Reactions of Tricresyl Phosphate with Bearing Materials

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Si_3N_4 and SiC do not react with TCP at 110°C in air, the same conditions used in typical steel-bearing pretreatment processes. At higher temperatures, there is some reaction, but the films formed are chemically different from those on steel. Bearing tests indicate that the reaction product is ineffective in extending the life of a lubricated, modified thrust bearing. Thus, pretreatment is unnecessary for Si_3N_4 and SiC bearing parts under the same conditions as used for steel.

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1. Introduction

Tricresyl phosphate (TCP) is an antiwear additive used in many tribological systems that contain steel parts. The exact mechanism by which the additive provides antiwear action is not understood, and is the subject of many investigations. In general, it is believed that TCP reacts with the steel surface to provide a wear-resistant phosphate coating.[1] The steel parts are often pretreated with the additive by submersion into either neat TCP or a solution containing TCP, and heating at about 110°C for several hours or overnight. TCP is also often added to the lubricating oil in the hopes that it will replenish the phosphate coating as it is worn off in use.

All-ceramic bearings, hybrid bearings (steel raceways plus ceramic balls), and ceramic-coated parts in bearings will be more prevalent in future systems. These new bearings are expected to provide longer life than steel bearings, particularly under adverse conditions. Their hardness provides wear resistance, and their less reactive surfaces don't promote oil degradation as effectively as steel. However, very few studies have been reported concerning the effects of traditional antiwear additives on ceramic or hybrid systems. The wear of silicon nitride-steel couples was found to be less with phosphorus-containing additives,[2,3,4] and iron phosphate was found on both surfaces.[3,4] TCP decomposed on silicon carbide at 700°C, but no chemical interaction between the ceramic and the additive was found even at such a high temperature.[5] Silicon nitride-silicon nitride couples have also been studied, and wear reduction with TCP-formulated oil has been found,[6,7,8] although there has been no evidence of silicon- or nitrogen-containing reaction products.[8]

In the work reported here, we have investigated the reaction of TCP with silicon nitride and silicon carbide in air, under conditions similar to those used for pretreatment of steel bearing parts. We have found that the reaction of TCP with these two materials is different from that with iron, but that under some conditions a phosphorous-containing layer is produced on the ceramic surface. We have performed tests of modified thrust bearings containing silicon nitride components in order to determine whether the aryl-phosphate layers produced on silicon nitride under these conditions are effective at lengthening the lifetime of working mechanical systems. The experiments reported here are intended to determine the effects of the pretreatment process and do not address the issue of tribo-chemistry in an operating bearing system, as do the works cited above.[2-4,6-8]

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2. Experimental

Two sets of experiments designed to elucidate the reactivity of TCP with silicon carbide and nitride under typical bearing pretreatment conditions were performed. In one set, reaction products in the liquid phase were detected; in the other, reaction products on the solid surfaces were detected. Fourier Transform Infrared Spectroscopy (FTIR) was used to detect and identify the products in both sets of experiments. In addition, some of the solid surfaces were examined using X-ray Photoelectron Spectroscopy (XPS) or Auger Electron Spectroscopy (AES) to confirm the presence of phosphorus on the surfaces. Tests were performed with modified thrust bearings using silicon nitride components to assess the utility of the films produced in extending the life of mechanical systems.

2.1 Reactivity Studies

2.1.1 Materials

Tricresyl phosphate from Spectrum Chemical Company was used in all the experiments. No specific grade or purity is claimed for this material. Liquid from the same bottle was used in all the experiments so lot-to-lot variations in the TCP would not be a concern.

High-surface-area powders were used in the liquid-phase product study in order to maximize the concentration of products in the liquid. α-Si_3N_4 (97% purity, 1-μm-diam. particles), α-SiC (99.8% purity, 1-μm-diam. particles), and Fe (99.9% purity, 6–9 μm-diam. particles) were obtained from Johnson Matthey and used as received. The powders are doubtless covered with some form of native oxide; no characterization of the surfaces was attempted.

Polished coupons were used in the solid-surface product study. The Si_3N_4 was hot-pressed material from The Norton Company, NC-132. The SiC was hot-pressed material obtained from ESK Engineered Ceramics. The steel coupons used were 52100 bearing steel. All of the samples were polished in air with diamond paste down to a 0.3 μm diamond particle size. The coupons were cleaned by rinsing in heptane before use, and probably were covered by native oxides; no characterization of the surfaces (by XPS, for instance) was attempted. The oxides on the powders and coupons may not be exactly the same, but we assumed they would be comparable enough to enable correlation of the liquid and solid surface results. As will be seen below, the results of the two studies do correlate; thus, our assumption is justified.

2.1.2 Procedure

All of the reactivity experiments were carried out in air. The reactants were mixed in a round-bottomed flask. A 2-ml aliquot of TCP was used in each of the experiments (the TCP was used neat and not diluted in oil); from 1 to 3 g of each powder was used in the liquid-phase experiments in order to get comparable surface areas for reaction (see below). In the solid-surface experiments, each coupon was submerged in 2 ml of TCP. The flask was attached to a water-cooled condenser and heated to the desired temperature (110, 150, or 175°C). Some experiments were carried out at room

temperature ($\approx$23°C). The contents of the flask were allowed to react overnight (22$\pm$2 h). Each experiment was performed at least twice; some were performed four times. We do not expect the glass reaction vessel to play a significant role in the measured degradation of TCP since the glass surface area is so small (only a few square centimeters).

The powders were separated from the liquid after reaction by adding heptane to the reaction mixture, stirring, and decanting. This procedure was repeated three times. The recovered liquid was concentrated by evaporation using a dry-nitrogen stream. (Heptane was chosen as the solvent since it is more volatile than the expected reaction products, i.e. cresol.) The remaining liquid was analyzed in a constant-path-length cell using the FTIR spectrometer in the absorbance mode. This detection method is quantitative (peak heights in absorbance mode are linearly proportional to the number of absorbers in the path).

TCP was heated in the absence of powders to determine the products of its thermal decomposition in air under the same conditions as the powder reactions.

The coupons were removed from the liquid, rinsed in toluene, cleaned in toluene in an ultrasonic bath, and allowed to dry. Toluene was used as a solvent since heptane did not remove all of the unreacted TCP from the surfaces (as observed using FTIR). The steel coupons were observed using grazing incidence of the incoming radiation; this technique accentuates the vibrations of adsorbed species on metallic substrates.[9] The Si_3N_4 and SiC coupons could not be observed this way because of dispersion of the peaks (typical of reflection from semiconductors). The Si_3N_4 coupons were pressed against a KRS-5 internal-reflection element and successfully analyzed by attenuated total reflectance (ATR). The dispersion of the peaks from the SiC coupons was too severe in this method also, and infrared spectra were not obtained for these samples. These two reflection methods are not quantitative. Several coupons were analyzed using XPS (steel and Si_3N_4) or AES (steel and SiC) to confirm the presence of P on the surfaces.

