Mechanism of Lubrication by Tricresylphosphate (TCP)

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Summary

The coefficient of friction was measured as a function of temperature on a pin-on-disk tribometer. Pins and disks of 440C and 52100 steels were lubricated with tricresylphosphate (TCP), 3.45 percent TCP in squalene, and pure squalene. M-50 pins and disks were lubricated with 3.45 percent TCP in squalene and pure squalene. Experiments were conducted under limited lubrication conditions in dry (<100 ppm H2O) air and dry (<20 ppm H2O) nitrogen at 50 rpm (equivalent to a sliding velocity of 13 cm sec⁻¹) and a constant load of 9.8 N (1 kg). Characteristic temperatures Tc were identified for TCP on 52100 steel and for squalene on M-50 and 52100 steels, where the friction decreased because of a chemical reaction between the lubricant and the metal surface. The behavior of squalene obscured the influence of 3.45 percent TCP solute on the friction of the system. Wear volume measurements demonstrated that wear was lowest at temperatures just above Tc. Comparison of the behavior of TCP on M-50, 440C, and 52100 steels revealed that the TCP either reacted to give Tc behavior or produced initial failure in the temperature range 223° ± 5° C. The 440C steel yielded a peak in friction; the 52100 and M-50 steels had assignable Tc values in this temperature range. Oxygen was essential for the reaction of TCP with the metal surface.

Introduction

The mechanism by which tricresylphosphate (TCP) functions as an antiwear, extreme-pressure lubricant has been studied since 1940, when Beeck, Givens, and Williams (ref. 1) proposed the formation of a eutectic layer of iron and iron phosphide. Twenty-five years later several workers demonstrated that this idea was not tenable. Barcroft and Daniels (ref. 2) proposed the existence of a phosphate layer; Godfrey (ref. 3) demonstrated the presence of FePO4 and FePO4·2H2O on the surface of TCP-lubricated steel by electron diffraction; Bieber, Tewksbury, and Klaus (ref. 4) addressed the source of the phosphate by proposing that reactive acidic and polar impurities in commercial TCP are responsible for the formation of the phosphate layer. Current opinion is that phosphate is indeed formed on the surface of metals under a variety of conditions (refs. 5 to 9).

The coefficients of friction for lubricants containing TCP have been measured under a variety of conditions (refs. 9 to 12) but only once (ref. 9) over a sufficient temperature range to achieve failure of the lubricant. Faut and Wheeler demonstrated the presence of a characteristic temperature for TCP lubricating M-50 steel, where the lubricant reacted with the steel to produce a phosphate layer on the metal (ref. 9). The present investigation was conducted to determine the chemical reactions of the lubricant with other steels. Therefore the coefficients of friction were measured for TCP lubricating 52100 and 440C steels. In addition, a 3.45 percent TCP solution in squalene was used to measure friction with the three steels: 440C, 52100, and M-50. Wear studies were conducted to further delineate the effect of the phosphate layer.

Experimental Procedure

Coefficients of friction were measured as a function of temperature by using a pin-on-disk tribometer equipped with an induction heater for the disk (fig. 1). The details of the experimental procedure are given in reference 9. All experiments in the present report were conducted under limited lubrication conditions (i.e., approx 1 cm³ of lubricant was placed directly on the rotating disk). Lubricants used for nitrogen atmosphere experiments were degassed and dehydrated as described in reference 9. The base fluid for preparation of the TCP solution was 2,6,10,15,19,23-hexamethytricosane, commonly known as squalene. The 3.45 percent TCP in squalene was prepared from commercial laboratory reagent-grade squalene and TCP. The commercial TCP had been prepared from an 80 percent para–20 percent meta mixture of cresols.

Wear studies were conducted by setting the temperature of the disk at a fixed level and then stabilizing the temperature with air or nitrogen flow. When the temperature of the disk was stabilized, the lubricant was placed on the rotating disk and the pin was loaded to 9.8 N (1 kg) for a fixed time. The sliding velocity was set at 50 rpm (equivalent to a sliding velocity of 13 cm sec⁻¹) for each experiment. After the experiment was concluded, the pins were removed, washed carefully with Freon to remove traces of the lubricant, and examined microscopically. Photographs were taken of the wear scars on the pins, and the wear scar diameters were determined from the photographs.

The air used contained less than 100-ppm water. The nitrogen used contained less than 20-ppm water. Smoothed friction-temperature curves are presented in this report. Primary data curves and the use of smoothed curves are discussed in reference 9. This same reference includes a discussion of the uncertainties in the temperature measurements.

