RESPONSES OF TRICRESYL PHOSPHATE IN DIFFERENT LUBRICATING SYSTEMS

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SUMMARY
Experience has shown that a pretreatment called oil aging can improve significantly the tribological performance of contacting metallic surfaces. Previous studies on oil aging SAE 52100 steel specimens, starting from solutions of tricresyl phosphate in hydrocarbon mineral oil, free of any polar impurities, indicated that an organic phosphate type of material was formed. In the present work, the oil aging investigation focused on the pretreatment of 20NiCrMo12 steel specimens. A similar organic phosphate complex, capable of reducing the friction coefficient of the base metal and to help effectively under conditions of lubricant starvation or in a boundary lubrication regime, was obtained. It is speculated that such a complex is formed through liquid-solid reactions involving a radical reaction mechanism.

Keywords: TCP, phosphide, phosphate, hydrocarbon oil, boundary lubrication

1 INTRODUCTION
The antiwear and antioxidation mechanisms of tricresyl phosphate (TCP) have been investigated for many decades and contradictory theories have been proposed. The tribological benefits of the TCP have been attributed at one time or another, by various researchers, to the formation of compounds such as phosphides [1, 2], oxides [3, 4], or phosphates [2, 5-7].

The results of previous studies [5, 8] by the author have indicated that many of these differences could be resolved through a more comprehensive analysis of all the variables associated with the experiments and not by seeking a single mechanism to explain the observed phenomena. The behaviour of TCP cannot, in fact, be understood independently of the environment (e.g. lubricating system) in which it operates. These studies, generally referred to as “oil aging”, have portrayed the ability of TCP to interact with a metal surface as a competition with other polar species, including oxidation products and aromatic components from the lubricating oil.

Thin fluid film static experiments were devised to simulate the actual use conditions of various lubricating systems containing TCP. In particular, micro oxidation methods [9] minimized the complex transport phenomena associated with most test systems [9] and realistic conditions were approximated by the proper choice of variables such as air flow rate, temperature and sample size, aiming at, ideally, generating a uniform thin oil film with no temperature or concentration gradients. Finally, the wear mechanism of boundary lubrication, due to metal to metal contact and consequent thermal energy and electrons transfer process, was related to that of argon ion sputtering. The correctness of the above assumption was supported by the formation of phosphorous bearing species, similar to the ones observed on the wear tracks of metal surfaces, after running under boundary lubrication regime.

The interactions of TCP with steel surfaces, utilizing micro oxidation methods, were studied by electron spectroscopy for chemical analysis (ESCA). Table 1 summarises the most important results of 52100 steel oil aging utilizing TCP, neat or dissolved in different lubricating systems.

<table>
<thead>
<tr>
<th>Sample Description</th>
<th>Treatment</th>
<th>ESCA Results</th>
</tr>
</thead>
<tbody>
<tr>
<td>TCP in hydrocarbon oil containing aromatics and/or polar functional groups</td>
<td>Aging</td>
<td>No phosphorous species on steel surface</td>
</tr>
<tr>
<td>TCP in synthetic hydrocarbon oil</td>
<td>Aging</td>
<td>No phosphorous species on steel surface</td>
</tr>
<tr>
<td>Neat TCP</td>
<td>Sputtering the steel surface with Ar ions</td>
<td>Phosphide on steel surface</td>
</tr>
<tr>
<td>TCP in paraffinic hydrocarbon oil free of aromatics and polar impurities</td>
<td>Aging</td>
<td>Organic phosphate complex on steel surface: P/Fe = 1 on outermost surface P/Fe = 3 toward the substrate</td>
</tr>
<tr>
<td>Organic phosphate complex formed upon aging</td>
<td>Sputtering the steel surface with Ar ions</td>
<td>Inorganic phosphate on steel surface</td>
</tr>
</tbody>
</table>

Table 1: Different tribological responses of tricresyl phosphate (TCP) on 52100 steel

It can be seen that neat TCP behaves quite differently from TCP dissolved in a hydrocarbon mineral oil and it leads to the formation of iron phosphide. Some researchers [2, 10, 11] have found presence of iron phosphide on the wear tracks of specimens, subjected to extremely severe wear conditions [10]. On the contrary, when TCP is dissolved in a hydrocarbon mineral oil without polar impurities, it is possible, under certain conditions, to form an organic phosphate with outstanding tribological characteristics. Production records, taken for several years, have shown at least
20% better performance (longer life) of the aged bearings with respect to the untreated units.