2.2 Bearing Tests

The bearing tests were performed using a test fixture that has been described previously[10] (see Figure 1). The bearings used for the study were modified thrust bearings. The top raceway was a standard C117 steel GT-1 thrust bearing raceway, but the bottom raceway was replaced by a disk of silicon nitride. Also, the steel balls of the standard bearing were removed from the steel retainer and replaced by silicon nitride balls. The disks were obtained from Cerbec (material NBD-200) and were polished to an arithmetic average roughness of less than 150 Å as measured by a Sloan DEKTAK profilometer. The balls were Grade 5 NBD-200 silicon nitride balls from Cerbec. (NBD-200 is very similar in chemical composition to the NC-132 used in the coupon studies described above. The major difference between the two materials is that NC-132 is hot-pressed, while NBD-200 is hot-isostatically pressed.)

As can be seen in Figure 1, the upper grooved raceway is mounted slightly off the axis of rotation of the rotating disk below it. This increases the amount of ball skidding at the ball-flat interface, and puts more stress on the lubricant at that interface than in a properly aligned thrust bearing, thus decreasing the wear life of the system. The bearing operates under mixed or boundary lubrication conditions. The tests are believed to fail by any or all of the following mechanisms: wear, lubricant

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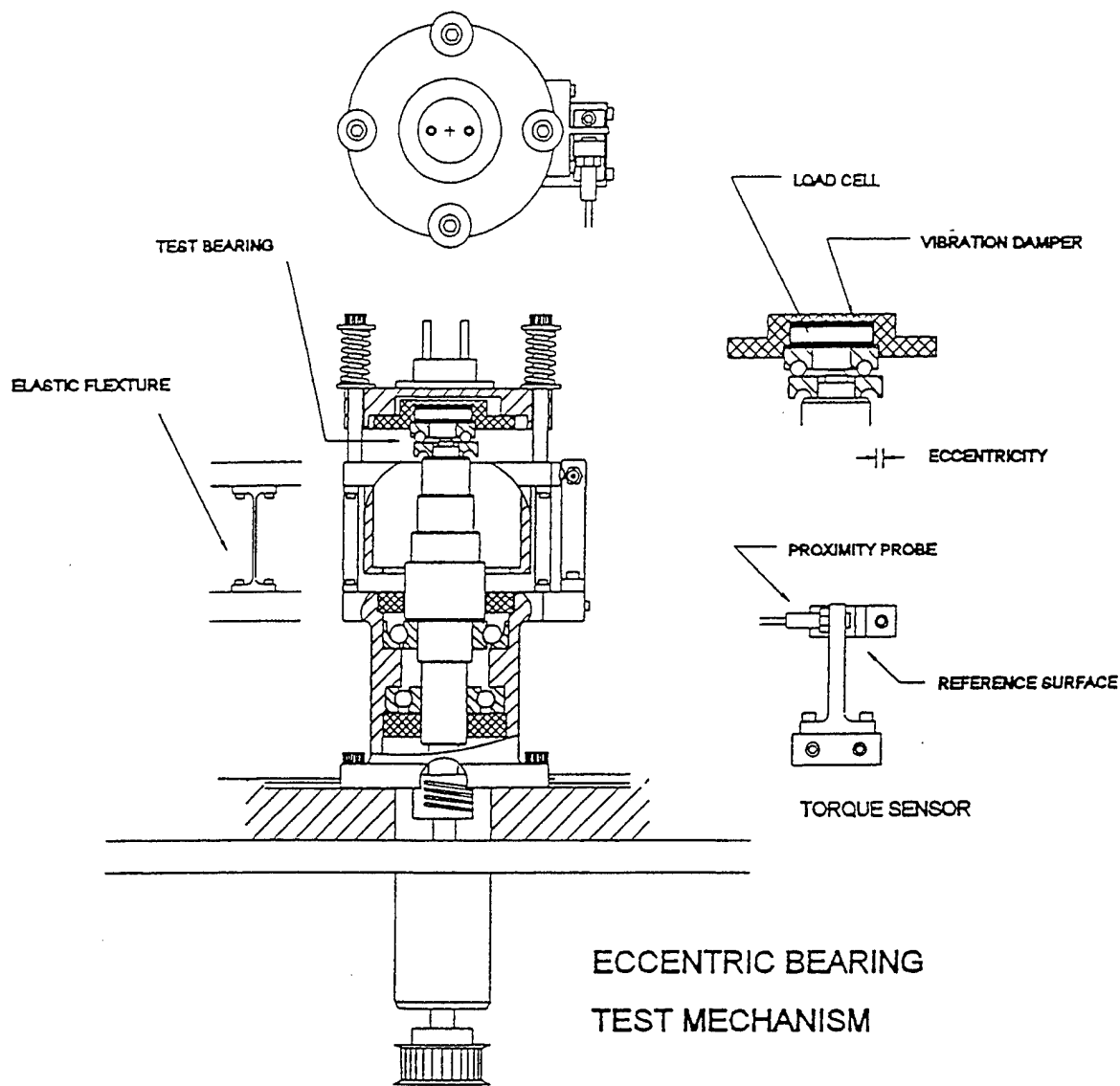
Figure 1. Lubricant screening test apparatus.

starvation, and lubricant degradation. Previous tests using this type of apparatus have shown differences in wear life between untreated and TCP-treated steel bearings[11,12] (see discussion below).

Before use, the bearing components were cleaned ultrasonically in heptane. The steel raceways and retainers were never treated with TCP. Some of the silicon nitride disks and balls were treated with TCP (obtained from Spectrum Chemical) by submerging them in a round-bottomed flask containing TCP (no oil) and a thermometer. A water-cooled condenser was attached, and the temperature of the TCP was raised to 150°C and maintained at that value overnight. After cooling, the parts were rinsed

three times in toluene to remove unreacted TCP and assembled into the bearing. All of the bearings were lubricated with 30 μL of unformulated Nye 2001 oil, a multiply alkylated cyclopentane.

The bearings were placed in the test fixture and loaded to 24 lb. This results in a mean Hertzian contact stress of approximately 290 ksi at the ball-flat interface. The tests were run in vacuum, at a pressure of about 2×10^{-6} torr. The bearings were run in by slowly raising the speed over 20 min to the final test value of 1800 r/min. The reaction torque of the test bearings was monitored on a continuous basis, and the test was automatically terminated when the reaction torque exceeded 1.5 times the initial torque. The test bearing was cooled by a copper block containing circulating water. The temperature measured by the thermocouple in the housing did not exceed 30°C. Three tests were conducted with untreated silicon nitride parts, and three were conducted with treated silicon nitride parts.

