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THE EFFECT OF TRICRESYL-PHOSPHATE (TCP) AS AN ADDITIVE ON WEAR OF IRON (Fe)

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SUMMARY

The present study investigates the effect of tricresyl phosphate (TCP) as an antiwear additive in lubricant trimethyl propane triheptanoate (TMPTH). The objective of this study was to combine examinations of: surface analysis, wetting, chemical bonding changes, and wear rate through steploading.

The investigation consisted of steploading wear studies by a pin on disk tribometer, the effects on wear related to wetting by contact angle and surface tension measurements of various liquid systems, the chemical bonding changes between lubricant and TCP chromatographic analysis, and by determining the reaction between the TCP and metal surfaces through wear scar analysis by Auger emission spectroscopy (AES).

The steploading curve for the base fluid alone shows rapid increase of wear rate with load. The steploading curve for the base fluid in presence of 4.25 percent by volume TCP under dry air purge has shown a great reduction of wear rate with all loads studied. It has also been found that the addition of 4.25 percent by volume TCP plus 0.33 percent by volume water to the base lubricant under N₂ purge also greatly reduces the wear rate with all loads studied. AES surface analysis reveals a phosphate type wear resistant film, which greatly increases load-bearing capacity, formed on the iron disk. Preliminary chromatographic studies suggest that this film forms either because of ester oxidation or TCP degradation. Wetting studies show direct correlation between the spreading coefficient and wear rate.

INTRODUCTION

Lubricants are those materials which are used to reduce friction and wear. In most applications such as automobile engines the base lubricant is not sufficient to give a long life. In order to reduce wear, additives must be included in the lubricants. In many applications the wear reduction mechanisms for these additives are not well known.

One such common antiwear additive is tricresyl phosphate (TCP). Much scientific effort has been devoted to understanding how TCP interacts with metal substrates, and, thus, lubricates their surfaces (refs. 1 to 18).

These studies suggest that the antiwear protection afforded by TCP results from the formation of a reaction film on the rubbing surfaces of the metals. Generally, these reaction films are composed of a number of metal phosphates or phosphides. A number of studies involve the use of surface analysis (ref. 19) to examine the surface composition. We perform step-loading studies (wear rate versus load) in order to establish the wear effectiveness of TCP and to define the operating conditions where surface films are formed. Auger electron spectroscopy (ref. 19) is used to examine surface composition.

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To answer this question, three objectives, and the ways in which they will be accomplished are listed:

- (1) To study the effect of step loading wear for the following solutions:
 - (a) Liquid lubricant, trimethyl propane triheptanoate (TMPH) by itself
 - (b) Liquid lubricant (TMPH) in the presence of 4.25 percent TCP by volume
 - (c) Liquid lubricant (TMPH) in the presence of 4.25 percent by volume, 0.33 percent by volume of water
 - (d) Liquid lubricant (TMPH) in the presence of 0.33 percent water

All solutions were examined under inert nitrogen atmosphere purge, under dry air purge, and under a room air with varying loads. A 0.33 percent water miscibility was determined experimentally. Wear studies were run at 2 percent by volume of TCP, at 4.25 percent by volume of TCP and at 10 percent TCP by volume. A concentration of 4.25 percent TCP was chosen since it gave the lowest wear rate of the concentrations examined. The wear studies were performed with a pin-on-disk tribometer.

- (2) To investigate the effects on wear of related physical properties.

Physical properties of the lubricant such as surface tension, contact angle between the metal and the lubricant solutions, were measured. Liquid chromatographic analysis on TCP-lubricant systems were also examined to examine if any chemical bonding changes in the base lubricant occurred as a result of adding TCP.

- (3) To determine reactions between the TCP, and the metal surfaces.

Wear scars were analyzed for the presence of phosphorous compounds, by Auger emission spectroscopy (AES).

MATERIALS AND MATERIAL PREPARATION

Materials used in this investigation were trimethyl propane triheptanoate (TMPH), a polyol ester and tricresyl phosphate (Fisher Scientific Company Technical grade T-342) consisting of 80 percent para TCP and 20 percent meta TCP.

The following solutions were used:

- (1) Lubricant TMPH alone
- (2) Lubricant in the presence of 0.33 percent by volume of distilled water
- (3) Lubricant plus 4.25 percent TCP by volume
- (4) Lubricant plus 4.25 percent TCP by volume and 0.33 percent by volume of distilled water.

The glassware used in the preparation of these solutions was first cleaned with hot water and soap, and then rinsed with hot tap water and rinsed six times with distilled water, and finally, rinsed three times with acetone and dried in an oven for 2 hr at 110 °C.

Solutions were mixed at room temperature for 3 hr. The solutions were then stored in brown bottles to eliminate possible light-induced degeneration.

The pin and disk used were pure iron and M₂ tool steel, respectively. The pure iron pin (less than 0.1 at % impurities) was given a final polish with 10 μm alumina. The pin was then annealed in a vacuum furnace above the recrystallization temperature and cooled slowly in order to give a uniform hardness for all of the pins. This procedure gives reproducible wear measurements to ±15 percent (ref. 2). The disk was lap ground and given a 600 μm SiC final polish. This material combination was selected to guarantee wear on the much softer pin and not on the hard disk and to have a simpler system chemically (i.e., pure Fe).