During these studies, samples of 52100 steel bearings were pre-treated under various sets of time and temperature with a super-refined hydrocarbon mineral oil containing 1-3% TCP. Gel permeation chromatography (GPC) analyses showed that the polymerisation of the base hydrocarbon oil was favoured, within certain limits, by lowering the temperature and increasing the length of the pre-treatment process. ESCA results indicated a direct relationship between the extent of the hydrocarbon polymerisation and the amount of phosphorus (atomic per cent) present in the coating left on the steel surface. The optimal sets of time and temperature were: 100 hours and 114°C. Oil was applied to each bearing in such a way not to exceed a film thickness of 150µm and each specimen was aged in a 8 cm³ petri dish, having a loose cover to allow the escaping of volatile compounds. It was formed an organic phosphate whose phosphorus concentration became richer going from the outermost surface toward the substrate. Such a phosphate retained, in toto or in part, the characteristic aromatic ring structure of the TCP; however, its binding energy showed a distinct chemical change from the original additive.

The present work concerned itself with twofold purposes: one dealt with the tribological characterization of the phosphate coating formed by aging a steel alloy utilized for automotive gears which possesses different characteristics of the previously investigated 52100 steel. The second purpose was to reach a basic understanding on the mechanism of TCP dissolved in hydrocarbon mineral oil in producing such a desirable phosphate coating.

2 EXPERIMENTAL PROCEDURES

2.1 Oil aging

The oil aging pre-treatment (100 hours at 114°C) was carried out on samples of 20NiCrMo12 steel, which is used for gearing components. This material had been thermally treated and case-hardened to reach a hardness of 550 Hv. The modified surface layer, richer in carbides, was about 1 mm deep. Specific surface analyses, ESCA and glow discharge optical emission spectrometry (GDOES), were carried out before and after the aging process to verify the actual formation of the phosphate protective coating.

2.2 Tribological characterization

Figure 1 shows the set-up of the tribological test apparatus. A point contact (ball on disc) geometry, instead of the actual linear contact existing between the straight teeth of a gear drive, was chosen, because it represented a more severe mechanical condition. The disc was constituted by the gearing steel, before and after the TCP/oil aging process; the ball was made up of SAE 52100 steel. Some of the tribological tests were run in absence of lubrication and other ones utilizing a uniform film of commercial gearing oil placed between ball and disc.

An analysis of the operating conditions of the gear system indicated that the absolute value of maximum sliding distance (length of teeth engagement) was around 4 mm and that maximum and minimum speeds to cover such a distance were 1.2 m/s and 0.4 m/s. Considering that the maximum stroke of our tribometer was 3 mm, the above speeds would correspond approximately to 392 Hz and 140 Hz, respectively. The higher frequency was discarded, because at elevated values of sliding speeds a hydrodynamic lubrication is predominant, during which the lubricant characteristics prevail with respect to the tribological properties of the contacting surfaces. For this reason the lower frequency was considered. However, in our tribological set-up, stroke, load, and frequency were not independent variables. In fact, even though the maximum stroke of 3 mm was set out, this was maintained at low (~50 Hz) frequencies only. Preliminary tests had indicated that at a frequency of 140 Hz, the sliding stroke was 0.36 mm only, although a 3 mm stroke had been planned out. Therefore, in addition to the 140 Hz, tests were run also at 50 Hz, which allowed a stroke slightly below 3 mm, much closer to the real operating conditions (4 mm) of the gear system. Moreover, assuming three engaged teeth and a 4 mm linear contact, it was estimated a load of about 3 x 10⁵ N on each tooth. In our case, taking also into account the more severe point contact typology, a load of 100 N was proved to be a sufficiently discriminating parameter.