After each test, the bearing was disassembled and rinsed with heptane. The parts were examined under a microscope. The heptane rinses were concentrated by evaporation of the solvent in a room-temperature, dry-nitrogen stream, and analyzed by infrared spectroscopy. The surface roughnesses of the cleaned disks were determined using a Sloan DEKTAK Profilometer.

3. Results and Discussion

3.1 Liquid-Phase Experiments

The infrared spectrum of TCP and its structure are given in Figure 2. The spectrum was obtained from the TCP used in this work. The $-CH_3$ group can be attached at the ortho, meta, or para position on the aromatic ring. The commercially available product contains mostly meta and para isomers. There are only very small amounts of the ortho isomer, which is carcinogenic. We did not attempt to obtain pure samples of the various TCP isomers since the purpose of the experiments was to examine a process typically used in bearing manufacture. The peaks around 3000 cm^{-1} are due to C–H stretching vibrations; the peaks between 1400 and 1600 cm^{-1} are due to aryl substitution bands and aryl–CH_3 vibrations;[13,14] the peak at 1300 cm^{-1} is due to the P–O stretching vibration of the phosphoryl group;[13,15] the peaks around 1140, 1190, and 1240 cm^{-1} are due to deformation vibrations of the aryl moieties involving in-plane C–H;[13,14,16] the peaks around 970 cm^{-1} are due to P–O–aryl vibrations;[13] and the peaks around 1000 and 950 cm^{-1} are due to the antisymmetric and symmetric vibrations of the PO_3 group, respectively.[13,17]

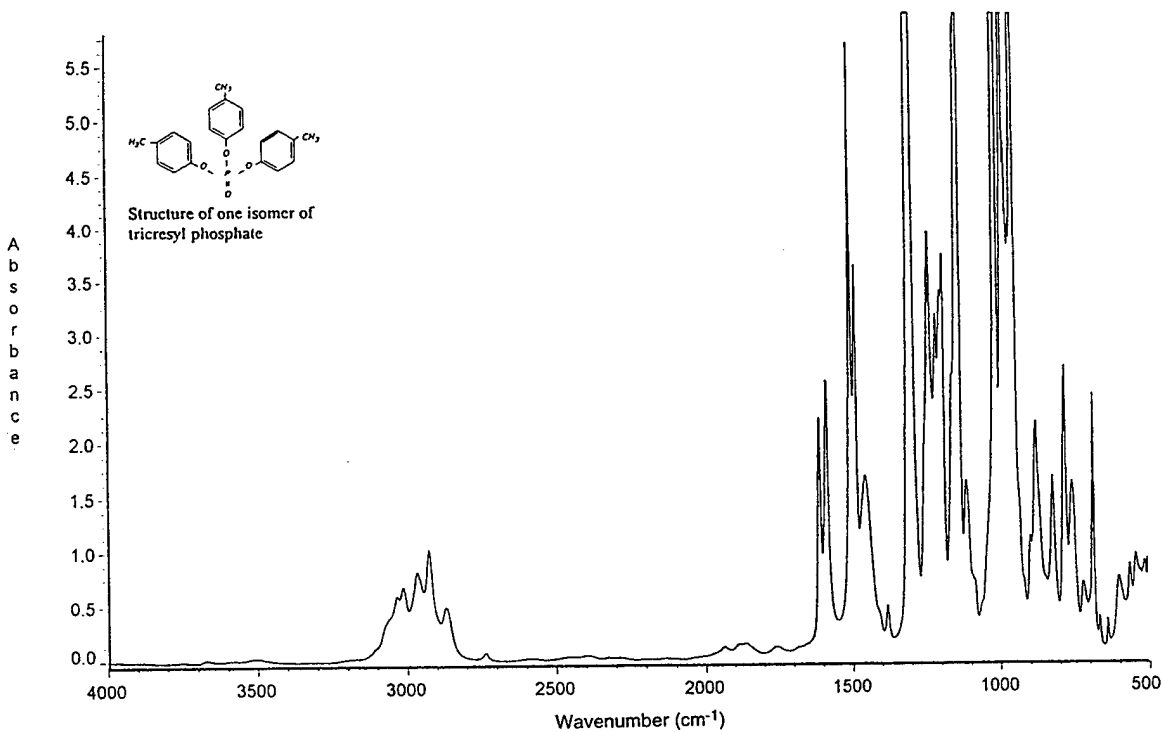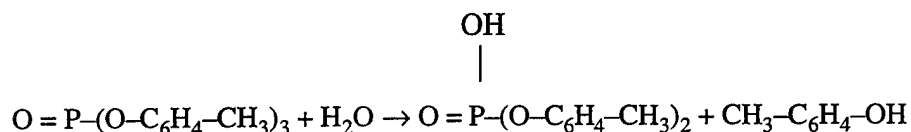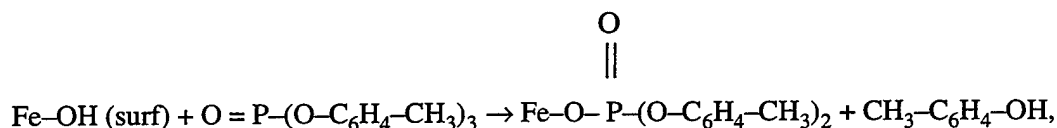Figure 2.   Infrared spectrum of tricresyl phosphate (liquid transmission cell, absorbance mode).

Figure 3 shows the region from 3000 to 4000 cm^{-1} in more detail. TCP has several vibrations in this region involving the oxygen atoms. The O–H stretching vibration of cresol appears at 3350 cm^{-1}. TCP and TCP heated in air to 110°C do not contain any observable cresol (Figure 3a and b). However, TCP heated in air to 150°C does contain cresol (Figure 3c). TCP heated in air to 110°C with a few drops of NaOH also contains cresol (Figure 3d). Thus, TCP begins to decompose in air, liberating cresol at 150°C, perhaps according to the reaction

$$\overset{\displaystyle OH}{\underset{\displaystyle}{|}}$$

$$O = P\text{–}(O\text{–}C_6H_4\text{–}CH_3)_3 + H_2O \rightarrow O = P\text{–}(O\text{–}C_6H_4\text{–}CH_3)_2 + CH_3\text{–}C_6H_4\text{–}OH$$

More than one cresol can be liberated, with a corresponding change in the phosphorus-containing product ("acid phosphate"). In the presence of a strong base such as NaOH, decomposition begins at lower temperatures because OH$^-$ is much more nucleophilic than H$_2$O.