TEST APPARATUS AND PROCEDURE

The wear studies were performed with a pin-on-disk tribometer apparatus shown in figure 1. This friction-and-wear apparatus was enclosed in a plexi-glass box which could be purged with dry air or nitrogen.

The angular speed of the M₂ tool disk was determined by reducing the speed until the friction coefficient rose and saturated at the lowest load, thus guaranteeing operation in the boundary lubrication region. The wear experiment was then performed by sliding an annealed 99.9 percent pure iron pin with a hemispheric tip of radius 0.476 cm on the hardened steel disk. Pin loads varying between 0.5 and 5.5 kg were applied by a pulley system. For each run of the experiment and for each of the four solutions, an unworn position of the pin and a different track on the disk were used. The lubricant was applied to the disk surface at a flow rate of approximately 0.5 ml/min, consequently constantly supplying fresh lubricant. The disk was completely covered with lubricant before initiating the test.

To study chemical changes in the liquid 40 to 50 ml samples of each solution were collected following wear studies at each load (from 0.5 to 5.0 kg). One sample of each was collected at 40 to 41 min; another was collected at 82 to 83 min. The first sample did not show much change under low loads; so the samples taken at 82 to 83 min were tested for surface tension, contact angle, and liquid chromatographic effects only at 5.0 kg.

The humidity was controlled by placing a desiccator in the plexiglass box and by purging with dry air or dry nitrogen at a positive pressure. The percent humidity saturated at a minimum of 10 to 16 RH as measured with a humidity stat., the wear experiments were initiated at this point. Wear volume was calculated from the pin wear scar diameters. Typical wear versus sliding distance curves at 5 kg load are shown in figure 2. The portion of the curve following run in was fitted to a straight line in order to determine wear rate (cm³/cm). This procedure was repeated for each load and each condition in an independent test. Then a plot of wear rate versus load was determined for each lubricant mixture and at each atmospheric condition.

Frictional force was measured by a strain gauge and was recorded on a strip chart as a function of time. The strain gauge was calibrated by hanging fixed weights by way of a pulley.

Surface tension was measured by an apparatus consisting of a 6.001 cm (circumference) platinum wire that was loaded with a spring and mounted above the balance (top loader). The lower tip of this wire rested in the lubricant held in a petrie dish on the disk. As this wire was slowly drawn from the lubricant in the dish it "popped" from the fluid at some specific point. The amount of weight that it had taken to release the platinum was used to determine the surface tension for each solution. The error for this method, established by multiple repetitions, was determined to be less than 1 percent.

Contact angle measurements were made from photographs of samples taken on the ground-and-lapped tool steel surface. The photographs were taken in the interval between 4.5 and 5.5 sec after initial contact, the rapid spreading of the lubricant on the steel surface made readings after this point difficult. The error of estimate is between 1 to 3 percent. This was considered acceptable as our main concern was to use this data in order to establish a relative spreading coefficient for the various lubricant/additive mixtures.

A Waters model 244 liquid chromatograph was used for chromatographic analysis of neat lubricants with varying percent of TCP. This liquid chromatographic instrument was used in combination with either an ultraviolet (UV) absorbance detector and differential refractive index (RI) detector, or with a refractometer. The UV detector monitors absorbances at a wavelength of 254 nm, at sensitivities ranging from 0.005 to 2.0 absorbance units, full scale (AUFS). The purpose of this study was to determine whether reactions between the lubricant and additive had taken place and whether changes in lubricant structure had taken place following wear. In order to examine the reaction of the TCP with the pins, wear scars were analyzed by Auger emission spectroscopy (AES). Following the wear test, the samples were mounted in an ultrahigh vacuum system with a base pressure of 1×10^{-10} torr. The wear scars were, next, AES analyzed by a standard cylindrical mirror analyzer with an integral electron gun operated at 2 keV beam energy, a beam current of 1 μ A, and a 25 μ m nominal electron beam diameter. In addition to AES analysis, the wear scars were depth profiled; i.e., AES analysis and ion bombardment were done simultaneously. The ion beam was operated with a 3 keV argon ion beam energy and a 5 μ A beam current with a nominal 2 mm (spot) diameter.

RESULTS AND DISCUSSION

We now proceed to discuss the results of the wear studies. In figure 3, we plot wear volume versus load times sliding distance for each condition. An interesting result is that each curve for the wear volume versus load times distance are close to linear. This result is consistent with the Archard wear equation (ref. 20). The Archard equation is the relation generally used to describe adhesive wear which we might assume to be the dominant wear mechanism in the boundary lubrication region. The fact that the presence of TCP greatly reduces the wear volume indicates that it is intervening in such a way to reduce the occurrence of an adhesive contact consistent with the Archard model.

Wear Volume

Another interesting feature of figure 3 is that the absolute volume worn reflects the same relative trends as the wear rate. First all curves without TCP showed a significantly higher wear volume than with TCP. Figure 3 shows that the lubricant solution with 4.25 percent TCP, had a wear volume that was significantly less under dry air than under N₂ purge with TCP. The lubricant plus TCP plus water curve shows an unexpected reduction of wear volume, with load, under N₂ purge relative to the nitrogen plus TCP curve. Reduction in wear may be caused by the oxygen in the water facilitating whatever reaction is taking place with the dry air results. The wear volumes for no TCP with different atmospheres give approximately the same wear volumes. Surprisingly, the N₂ plus water curves show an increased wear volume over these. At this point it is not clear why this should be the case.