The hardness of each pin and disk was measured before and after each experiment. It is well known that friction can change as the hardnesses of the metals change (ref. 13). Therefore only those results are presented in which the hardnesses changed by less than 10 percent during the course of the experiment. Indeed, the experiments that required heating the disks to
approximately 700° C in order to remove or react adsorbed oxygen could not be performed for 52100 steel because of the great variation in hardness with temperature (ref. 14).

**Experimental Results**

The results of the friction-temperature measurements are presented in figures 2 to 7. Table I summarizes the experiments presented in this report.

**Pure TCP**

The friction-temperature curves for 44OC steel lubricated by pure TCP in dry air are shown in figure 2(a) and exhibit a peak in friction at 225° to 230° C for the two experiments. After the peak the friction decreased before failure, which occurred at temperatures as low as 235° C. The friction-temperature behavior of 44OC steel can be compared with that of 52100 steel in figure 2(b). For 52100 steel the friction underwent a pronounced decrease beginning at 220° C and reached a minimum at 230° C. This minimum was followed by a peak in friction at 320° to 330° C. The minimum beginning at 220° C is attributed to the characteristic temperature \( T_r \), and is associated with a chemical reaction between the lubricant and the metal surface (refs. 9 and 15). Note particularly that no \( T_r \) value can be assigned to the 44OC steel curve since no sharp decrease in friction occurred before the peak at 225° C.

**TABLE I. SUMMARY OF EXPERIMENTS PERFORMED**

<table>
<thead>
<tr>
<th>Steel used</th>
<th>Lubricant used</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>44OC</td>
<td>Pure TCP</td>
<td>Dry air</td>
</tr>
<tr>
<td>52100</td>
<td>Pure TCP</td>
<td>Dry air</td>
</tr>
<tr>
<td>44OC</td>
<td>Pure TCP</td>
<td>Dry nitrogen</td>
</tr>
<tr>
<td>52100</td>
<td>Pure TCP</td>
<td>Dry nitrogen</td>
</tr>
<tr>
<td>44OC</td>
<td>Pure squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>52100</td>
<td>Pure squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>M-50</td>
<td>Pure squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>44OC</td>
<td>Pure squalene</td>
<td>Dry nitrogen</td>
</tr>
<tr>
<td>M-50</td>
<td>Pure squalene</td>
<td>Dry nitrogen</td>
</tr>
<tr>
<td>44OC</td>
<td>3.45 Percent TCP in squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>52100</td>
<td>3.45 Percent TCP in squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>M-50</td>
<td>3.45 Percent TCP in squalene</td>
<td>Dry air</td>
</tr>
<tr>
<td>M-50</td>
<td>3.45 Percent TCP in squalene</td>
<td>Dry nitrogen</td>
</tr>
</tbody>
</table>
Figures 3(a) and (b) present the coefficient of friction as a function of temperature for 440C and 52100 steels, respectively, lubricated with pure TCP in a dry nitrogen atmosphere. The 440C curves exhibit multiple peaks in friction beginning at 220°C. The 52100 curves show initial sharp peaks in friction at approximately 230°C. It is interesting that these peaks occur in the same temperature range as the $T_f$ values obtained for 52100 steel with TCP in dry air. It is also noteworthy that 440C steel begins its multiple peak behavior near the temperature where the peak is found for 440C in dry air.

Squalene

The great majority of published work involving TCP deals with solutions in which TCP is a minor component (i.e., the solute). The coefficient of friction has not been
studied as a function of temperature over large temperature ranges for such solutions. To determine the behavior of TCP solutions, we chose a single compound as the solvent, one whose frictional behavior as a function of temperature could be carefully characterized. Figures 4(a) to (c) present friction-temperature curves for 440C, 52100, and M-50 steels, respectively, lubricated with pure squalene in dry air. The 440C curves in figure 4(a) contain no easily assignable \( T_r \) values, but the 52100 and M-50 steel curves do exhibit assignable values. The 52100 steel shows sharp decreases in friction at 203° and 208° C in figure 4(b). These temperatures were assigned as the \( T_r \) values for squalene lubricating 52100 steel in dry air. The M-50 behavior in figure 4(c) is similar, with \( T_r \) values assigned as 170° and 190° C.

Figures 5(a) and (b) present friction-temperature curves for squalene on 440C and M-50 steels, respectively, in dry nitrogen. Characteristic temperatures were assigned for these steels as follows: 440C as 155° and 160° C, and M-50 as 170° C for both curves.