The decomposition of TCP in the presence of iron powder (Figure 3e) is similar to that of TCP in the presence of base. There is no observable reaction at room temperature, but decomposition begins at 110°C. This suggests that basic sites on the iron surface participate in the decomposition of TCP. The reaction is even more extensive at 150°C. This reaction might be described as

$$\overset{\displaystyle O}{\underset{\displaystyle}{\|}}$$

$$Fe\text{–}OH \text{ (surf)} + O = P\text{–}(O\text{–}C_6H_4\text{–}CH_3)_3 \rightarrow Fe\text{–}O\text{–} P\text{–}(O\text{–}C_6H_4\text{–}CH_3)_2 + CH_3\text{–}C_6H_4\text{–}OH,$$

where Fe–OH (surf) is the designation for a basic surface site. The reaction is written for loss of one cresol; one, two, or three may actually leave.

The decomposition of TCP in the presence of silicon nitride or silicon carbide powders is similar to that of TCP without the presence of base. There is no cresol produced at room temperature or 110°C (Figure 3f). There is a small peak visible at about 3350 cm^{-1} in the spectrum reproduced in Figure 3f, but it is not reproducible in all the repetitions of the experiment. We established an absorbance value of 0.005 as a threshold for reporting the presence of cresol. Cresol is present in the liquid from the 150°C reaction mixture. This indicates that there are no sites on the silicon nitride or carbide surfaces that are sufficiently reactive to initiate the decomposition reaction at temperatures as low as 110°C.

At 175°C, TCP, whether pure or combined with powders, decomposed to a black tarry substance that could not be analyzed for products in the "liquid" phase.

The relative amount of cresol produced in each reaction can be inferred from the intensity of the absorption peak. The absorbances are given in Table 1 (each value is the average of all the experiments for a given set of conditions and the standard deviation from the average). It is clear that the
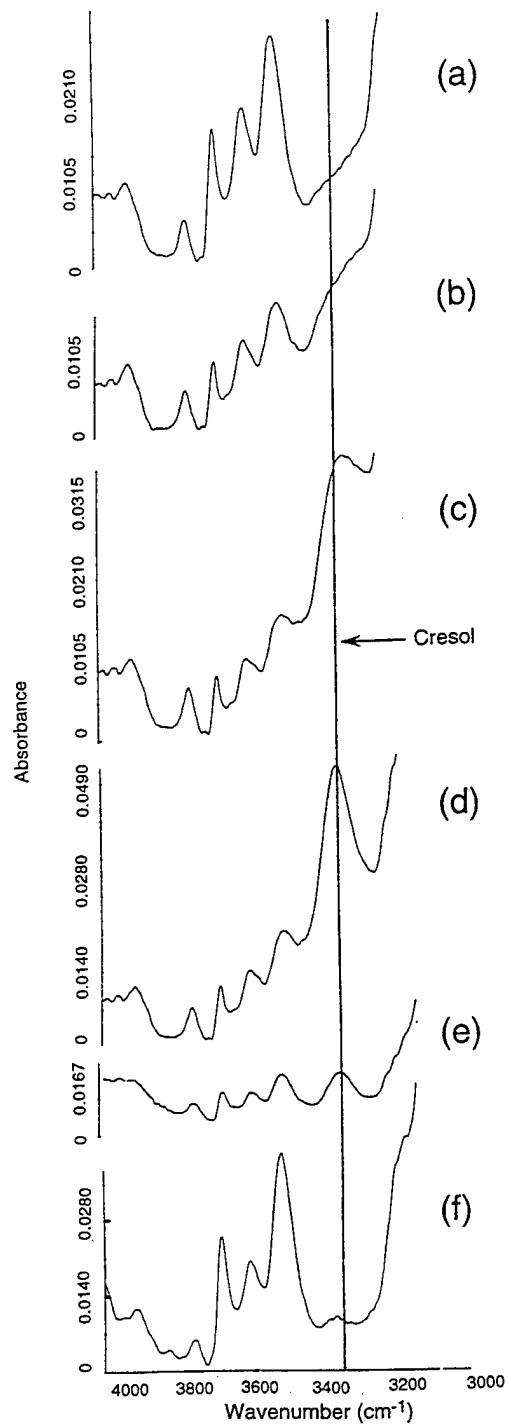
Figure 3. Infrared spectra of tricresyl phosphate (liquid transmission cell, absorbance mode; note changes in absorbance scale). (a) TCP; (b) TCP heated to 110°C; (c) TCP heated to 150°C; (d) TCP heated to 110°C with NaOH; (e) TCP heated to 110°C with iron powder; (f) TCP heated to 110°C with silicon nitride powder.

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amount of cresol produced by heating TCP with Si_3N_4 or SiC is about the same as that produced by heating TCP alone. On the other hand, cresol is produced by heating TCP with Fe at 110°C. In this case, the surface of the powder is involved in the reaction. Therefore, in order to compare the results, the absorbances must be normalized by the surface areas. These values are reported in the last two columns of Table 1. The normalization is based on the approximate size of the powder particles reported by their manufacturers; the true surface area of the powders was not determined. Bearing in mind the approximate nature of the surface areas used, the normalized values of absorbance show an interesting trend: they are much smaller for Si_3N_4 and SiC than for Fe. Since the absolute absorbances for the Si_3N_4 and SiC powder reactions are similar to those of the thermal decomposition of TCP itself, it is likely that the surfaces play no role in the degradation. That is, the basic surface sites on the Si_3N_4 and SiC surfaces are not as strong as those on the Fe surfaces, and cannot initiate reaction with TCP.

Table 1. Amount of Cresol

Powder	Absorbance		Absorbance/Surface Area (cm^{-2})	
	110°C	150°C	110°C	150°C
TCP—neat	0	0.011 ± 0.001	—	—
Fe	0.014 ± 0.001	0.057 ± 0.008	5×10^{-6}	2×10^{-5}
Si_3N_4	0	0.02 ± 0.01	0	7×10^{-7}
SiC	0	0.010 ± 0.006	0	3×10^{-7}

3.2 Surface Products: Silicon nitride and carbide

Phosphorus-containing reaction products were detected by ATR on silicon nitride coupons that had been treated with TCP under some conditions. Spectra in the 900 to 1300 cm^{-1} range for samples produced under different reaction conditions are summarized in Figure 4. This region contains peaks for Si–O and P–O bonds, which can be used to determine the extent of reaction on the surface. The spectra change markedly with reaction temperature, and will be discussed individually below.