Wear Rate

The principle result of the present paper is shown in figure 4. Here we have plotted the wear rate versus load for each load, atmospheric, and additive combination. The curves are only included as a guide to the eye. Each point in the plot is difficult to obtain, since each requires obtaining the wear rate from a wear volume versus sliding distance curve (fig. 2). The effects of the TCP on the wear rate are quite clear. The base fluid step loading curve shows a rapid increase in wear rate with load. The addition of TCP with a dry nitrogen shows a great reduction of wear at lower loads and then a breakdown of antiwear effect and a return to a wear condition with approximately the same slope as the no additive curve. We see a similar result with dry air except the load-bearing capacity is substantially increased. The addition of water gives a large reduction in wear rate over the base fluid but with a higher initial wear rate than the dry air or nitrogen.

A principal objective of this study was to combine surface analysis with the step loading studies, revealing a different composition of wear resistant films in the low and high wear regimes. The wear rate results (fig. 4) clearly suggest that reaction films are formed which greatly increase the load bearing capacity of the contact.

The dry nitrogen versus dry air results suggest that the presence of oxygen alters film composition, possibly from a phosphide to a phosphate, which further improves the load bearing capacity. The addition of water, which is included since it is often present in real lubrication situations, also creates differences in load bearing capacity. The somewhat higher wear rate is possibly due to a competing corrosive wear component caused by a reaction between the TCP and the water forming an acidic component. Figure 5 shows an average wear rate bar curve for various lubricant systems at 5 kg load.

In figure 6, we shown the AES spectrum for several additive load and ambient atmosphere conditions. Figure 6(a) shows a typical spectrum over the entire energy range with TCP. This spectrum was taken at a 5 kg load and a dry air atmosphere. In figure 6(b), we show the low energy spectrum for the same conditions. In figure 6(c), we show the low energy spectrum for TCP, 1.2 kg load, and dry air. In figure 6(d), we show the low energy spectrum for TCP, 1.2 kg load, and dry nitrogen. The lower energy part of the spectrum is emphasized, since the phosphorus and low energy iron peak shapes give chemical

information. These peak shapes are similar to those obtained by Murday and Shafrin (ref. 1) for iron phosphate.

The various spectra show that the surface contains an iron phosphate under each load and atmosphere conditions. This is surprising since little air was present with the nitrogen purge. This suggests that the phosphate in the TCP or oxygen present as an oxide on the surface are critical components. The ambient oxygen atmosphere is important, since the load bearing capacity is lower in the nitrogen atmosphere than with air (fig. 4). The high load spectrum taken at 5 kg where the in air wear starts to increase still shows a phosphate film. Consequently, at this point, we do not see a chemical difference in the AES spectrum where the load bearing capacity changes in figure 4.

In figure 7 we show a depth profile for TCP, 1.2 kg load and dry air, this profile gives the rather surprising result that no thick film is present on the surface in the low wear rate region. This is contrary to the results of Ferrante and Brainard (ref. 2) who observed thick reaction films with zinc-dialkyl-dithiophosphate as an additive in a mineral oil base stock. The depth profile result leads to some interesting speculations. The lack of a thick phosphorous containing films suggests that either the TCP works through a true monolayer mechanism to reduce wear or that protective films are formed which shear readily. The latter could be established by collecting wear debris and determining its composition. These results are preliminary and further studies should be performed including the effects of varying TCP concentration. Since a flowing lubricant system was used with the lubrication, it may be necessary to perform the experiment with a fixed reservoir of lubricants in order to optimize the amount of wear debris per unit volume.

It is interesting to compare these results with other similar tests with TCP. The Godfrey (ref. 7) study of TCP-white mineral oil base stock indicates that TCP reduces wear by formation of iron phosphate film on Fe-surfaces. The presence of iron phosphate has been shown by electron diffraction analysis and molybdate titration tests.

Bieber, Klaus, and Tweksbury (ref. 8) studied wear improvement behavior by increasing transition loads in presence of TCP in mineral oil and ester base fluids. They concluded that the antiwear behavior in the finished lubrication formation appears to be due to acid phosphate impurities of intermediate polarity in the TCP. The TCP acted as a reservoir for the formation of polar impurities during the life of the lubricant.

Cho and Klaus (ref. 13) studied mineral oil and phosphate ester based lubricants with and without additive packages. They evaluated oxidation of phosphate esters based on reaction rate and product analysis. Their findings show that aryl phosphate esters have more oxidative stability. It can be inferred from Cho and Klaus' study that addition of TCP to the polyol based esters can improve oxidative stability.

Goldblatt and Appledoorn (ref. 14) have performed similar studies to the present work with TCP in air and inert atmosphere with and without moisture present and with different base stocks. The base stocks varied between aliphatic and aromatic. The ester in the present study was most similar to the aliphatic oils but not precisely the same. These authors were sliding at much higher speeds. In addition, Goldblatt and Appledoorn used 52100 steels in a four-ball tester and a ball on a cylinder study, which is much harder than the

present annealed iron bullet. We compare wear test results only, since scuffing was not observed in the present study. Also, Goldblatt and Appledoorn's observed wear scar diameter, rather than wear rate. Their wear scar diameter results were similar to our wear volume results.