3.45 Percent TCP in Squalene

Figure 6 presents friction-temperature curves for 3.45 percent TCP in squalene in dry air. Again the 440C steel (fig. 6(a)) exhibits multiple peaks without a significant decrease in friction assignable to \( T_r \). These multiple peaks occur in the temperature range 150° to 180° C, the same range where friction increased for pure squalene on 440C in dry air. In effect, the 3.45 percent TCP seems to have no effect on the friction of 440C steel in dry air. In contrast, 52100 steel (fig. 6(b)) exhibits a decrease in friction at assignable \( T_r \) values of 205° and 212° C. This is in the same temperature range as squalene alone but is also only about 10 degrees below the \( T_r \) values for TCP alone on 52100 steel in dry air (fig. 2(b)). It seems reasonable to suggest that the 3.45 percent TCP in squalene had no effect on the friction experienced by the 52100 steel in dry air, but the proximity of the pure-TCP \( T_r \) values makes this suggestion a tentative one. The M-50 steel (fig. 6(c)) exhibits a decrease in friction similar to that observed for squalene alone in figure 4(c) (i.e., \( T_r \) values of 175° to 180° C). These \( T_r \) values are in the same temperature range as squalene alone but well below the \( T_r \) values found for pure TCP (fig. 5(b)). This suggests that the 3.45 percent TCP has no observable effect on the friction experienced by M-50 steel. Figure 7 presents the curves for 3.45 percent TCP in squalene on M-50 steel in dry nitrogen. No \( T_r \) values were assignable and failure temperatures were 162° and 169° C. These temperatures matched very well with those for squalene alone (fig. 5(b)), an indication that the TCP did not affect the friction in this experiment.

Wear Volumes

Wear volumes for 52100 and 440C steels lubricated with TCP were determined. They are summarized in table II. The photographs from which the data in table II were gathered are presented in figures 8 and 9.

The temperatures used for the wear analysis were chosen on the basis of the friction-temperature curves in figures 2(a) and (b). The low temperature ranges were selected as representative of the lubrication before any dramatic change in the friction. The middle temperature ranges were chosen to be as close as possible to the first
Figure 6. - Coefficient of friction as a function of temperature for 440C, 52100, and M-50 steels under limited lubrication by 3.45 percent TCP in squalene in dry air. Each curve represents an independent experiment.

(a) 440C Pins sliding against 440C disks.
(b) 52100 Pins sliding against 52100 disks.
(c) M-50 Pins sliding against M-50 disks.

Figure 7. - Coefficient of friction as a function of temperature for M-50 pins sliding against M-50 disks under limited lubrication by 3.45 percent TCP in squalene in dry nitrogen. Each curve represents an independent experiment.

<table>
<thead>
<tr>
<th>Steel used</th>
<th>Temperature range, °C</th>
<th>Wear volume, cm³</th>
</tr>
</thead>
<tbody>
<tr>
<td>52100</td>
<td>168-172</td>
<td>55×10⁻⁸</td>
</tr>
<tr>
<td></td>
<td>229-231</td>
<td>14</td>
</tr>
<tr>
<td></td>
<td>329-336</td>
<td>1300</td>
</tr>
<tr>
<td>440C</td>
<td>167-170</td>
<td>120</td>
</tr>
<tr>
<td></td>
<td>234-237</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td>353-357</td>
<td>4700</td>
</tr>
</tbody>
</table>

*Each experiment was run for 15 min.

TABLE II. - WEAR VOLUMES USING PURE TCP IN DRY AIR*

minimum in friction (52100 steel) or just past the first peak in friction (440C steel). The high temperature ranges represent the failure portion of the curves. For both 52100 and 400C steel samples the lowest wear occurred in the middle temperature range and the highest wear at the failure temperatures.

The photographs of the wear scars show more severe striations in the 52100 steel at the low temperatures than occurred in the 440C steel. The 52100 sample also had some evidence of material transfer. The highest temperature photographs show the most severe wear for both 52100 and 440C steels.
Discussion of Experimental Results

One of the most striking features of the friction-temperature studies using pure TCP is the persistent occurrence of either failure temperatures or characteristic temperatures associated with a chemical reaction on the surface $T_r$ in the temperature range 220° to 230° C. Table III presents these data for the three steels.