The silicon nitride surface after room-temperature treatment with TCP (Figure 4a and 5a) is unchanged from the untreated surface (Figure 5b). No reaction has occurred, which is consistent with finding no cresol in the liquid phase at this temperature. Any TCP that was on the surface in the reaction mixture was not very strongly adsorbed because it was removed with the toluene solvent. The two peaks (1020 and 1070 cm^{-1}) are due to Si–O stretching, and are typical of a thin oxide coating on Si-containing materials. Bridging Si–O–Si vibrations occur between 1060 and 1080 cm^{-1} in thin vitreous glass films[18] and at 1020 and 1085 cm^{-1} in long, linear and cyclic siloxanes.[19] Nonbridging Si–OH vibrations also occur around 1030 to 1050 cm^{-1}.[20]
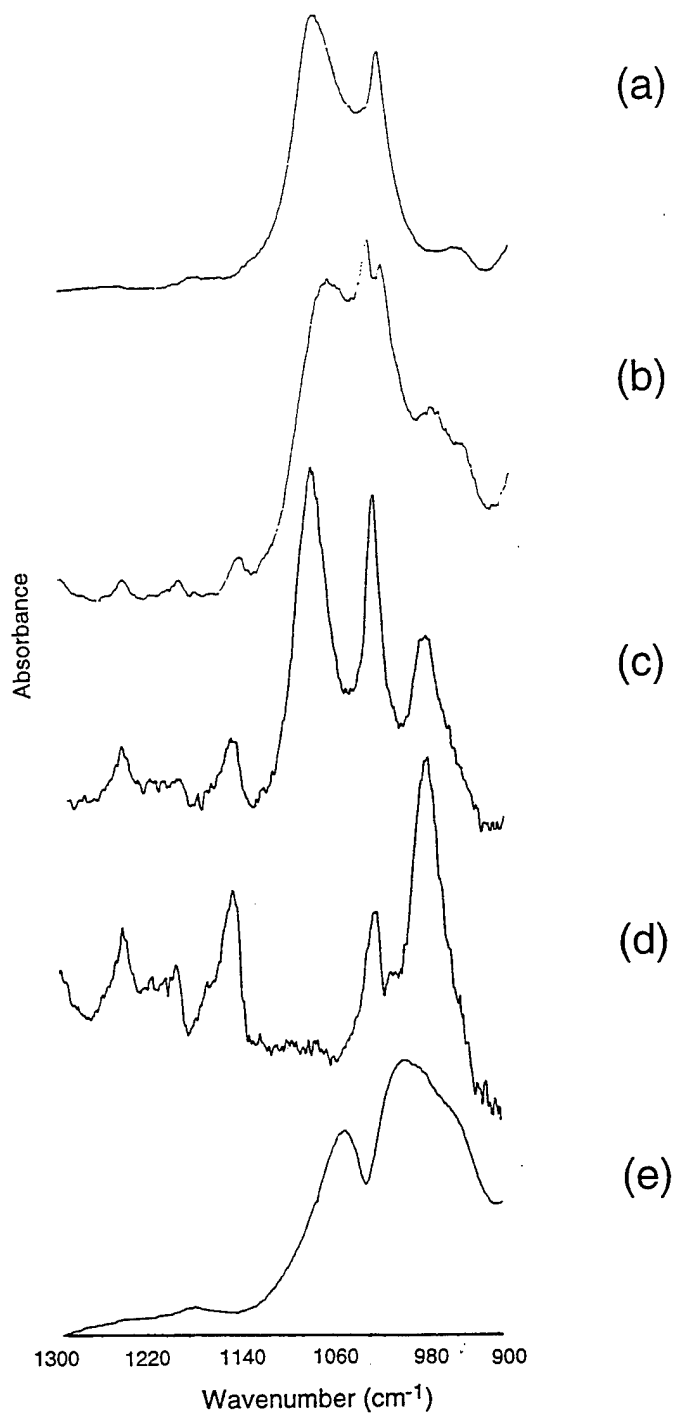
Figure 4. Infrared spectra of surfaces of silicon nitride coupons treated with tricresyl phosphate at the temperatures indicated (coupons pressed against IRE, absorbance mode). (a) room temperature; (b) 110°C; (c) 140°C; (d) 140°C, excursion to 200°C for 10 min; (e) 175°C.
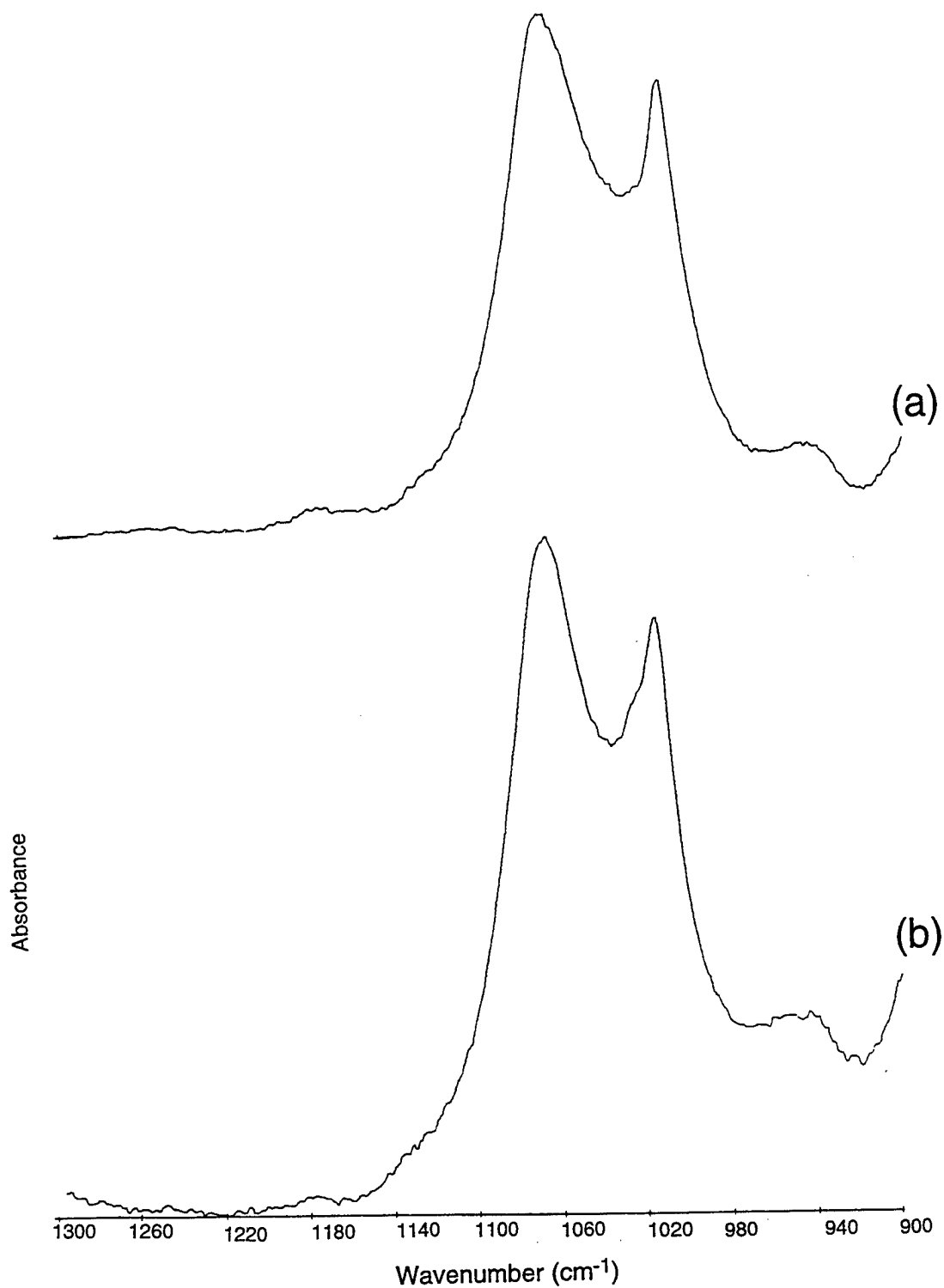
Figure 5.   Infrared spectra of surfaces of silicon nitride coupons (coupons
pressed against IRE, absorbance mode). (a) treated with tricresyl
phosphate at room temperature; (b) untreated.