As in the present study, wear was related to atmosphere and moisture content. We found that TCP improved the load bearing capacity of the aliphatic lubricant. Goldblatt and Appledoorn agree that the primary antiwear protection came from the phosphate. Moisture had a slightly detrimental effect, possible due to corrosive wear, as in the present result. Similar to the present results, in an inert atmosphere TCP still had a beneficial effect. However, we found that the presence of oxygen seemed to have an important effect on the load bearing capacity of the film. Goldblatt and Appledoorn have evidence for film formation through electrical contact measurements. Their results indicate that a poorly adherent phosphate film may be present, since a monolayer film would not give appreciably different contact resistances from the metal surfaces. Although Goldblatt and Appledoorn's tests were somewhat different, their findings agree for the most part with the present study.

M. Kawamura and K. Fujita (ref. 18) have recently investigated lubrication properties of a series of organic sulfur and phosphorous compounds (including TCP) as additives in a paraffinic base oil. The additive concentration level used in the base lubricant was approximately the same range as in the present study. Kawamura and Fujita found that the additives react with sliding metal surfaces, forming a surface film of phosphates or phosphite, perhaps by adsorption. Their study shows that a surface film of phosphates or phosphites reduces wear, as has been found in our present study.

Next we would like to consider some wear and surface treatment studies where TCP was used along with surface analysis. Yamamoto and Kirano (ref. 15) examined friction and scuffing with pure TCP and TCP in paraffin base stocks using a carbon steel. Arezzo (ref. 17) and Murday and Shafrin (ref. 1) did "oil aging," or presoaking, studies on 52100 steel. Yamamoto and Hirano used a ball ring apparatus for their measurements. They concluded that wear and scuffing protection are obtained by formation of a protective film. Interestingly, they also found that the friction coefficients are also roughly independent of load, as we found in the present study. They also identify that the surface film is composed of FePO_4 after rubbing.

F. Arezzo (ref. 17) in his aging studies also found phosphates present on the surface of the 52100. Additionally, he found that aromatics present on polar compounds competed with the TCP for available adsorption sites on the steel surface. He also found that the composition of the surface film contained only 5 at % phosphorous. This is lower than would be expected from pure phosphate (FePO_4) - which would be 16 at %. Murday and Shafrin (ref. 1) also found that a surface film formed, as shown by AES. Their concentration was characteristic of a phosphate with a 4 to 6 at % phosphorus concentration, which was also lower than expected from the pure compound. This is less significant than in the XPS studies, since AES is, at best, semi-quantitative. Murday and Shafrin make an interesting point from their AES depth profile. This is that an exponential fall off of concentration with depth is indicative of monolayer films; whereas a plateau in the profiles indicates thicker films. In the present study (fig. 7) the fall off of the phosphorous peak was exponential, indicating, at best, a thin film. A quantitative

evaluation of the surface composition is not possible because of the roughness of the wear surface (ref. 19).

The effectiveness of TCP as an antiwear additive in lubricants, due to surface wetting phenomena, was also studied. This experiment included the measurement of interfacial wetting between solid and liquid components. Wetting is defined as the formation of solid liquid interface when solid substrates and a liquid come in contact. If the addition of TCP enhances wetting of the surface it would contribute to reduction in wear. On solid substrates various types of wetting reactions have been observed. They are the following:

- (1) No attachment (between liquid and solid)
- (2) Loose liquid attachment
- (3) Partial surface spreading and wetting
- (4) Complete spreading and wetting
- (5) Absorption of the liquid into the solid (see fig. 8)

Types of wetting are determined by energy changes taking place when the lubricant solutions come in contact with the iron pin and disk. These energy changes are related, and determined by, contact angle and interfacial tension (see fig. 8). Interfacial tension (symbol γ , fig. 7) in this study is defined as the work done in extending the area of a liquid surface 1 cm².

Zisman (ref. 21), and others (refs. 22 to 26), have studied the relation between the contact angle of a solid-liquid interface and the work of adhesion (W_A) and cohesion (W_C). Several equations have been used to describe these relationships. The equations used for this study are the following:

$$\gamma_{SV} \approx \gamma_{SL} + \gamma_{LV} \cos \theta \quad (1)$$

$$W_A \approx \gamma_{LV} (\cos \theta + 1) \quad (2)$$

$$W_C \approx 2\gamma_{LV} \quad (3)$$

$$*S \approx W_A - W_C \quad (4)$$

where γ_{SV} , γ_{LV} , and γ_{SL} are free energies per square centimeter of the solid-vapor, liquid-vapor, and solid-liquid interfaces, i.e., their surface tensions. W_A is the work of adhesion, i.e., the work required to separate the liquid from a solid of 1 cm² in cross section. W_C is the work of cohesion, i.e., work done in pulling apart a column of liquid, made up of two layers of the same liquid 1 cm² in cross section. θ is the contact angle and S is the spreading coefficient. The most useful equations are (2) and (4), as they contain only measurable quantities.

Table I summarizes the relationship between surface chemical changes and wear rate of neat lubricant, and lubricant with 4.25, 10, and 45 percent of TCP. This table shows the adhesion-cohesion relation of various lubricant combinations. The surface tension, contact angle, and spreading coefficient changes with the increased concentration of TCP containing lubricants. The table also shows that the wear rate is minimized by the solution containing the

lubricant and 4.25 percent TCP by volume, under both dry air and N₂ purge. This correlates with the surface chemical properties of surface tension and contact angle. Moreover, when 4.25 percent TCP is added to the lubricant, the work of adhesion also reaches a maximum, indicating that complete spreading wetting is occurring (see table I).