3 RESULTS

3.1 Oil aging

ESCA analysis of the TCP/oil treated gearing steel surface showed a phosphorus based protective layer with a 2p binding energy of 133.7 eV, which is consistent with values of binding energy ranging between 133.9 and 133.6 previously found on 52100 steel treated surfaces [5]. The presence of phosphorous bearing species was confirmed also by GDOES analysis. Typical GDOES concentration profiles for gearing steel samples in the as-received condition and after TCP/oil treatment are shown in Figures 2 and 3, respectively.
3.2 Tribological characterization

In the lubricated tests, at a frequency of 140 Hz, the friction coefficient of untreated samples, flounced up and down during the first minutes of the test; then it stabilized at about 0.13, while in the case of treated samples it maintained a constant value of about 0.13 for all the length of the test.

In the unlubricated tests, at the same frequency of 140 Hz, both treated and untreated samples reached a friction coefficient of 0.6, which was the maximum value detectable by the tribometer, and for this reason at this point the tests were discontinued. However, lengths of time to reach the 0.6 value were quite different in the two cases: 18 s for the untreated samples, 100 s for the treated ones, as shown in Figure 4.

In the lubricated tests, carried out at a frequency of 50 Hz, treated and untreated samples showed the same value (0.10) of friction coefficient and in both cases the stroke dropped from 3 mm to 2.8 mm.

In absence of lubrication, at a frequency of 50 Hz, both treated and untreated samples showed a rapid increase of the friction coefficient over the limit (0.6) of the apparatus. In this case, the stroke resulted to be the discriminating parameter. In fact, in the case of untreated samples, the stroke dropped as soon as the test was initiated and this had to be discontinued after 15 s only, due to early indications of seizure. On the contrary, in the case of treated samples, the stroke from 3 mm dropped after a few seconds to 2.7 mm and stayed constant for about 7 min. Such a behaviour is illustrated in Figure 5.

The results of tribological tests are summarised in Table 2.
4 DISCUSSION

In nearly all practical cases the wear of sliding pairs depends on a delicate balance of chemical reactivity and lubricant-film breakdown as well as the detailed mechanism of the interaction between the surfaces. In a paraffinic oil the molecules have balanced electrical charges and, therefore, they are physically adsorbed in random positions. In this case, the adhesion and cohesion forces are weak, and although the adsorbed molecules reduce the surface energy of the tribological pair, the lubricating characteristics generally are not satisfactory. Let’s now consider the situation when a small percentage (e.g. 1-3 %) of an extreme pressure additive such as TCP is added to the above lubricant.

Considering the low concentration, all the TCP is dissolved in the oil. Moreover, the relative surface tensions indicate that it will not be present as a surface excess, but it will tend to accumulate in the interior of the solution. It finds itself where it’s mostly needed, for reacting with the carboxylic acid, as soon as it forms due to microoxidation of the hydrocarbon oil. The result is the formation of some kind of phosphate complex which, as indicated by surface analyses, retains the aromatic ring structure, that is a characteristic of TCP, and the carbonyl functional group, typical of a carboxylic acid derivative.

Two hypotheses have been made in the attempt of elucidating the chemical nature of such a phosphate complex. The first one considered the possibility that the enolic form of TCP, would react with the carboxylic acid through an addition and elimination bimolecular reaction mechanism (SN2), catalysed by an acid. A source of H+ ions is constituted by water which is present in large excess with respect to TCP. In fact, 3 % TCP in 150 µl of hydrocarbon oil correspond to 0.011 moles, while about 4 moles of water would be present within the 8 cm³ of the oil aging apparatus, assuming a 40% humidity. The second hypothesis considered the extraction of hydrogen from one or more of the methyl groups in the para position of the TCP molecule, forming, thus, free radicals leading to the addition of a long chain carboxylic acid. An example of a hypothetical product originated from such a radical reaction is shown in Figure 6.