After heating silicon nitride coupons in TCP to 110°C, some TCP remains on the silicon nitride surface (Figure 4b and 6a). The spectrum looks very much like that of a thin TCP layer adsorbed on the surface. Such a film was produced for comparison by evaporating a solution of TCP in heptane on a silicon nitride surface at room temperature (Figure 6b). In the spectra in Figure 6, the Si–O stretches at 1020 and 1070 cm^{-1} are visible. In addition, there are peaks from TCP at 940, 970, 1030, 1140, 1190, 1240, and 1300 cm^{-1}. The peaks at 940 and 1030 cm^{-1} can be assigned to the symmetric and antisymmetric stretches of the pyramidal, C_{3v} PO_3 group (these vibrations occur at 920 to 990 and 970 to 1090 cm^{-1}, respectively, in many compounds containing the PO_3 group.)[13,17] We assign the peak at 970 cm^{-1} to the P–O–aryl vibration.[13] The peaks at 1140, 1190, and 1240 cm^{-1} are in-plane C–H deformations in the aryl moiety and aryl–CH_3 vibrations.[13,14,16] The peak at 1300 cm^{-1} is due to the P–O stretch of the phosphoryl group.[13,15]

The TCP appears to be molecularly chemisorbed to the silicon nitride surface after heating to 110°C. It was not entirely removed by the toluene solvent, indicating a stronger attachment to the surface than in the case of room-temperature contact. No change has occurred in the adsorbed molecule to indicate reaction, and no cresol was found in the liquid at this temperature. The presence of the PO_3 vibrations confirm that no substituents have left the adsorbed TCP molecule.

Heating to 140°C initiated a reaction (Figures 4c and 4d). TCP decomposes in the liquid at this temperature, releasing cresol. Reaction products remain on the silicon nitride surface after the toluene rinse. Whether the decomposition of TCP occurs in the liquid and the products then react with the surface, or the decomposition and reaction occur on the surface cannot be determined from these experiments. Since the same amount of cresol was produced in the liquid-phase experiments with and without Si_3N_4 powder, decomposition in the liquid phase might be more likely.

The PO_3 peaks at 940 and 1030 cm^{-1} are gone, indicating that the material on the surface no longer has three P–O–aryl groups(Figures 4c and 4d). However, the 970 cm^{-1} peak of the P–O–aryl vibration remains, as do the 1140, 1190, and 1240 cm^{-1} peaks indicative of the aryl group. Thus, there are one or two P–O–aryl groups left on the surface. If there are two such identical groups, the molecule might have C_{2v} symmetry; in which, case vibrations at 1320 to 1140 cm^{-1} (antisymmetric stretch of PO_2) and 1170 to 1000 cm^{-1} (symmetric stretch of PO_2) should be observed.[13] We do not see these vibrations in our spectra. This could be because they coincidentally lie beneath other peaks, or because the molecule does not have C_{2v} symmetry on the surface under these conditions. The P–O stretch of the phosphoryl group at 1300 cm^{-1} remains (not shown in the figure). This combination of spectral changes suggests that the molecule lost one or two aryl groups as cresols, and the remainder of the molecule attached itself to the surface via the available P– bond, as in the reactions
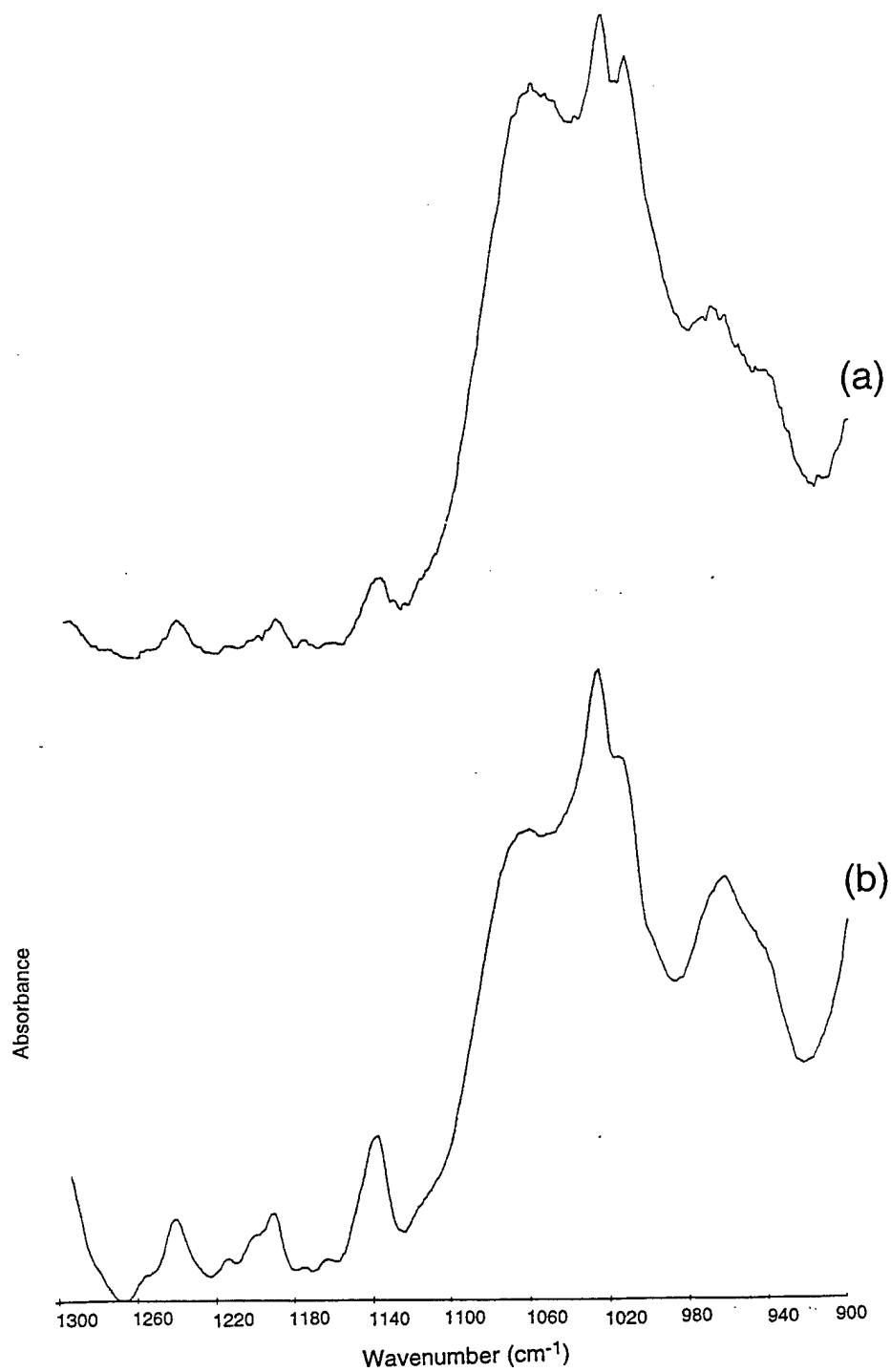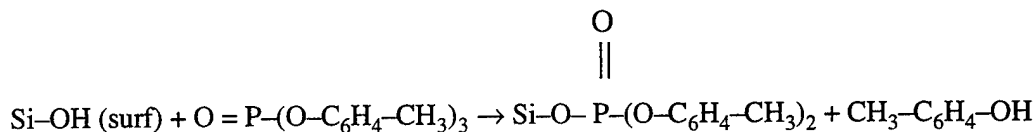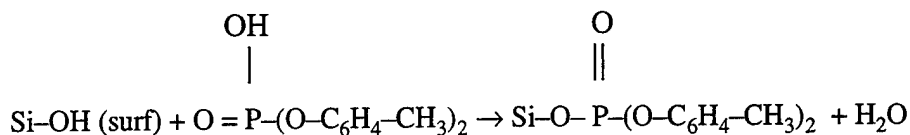
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Figure 6. Infrared spectra of surfaces of silicon nitride coupons (coupons pressed against IRE, absorbance mode). (a) treated with tricresyl phosphate at 110°C; (b) thin layer of TCP produced by evaporating a heptane solution of TCP at room temperature.