It is most important to determine whether the TCP is coating the surface of the pin and disk by adsorption or by chemical reactions between TCP and Fe. AES analysis indicates that a phosphate is formed on the surface of the pin. Depth profiles suggests they are not thick films (i.e., hundreds of angstroms). Although it has demonstrated that surface chemical changes accompany reduction in wear rates, the nature of the surface film cannot be understood from this study alone. At this time it can only be said that TCP binds with the lubricants and may create an interfacial bonding layer by reaction with the surface.

One method by which TCP may be involved in forming antiwear surface coating was found from preliminary liquid chromatograph analyses. These analyses indicate that there is a molecular weight increase in the base lubricant indicated by the detection of new UV absorbance peaks in the TCP-containing lubricants as shown in figure 9. These analyses also indicate that there is very little UV absorbance due to lubricant, but most of the UV absorbance is due to TCP. It can be said that a noticeable amount of change of UV absorbance could be due to ester-oxidation or TCP degradation giving the needed phosphate.

CONCLUSIONS

The results of this investigation into the effects of TCP as an antiwear additive in ester lubricants permits the following conclusions:

1. The steploading curve for the base lubricant alone shows a direct increase of wear rate with load.
2. The steploading curve for the base lubricant plus 4.25 vol % by TCP under a dry air purge and base lubricant plus 4.25 TCP with and without plus 0.33 percent water under N₂ purge shows a great reduction of wear rate with all loads studied.
3. AES surface analysis reveals that a thin phosphate formed on the iron disk. Preliminary chromatographic studies suggest oxidation of the ester occurs due to TCP degradation.
4. Wetting studies show a direct correlation between the spreading coefficient and wear rate indicating that wetting of the surface is improved at the TCP concentration which minimizes wear rate.

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TABLE I. - ADHESION-COHESION RELATION OF VARIOUS LUBRICANTS FOLLOWING WEAR AT 5.0 kg LOAD

Percent TCP by volume	Surface tension	Contact angle	Wear rate, $\times 10^{-10}$		Work of adhesion	Work of cohesion	Spreading coefficient
			Under air	Under nitrogen			
0	31.8	12.2	11.3	4.9	62.9	63.6	-0.7
4.25	31.0	8.9	1.3	2.8	61.6	62.0	-.4
10.00	33.0	9.8	3.4	3.6	65.5	66.0	-.5
45.00	34.6	14.7	8.5	10.3	68.1	69.2	-1.1

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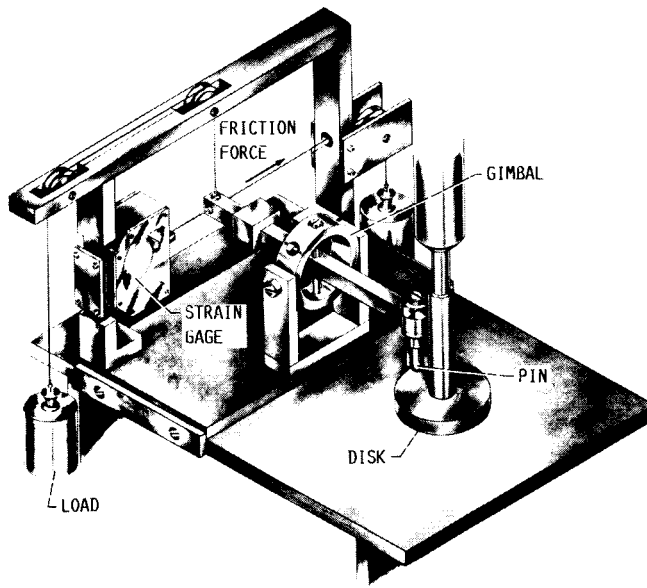


FIGURE 1. - FRICTION AND WEAR TRIBOMETER.

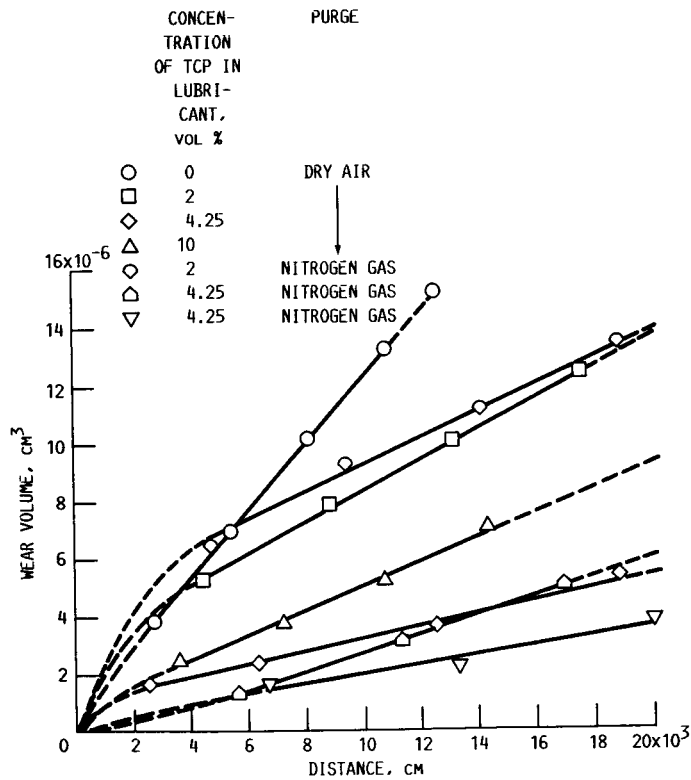


FIGURE 2. - WEAR VOLUME VERSUS SLIDING DISTANCE FOR VARIOUS CONCENTRATIONS OF TRICRESYL PHOSPHATE (TCP) IN LUBRICANT AT VARIOUS LOADS UNDER DRY AIR AND NITROGEN.