In each case noted in table III the frictional behavior was smooth and regular until the temperature reached the 220° C range. At this point the friction either decreased at a characteristic temperature $T_r$ or failure occurred.
Faut and Wheeler (ref. 9) presented evidence that a chemical reaction occurs between TCP and M-50 steel to form a phosphate at $T_r$. It will be useful to compare the behavior of M-50 steel lubricated by TCP in dry air with the behavior of 440C and 52100 steels under the same conditions. The M-50 steel curves show a pronounced decrease in friction beginning at $T_r$. Any increase in friction occurring before final failure reached a maximum at friction values no higher than those observed before $T_r$. The 52100 steel curves exhibit a less
When the results of the experiments with characteristic temperature of the antiwear action of TCP steels were added to this analysis, a mean temperature of has been suggested (ref. 9) that temperature or the failure temperature. Indeed the protective films were formed in the dry air at temperatures slightly above atmosphere, not in the nitrogen atmosphere. For 44OC steel there was no Tn, only a failure temperature, 44OC, steel also may form a protective film. For 44OC steel the adsorbed lubricant film appeared to fail before the chemical reaction occurred to form the protective film. In effect, the chemical reactivity of TCP toward these steels seems to be of the order M-50 > 52100 > 44OC. The latter two are in the order suggested by previous investigators (refs. 6 and 7).

Comparing the friction behavior for TCP lubricating 440C and 52100 steels in dry air and in dry nitrogen confirmed the essential role of oxygen in forming the protective film at Tn. The dry air experiments produced assignable Tn values because a protective film formed on the metal surface, but the dry nitrogen experiments produced failure behavior in the same temperature range. The 440C steel also exhibits the effects of oxygen in figures 2 and 4. The dry air experiment with 440C steel produced a decrease in friction after the initial peak at 227°C, but the dry nitrogen experiments produced no such decrease.

The TCP did appear to form a protective film with each steel. For M-50 and 52100 steels this layer began to form at Tn. For 440C steel there was no Tn, only a failure in the same range. However, because the wear volume analysis indicated minimum wear just past the failure temperature, 440C steel also may form a protective film. The protective films were formed in the dry air atmosphere, not in the nitrogen atmosphere. Indeed the wear for both 52100 and 440C steels was significantly less at temperatures slightly above 230°C than at the lowest temperature or the failure temperature. On the basis of the behavior of TCP on M-50 steel, it has been suggested (ref. 9) that 220°C C is the characteristic temperature of the antiwear action of TCP.

223°C C with a standard deviation of 5 degrees was found. Therefore under limited lubrication conditions TCP will react with steel surfaces at 223°C ± 5°C. The use of this temperature for the limiting usefulness of TCP will vary with the hardness of the metal. All of the data used for temperature calculations were from steels with hardness between 55 and 60.

Friction can also vary with composition. It is reasonable to expect that the chemical reaction on the metal surface will be with iron, the major component of the steels. The 440C steel is the most questionable in this regard because it has a high chromium content. However, Ferrante (ref. 16) has shown that the surface of 440C steel is composed of iron oxides up to about 700°C. (After 700°C C the chromium oxides become the major surface material.) Therefore we can expect any chemical reaction between TCP and the steels to be essentially a reaction with iron or iron oxides.

The friction-temperature behavior for squalene lubricating 52100 and M-50 steels in air exhibits assignable Tn values. If these temperatures are correctly assigned to the occurrence of a chemical reaction between the lubricant and the metal surface, some type of reaction must also occur between the squalene and the steel surface. It is well known (refs. 17 and 18) that hydrocarbon lubricants can react with oxygen to form a variety of compounds including carbonylels and alcohols. The squalene has six tertiary hydrogen atoms in its structure that will be particularly reactive as compared with secondary and primary hydrogen atoms (ref. 19). Therefore reaction with oxygen should be easier for squalene than for unsubstituted straight-chain hydrocarbon lubricants. The presence of assignable Tn values is most likely due to oxidation products of squalene reacting with the steel surfaces. The 440C steel was not sufficiently reactive to allow measurable reaction; this is in accord with the behavior already discussed for TCP. The lubrication by squalene in dry nitrogen atmosphere did not result in measurable Tn values, as would be expected if oxidation products were reacting with the steel.
When TCP is used as an additive in liquid lubricant systems, it is usually present in concentrations below 10 percent, frequently less than 5 percent. Using TCP as an additive reduces wear (refs. 5, 10, 11, 20, and 21), but not friction (refs. 10 and 12) although Wiegand and Broszeit (ref. 11) have observed a reduction in friction as a function of load for 1 percent TCP in paraffin. The presence of 3.45 percent TCP in squalene did not result in any significant difference in friction from that with squalene alone. The ability of the oxidation products to react with the metal surface apparently obscured any reaction by the smaller amount of solute (TCP). The observations of Weigand and Broszeit are not in conflict with this suggestion if the paraffin solvent used by them contained no tertiary hydrogen atoms. The secondary hydrogen atoms necessarily present in any unsubstituted straight-chain hydrocarbon molecules react with greater difficulty than the tertiary hydrogen atoms. The reactivity of TCP would then be stronger than the reactivity of oxidation products of the solvent and thereby produce a decrease in the friction.