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$$\text{Si–OH (surf)} + \text{O} = \overset{\displaystyle\text{O}}{\overset{\displaystyle\|}{\text{P}}}\text{–}(\text{O–C}_6\text{H}_4\text{–CH}_3)_3 \rightarrow \text{Si–O–} \overset{\displaystyle\text{O}}{\overset{\displaystyle\|}{\text{P}}}\text{–}(\text{O–C}_6\text{H}_4\text{–CH}_3)_2 + \text{CH}_3\text{–C}_6\text{H}_4\text{–OH}$$

or

$$\text{Si–OH (surf)} + \text{O} = \overset{\displaystyle\text{OH}}{\overset{\displaystyle|}{\text{P}}}\text{–}(\text{O–C}_6\text{H}_4\text{–CH}_3)_2 \rightarrow \text{Si–O–} \overset{\displaystyle\text{O}}{\overset{\displaystyle\|}{\text{P}}}\text{–}(\text{O–C}_6\text{H}_4\text{–CH}_3)_2 + \text{H}_2\text{O}$$

Si–OH (surf) is merely one example of a surface site that might be attacked by TCP or its acid phosphate.

The Si–O vibration at 1070 cm^{-1} appears to be removed before that at 1020 cm^{-1}. The exact identities of these two vibrations are not known at the present time, but their removal does seem to indicate that the Si–O–Si and Si–OH groups are being replaced by something else. P–O–Si bonds[21] should absorb between 925 and 1000 cm^{-1}; there is already a peak at 970 cm^{-1} that would make their observation difficult.

Above 175°C, the reaction is complete (Figure 4e). The liquid in the reaction flask was a black, tarry substance. Most of this could be rinsed from the surfaces by using toluene with ultrasonic agitation. The surfaces were a matte-black color, no longer shiny and reflective. The Si–O vibrations are gone from the IR spectrum, as are the aryl and phosphoryl vibrations. There are peaks at 940, 970, and 1040 cm^{-1}. The peaks at 940 and 1040 cm^{-1} could be due to PO$_3$ group vibrations as discussed above. There are several different bonds that could absorb in the region around 970 cm^{-1}. P–O–Si bonds, P– O–P bonds,[13,22] P–OH bonds[13,20] are all possibilities. All of these bonds are reasonable in some sort of phosphate surface layer.

The surfaces of samples treated with TCP at 150 and 175°C were examined with XPS. P was present on the surfaces, and the P 2p peak appeared at an energy characteristic of phosphates (133.0–134.3 eV). Carbon was also found; some was probably adventitious carbon that is observed on all unsputtered surfaces in XPS; some was probably due to the decomposition of TCP. Silicon and nitrogen were also found, indicating that the films are either thin or patchy, allowing substrate photoelectrons to be detected.

The surfaces of the SiC coupons could not be examined using FTIR because of the dispersion of the spectra. They were examined with AES; P, Si, and C were found on samples treated with TCP at 150°C.

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These experiments show that Si_3N_4 and SiC do not react readily with TCP, confirming the work of other groups. Using very surface-sensitive techniques, we can distinguish some surface reaction at high temperatures, but it is not extensive.

3.3 Surface Products: Steel

Reaction products were detected on the surfaces of steel coupons that had been treated with TCP at 110 and 150°C. The products are not the same as those detected for Si_3N_4 surfaces. After room-temperature exposure, all the TCP is removed from steel surfaces by the toluene rinse, just as for Si_3N_4 and SiC surfaces; there is no chemisorbed material. At 110°C, reaction has occurred, leaving no trace of the vibrations of molecular TCP.

Figure 7 shows the IR spectral region from 900 to 1400 cm^{-1} for steel coupons that had been treated with TCP at 110°C (Figure 7a) and 150°C (Figure 7b). The spectra do not resemble those of TCP or any of the films on the unreactive surfaces. In both spectra from the steel surfaces, there are peaks at 1130, and 1170 cm^{-1}. These peaks could be due to PO_2 groups,[13] or hydrogen-bonded phosphoryl groups.[13,23] There are no TCP-like phosphoryl peaks (1300 cm^{-1}), P–O–aryl peaks (970 cm^{-1}), or peaks for PO_3 groups (940 and 1130 cm^{-1}), indicating that the TCP has completely decomposed. There is a shoulder in each spectrum at about 1040–1070 cm^{-1}. It is probably due to iron phosphate, which contains tetrahedral PO_4 groups that absorb in that region.[24]

XPS confirms the presence of P in a phosphate-like species on the steel surfaces at 110°C. AES indicates P on steel surfaces at 110°C and 150°C, but not at room temperature.