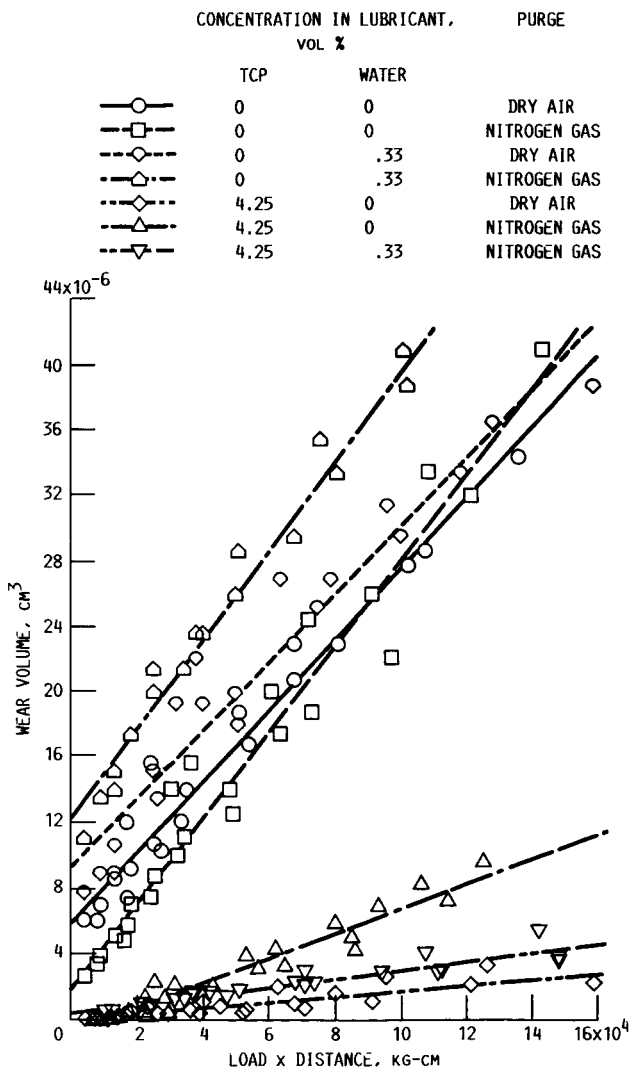


FIGURE 3. - WEAR VOLUME VERSUS LOAD TIMES DISTANCE FOR VARIOUS CONCENTRATIONS OF TRICRESYL PHOSPHATE (TCP) IN LUBRICANT UNDER VARYING CONDITIONS.

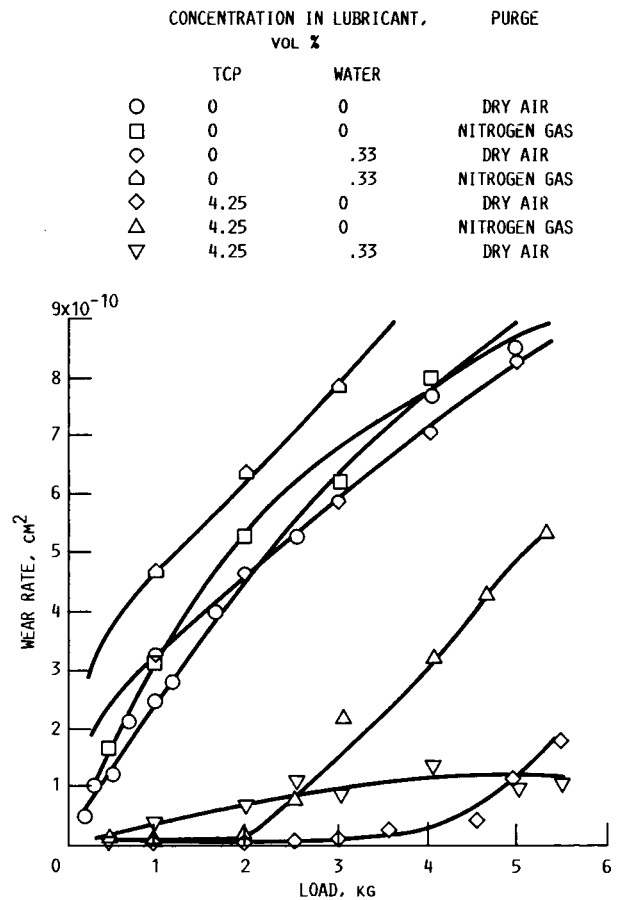


FIGURE 4. - WEAR RATE VERSUS LOAD FOR VARIOUS CONCENTRATIONS OF TRICRESYL PHOSPHATE (TCP) AND WATER IN LUBRICANT UNDER ATMOSPHERIC VARYING CONDITIONS.

