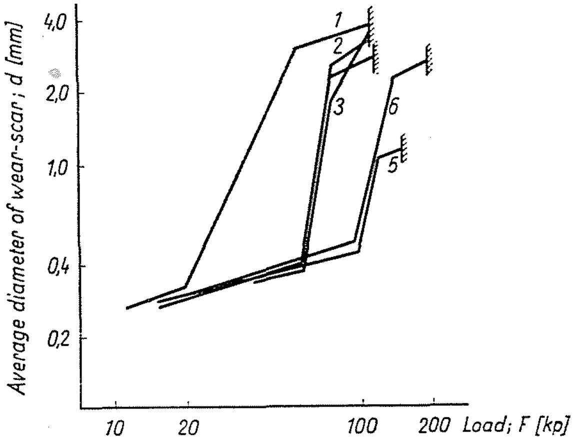

Fig. 10. Four-ball tests of EP additives containing phosphorus (1%). 1. Base oils; 2. tri-n-octyl-phosphite; 3. tri-n-octyl-phosphate; 4. di-ethyl-hexyl-phosphate; 5. tri-n-butyl-phosphate; 6. tri-n-butyl-phosphite

The reduction of wear-scar diameter may be explained by the above-mentioned phosphate layer formation, but the cause of improvement of welding limit needs further investigation.

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Summary

Investigations were carried out to correlate the wear reducing effect of EP additives containing Cl, S and P and their thermal stability. Thermal decomposition was investigated by simultaneous TG, DTA and DTG measurements, tribological behaviour was tested in a Shell-four-ball apparatus. Volatile additives were dissolved in heavy residual oils and tested subsequently. This method permitted to study thermal decomposition of additives, which otherwise would have evaporated at atmospheric pressure without decomposition. Antiwear effect was in correlation with the thermal decomposition peaks of additives, taking also the qualitative analysis of gases sucked off into consideration. Starting temperatures of the thermal decomposition of aliphatic compounds containing S and Cl did not differ substantially, and their effect resulted from the formation of H_2S and HCl.

Chlorine contained in aromatic bonds is only effective if the bond is weakened by further substitution. Compounds containing P seem to form a residue containing phosphoric acid, which acts as oiliness agent but sometimes also as an EP agent.

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