The first hypothesis was discarded in favour of the second one, because this seemed to be more consistent with the experimental results. In fact, in the case of an SN2 type mechanism, the shorter are the chains of carboxylic acid, the easier is their addition to the P atom. However, the experimental evidence showed the phosphorous content increasing with the degree of hydrocarbon polymerisation, suggesting a different mechanism taking place.

<table>
<thead>
<tr>
<th>Sample (disc)/treatment</th>
<th>Frequency (Hz)</th>
<th>Lubrication</th>
<th>Stroke (mm)</th>
<th>Friction coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>Set out</td>
<td>Actual</td>
</tr>
<tr>
<td>gear steel after TCP/oil aging 140</td>
<td>thin oil film</td>
<td>3.0</td>
<td>0.36</td>
<td>0.13</td>
</tr>
<tr>
<td>gear steel as received 140</td>
<td>thin oil film</td>
<td>3.0</td>
<td>0.36</td>
<td>floucing during first 4 min. 0.13 afterwards</td>
</tr>
<tr>
<td>gear steel after TCP/oil aging 140</td>
<td>none</td>
<td>3.0</td>
<td>0.36</td>
<td>ranging between 0.47-0.60 during the first 100 s</td>
</tr>
<tr>
<td>gear steel as received 140</td>
<td>none</td>
<td>3.0</td>
<td>0.36</td>
<td>&gt;0.60</td>
</tr>
<tr>
<td>gear steel after TCP/oil aging 50</td>
<td>thin oil film</td>
<td>3.0</td>
<td>2.8</td>
<td>0.10</td>
</tr>
<tr>
<td>gear steel as received 50</td>
<td>thin oil film</td>
<td>3.0</td>
<td>2.8</td>
<td>0.10</td>
</tr>
<tr>
<td>gear steel after TCP/oil aging 50</td>
<td>none</td>
<td>3.0</td>
<td>2.5</td>
<td>&gt;0.60 (after 7 min.)</td>
</tr>
<tr>
<td>gear steel as received 50</td>
<td>none</td>
<td>3.0</td>
<td>0.1</td>
<td>&gt;0.60 (after 15 s)</td>
</tr>
</tbody>
</table>

Table 2: Results of tribological tests

In support of the radical mechanism, it can be observed that the oxidation of the hydrocarbon oil proceeds through the formation and reaction of free radicals. The CH₂ radical in para position in the cresyl group is quite stable. Such a stability derives by virtue of the inductive and hyper conjugation effects of the methyl groups, within the TCP molecule. When a carbon sp³ orbital is attached to an sp² orbital of carbon, there is an electron donation in the direction of the sp² carbon. That makes feasible the formation of the above radical even at the relatively low temperature of the aging treatment. This point of view is supported also by the observation that TCP with methyl groups in para position only leads to the phosphate complex. Finally, the structure of such organic phosphate appears consistent with its conversion.
to inorganic iron phosphate because of the thermal energy [12, 13] and electron transfer [14] mechanism associated with boundary regime of lubrication.

Chemical analysis of tribological films is not an easy task, however, in our opinion, clues such as the ones discussed in this work may contribute to a better understanding of the chemical interactions among additives, lubricant, and metal surface and, thus, to improve the tribological systems.

5 CONCLUSIONS

- The results of this work have confirmed that it is possible to deposit on contacting tribological surfaces – through liquid-solid reactions taking place during the so-called oil aging process – a phosphorous bearing protective layer. This last one can be deposited in different types of substrate materials, i.e. 52100 and 20NiCrMo12 steels for bearing and gear components, respectively.

- It appears that the protective layer is constituted by an organic phosphate complex originating by a radical reaction between TCP and long chain carboxylic acid

- The phosphate complex is capable of reducing the friction coefficient of the base metal and to help effectively under conditions of lubricant starvation and in the transitory intervals of time within which drastic changes (e.g. sudden acceleration and deceleration) take place or when in general a boundary lubrication regime is established.

- The phosphate protective layer could also lead to the optimisation of the amount and viscosity grade of the various lubricants depending on the service conditions of a given tribological system.

6 ACKNOWLEDGEMENTS

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7 REFERENCES