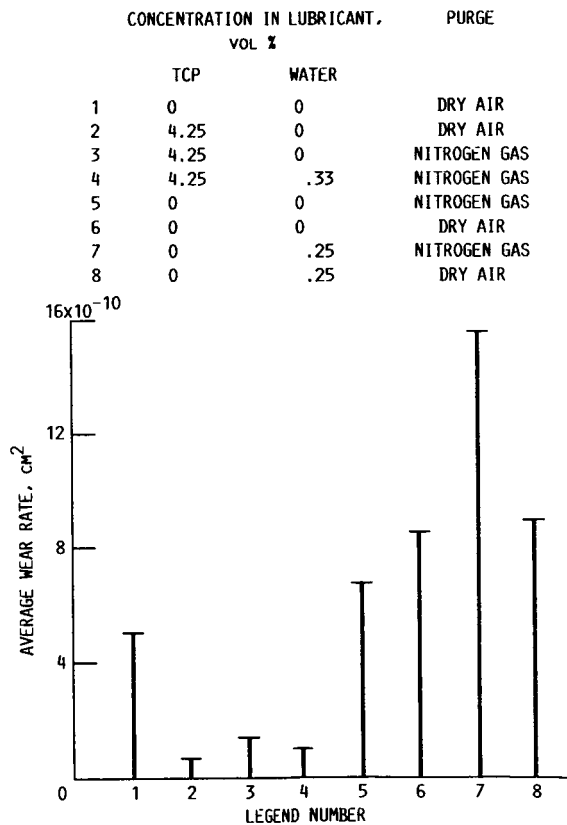
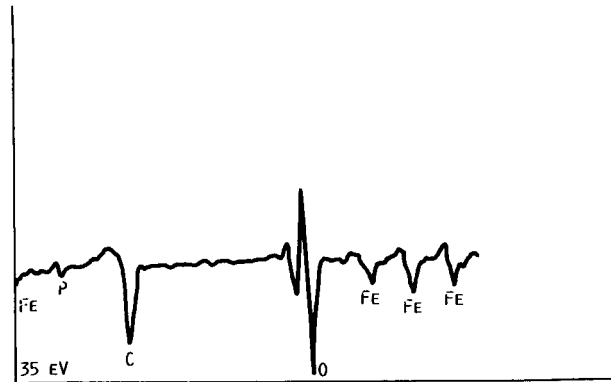
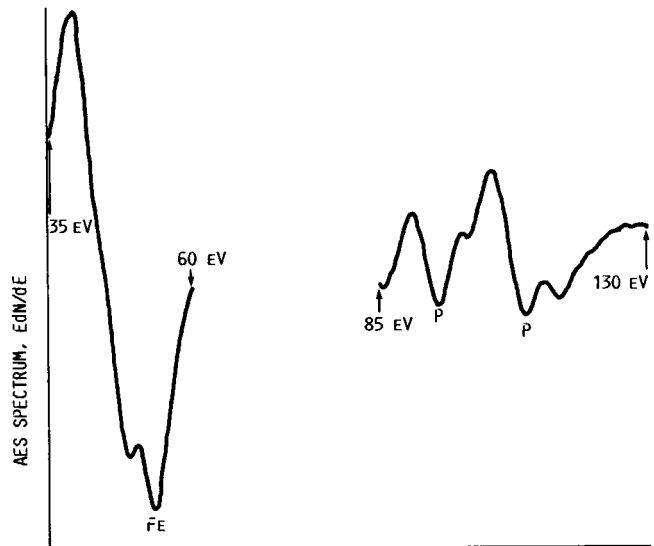


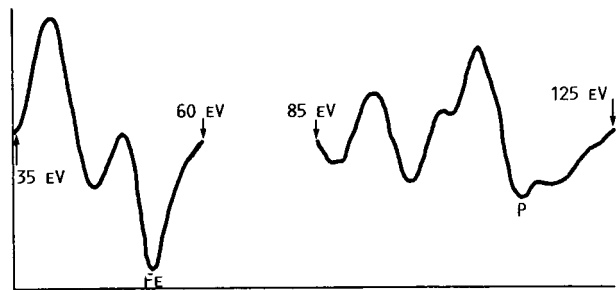
FIGURE 5. - AVERAGE WEAR RATE FOR VARIOUS LUBRICANTS, LOAD, 5 KG.



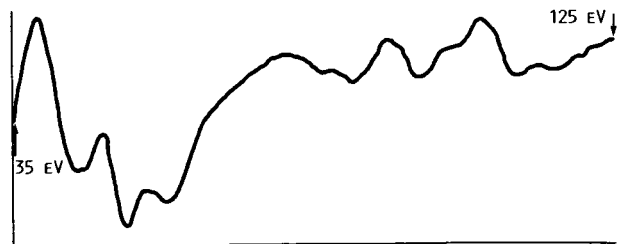
(A) TOTAL AES SPECTRUM; 5-KG LOAD; DRY AIR.



(B) LOW-ENERGY AES SPECTRUM; 5-KG LOAD; DRY AIR.



(C) LOW-ENERGY AES SPECTRUM; 1.2-KG LOAD, DRY AIR.