The TCP mechanism suggested by the preceding analysis can be summarized as follows: TCP is adsorbed onto the surface of the steel. The adsorbed layer undergoes limited reaction with the surface until \( T_r \) is attained. Then the TCP is either desorbed, leading to a failure behavior as in 440C steel, or reacts with the surface, leading to a decrease in friction and an assignable \( T_r \) value, as with M-50 and 52100 steels. The reaction with 52100 steel is sufficiently limited to allow the desorption of the TCP from the reacted layer to influence the friction (i.e., to produce the peak in friction immediately after the \( T_r \) behavior). The TCP continues to react with the surface to form a protective coating. Failure occurs when the liquid film is exhausted and the protective layer has worn through.

The fact that \( T_r \) occurs within a very narrow temperature range for the three steels points to a lack of sensitivity by the TCP for the surfaces. However, it is known that all three steels present iron oxide surfaces to the lubricant at the temperatures studied, and the narrow temperature range can be expected. The next step is an examination of an iron surface with TCP adsorbed onto it. A detailed examination of this type is currently in progress.

**Conclusions**

The following conclusions can be drawn from our study of the friction and wear of 440C, 52100, and M-50 steels lubricated with TCP, 3.45 percent TCP in squalene, and pure squalene as functions of temperature:

1. Tricresylphosphate (TCP) reacts with 52100 steel in dry air to form a protective film. This reaction begins at 220° C, the assignable characteristic temperature \( T_r \), which is almost the same as the \( T_r \) value for TCP reacting with M-50.

2. TCP reacts with 440C steel in dry air to form a protective film but only after the adsorbed TCP film is ruptured. There is no assignable \( T_r \) value because the friction peaks at 227° C.

3. TCP reacts with M-50, 440C, and 52100 steels under limited lubrication conditions in dry air at 223°±5° C. The reaction temperature is independent of the steel composition.

4. The presence of 3.45 percent TCP in squalene has no discernible influence on friction as a function of temperature for M-50, 440C, or 52100 steels in dry air.

5. Squalene exhibits characteristic temperatures that are sensitive to the steel surface. The 440C steel shows no assignable \( T_r \) value, 52100 steel has a \( T_r \) of 205° C, and M-50 steel has a \( T_r \) of 180° C. The reaction with the surface is attributed to oxidation products of squalene generated at the tertiary hydrogen sites in the molecule.

6. TCP does not react with 440C steel in dry nitrogen; failure behavior was observed at 220° C. TCP-lubricated 52100 steel exhibits a sharp peak in friction in dry nitrogen. Squalene-lubricated 440C fails very early in dry nitrogen, at 70° C; M-50 steel fails at 170° C.

7. Wear volume measurements demonstrate that the lowest wear for limited TCP lubrication of 440C and 52100 steels is achieved in the 229° to 237° C temperature range.

8. Oxygen is essential for the reaction of TCP with both 52100 and 440C steels.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, October 13, 1983

**References**


The coefficient of friction was measured as a function of temperature on a pin-on-disk tribometer. Pins and disks of 440C and 52100 steels were lubricated with tricresylphosphate (TCP), 3.45 percent TCP in squalene, and pure squalene. M-50 pins and disks were lubricated with 3.45 percent TCP in squalene and pure squalene. Experiments were conducted under limited lubrication conditions in dry (<100 ppm H2O) air and dry (<20 ppm H2O) nitrogen at 50 rpm (equivalent to a sliding velocity of 13 cm sec−1) and a constant load of 9.8 N (1 kg). Characteristic temperatures \( T_r \) were identified for TCP on 52100 steel and for squalene on M-50 and 52100 steels, where the friction decreased because of a chemical reaction between the lubricant and the metal surface. The behavior of squalene obscured the influence of 3.45 percent TCP solute on the friction of the system. Wear volume measurements demonstrated that wear was lowest at temperatures just above \( T_r \). Comparing the behavior of TCP on M-50, 440C, and 52100 steels revealed that the TCP either reacted to give \( T_r \) behavior or produced initial failure in the temperature range 223±5°C. The 440C steel yielded a peak in friction; the 52100 and M-50 steels had assignable \( T_r \) values in this temperature range. Oxygen was essential for the reaction of TCP with the metal surface.
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