(D) LOW-ENERGY AES SPECTRUM; 1.2-KG LOAD; DRY NITROGEN.

FIGURE 6. - TOTAL AND LOW-ENERGY AES SPECTRA OF LUBRICANT WITH TCP ADDITIVE UNDER TWO DIFFERENT LOADS IN TWO DIFFERENT ATMOSPHERES.

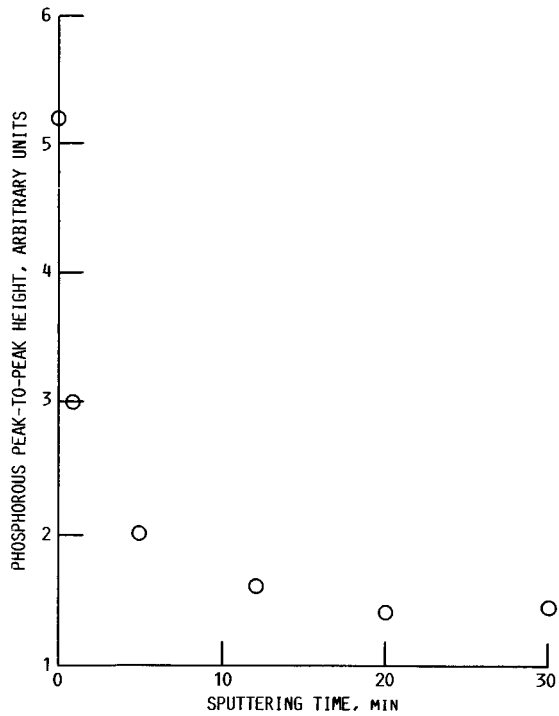


FIGURE 7. - AES DEPTH PROFILE OF LUBRICANT WITH TCP ADDITIVE. LOAD, 1.2 KG; PURGE, DRY AIR.

REGION	CONTACT ANGLE RANGE OF REQUIREMENT, DEG	MAXIMUM W_A , (EQ. (2)), DYN/CM	SKETCH
NONATTACHMENT	150 - 180	0.13γ	
ATTACHMENT	90 - 150		
PARTIAL WETTING AND SPREADING	30 - 90	1.87γ	
COMPLETE SPREADING AND WETTING	0 - 30	$\approx 2 \gamma$	
ADSORPTION PROCESS AND WETTING	0	$\geq 2 \gamma$	

FIGURE 8. - MODEL OF TYPES OF WETTING.

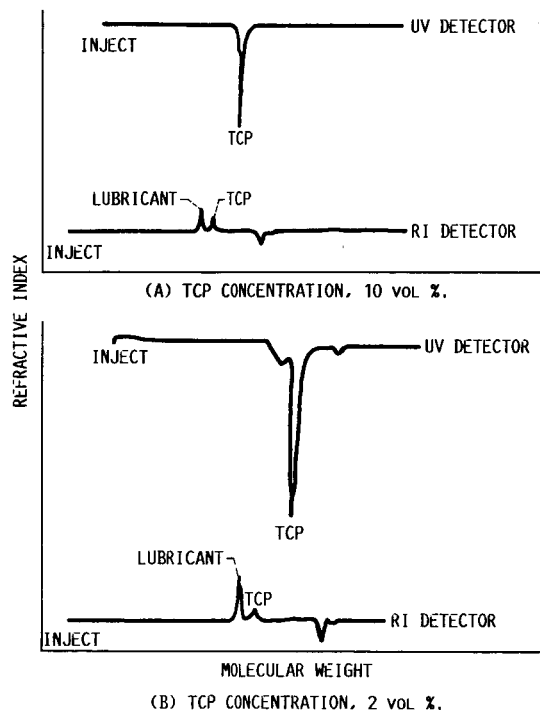


FIGURE 9. - LIQUID CHROMATOGRAPHIC ANALYSIS OF TCP IN LUBRICANTS.

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15. Supplementary Notes Hiren M. Ghose and Frank S. Honeyc, NASA Resident Research Associates; John Ferrante, NASA Lewis Research Center.					
16. Abstract <p>The present study investigates the effect of tricresyl phosphate (TCP) as an antiwear additive in lubricant trimethyl propane triheptanoate (TMPH). The objective of this study was to examine step loading wear by use of surface analysis, wetting, and chemical bonding changes in the lubricant. The investigation consisted of steploading wear studies by a pin on disk tribometer, the effects on wear related to wetting by contact angle and surface tension measurements of various liquid systems, the chemical bonding changes between lubricant and TCP chromatographic analysis, and by determining the reaction between the TCP and metal surfaces through wear scar analysis by Auger emission spectroscopy (AES). The steploading curve for the base fluid alone shows rapid increase of wear rate with load. The steploading curve for the base fluid in presence of 4.25 percent by volume TCP under dry air purge has shown a great reduction of wear rate with all loads studied. It has also been found that the addition of 4.25 percent by volume TCP plus 0.33 percent by volume water to the base lubricant under under N₂ purge also greatly reduces the wear rate with all loads studied. AES surface analysis reveals a phosphate type wear resistant film, which greatly increases load-bearing capacity, formed on the iron disk. Preliminary chromatographic studies suggest that this film forms either because of ester oxidation or TCP degradation. Wetting studies show direct correlation between the spreading coefficient and wear rate.</p>					
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