3.4 Bearing Tests

Bearing tests were run with unformulated oil and silicon nitride parts either treated or untreated by TCP at 150°C. The parts pretreated with TCP at 150°C have partially decomposed TCP attached to the surface. We did not pretreat the bearing parts at 175°C, at which temperature there was even more extensive decomposition of TCP since the surfaces after 175°C pretreatment were no longer smooth and reflective. Surface roughness variations can affect the results of bearing tests.

A typical torque trace is reproduced in Figure 8. The data are from Test 3, using untreated silicon nitride parts. The torque initially decreases as the bearing runs in. The failure is abrupt, so the arbitrary choice of failure being when the torque reaches 1.5 times its original value (rather than 2 or 3 times) does not greatly affect the test life reported.
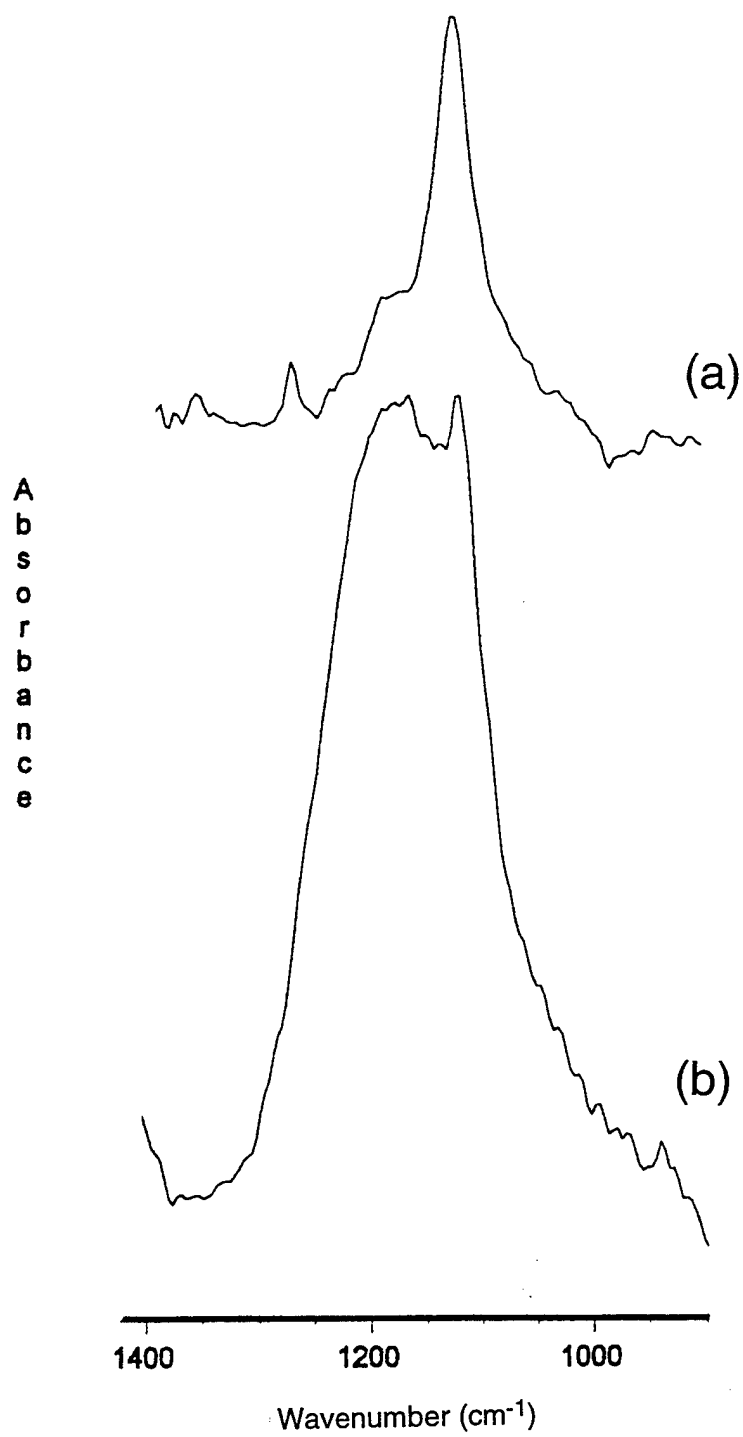
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Figure 7. Infrared spectrum of surfaces of steel coupons treated with tricre-
syl phosphate (grazing incidence reflection, absorbance mode). (a)
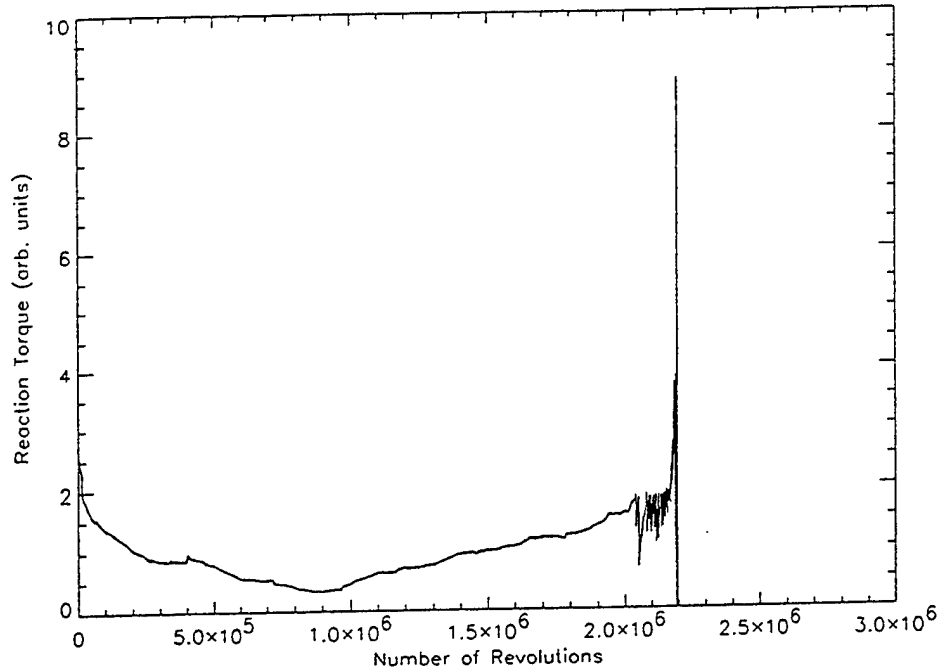heated to 110°C; (b) heated to 150°C.

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Figure 8. Typical torque during a test (Test 3, untreated parts).

The test results are presented in Table 2. The test life ranges from 1.2×10^6 to 5.4×10^6 revolutions. Statistical analysis of the results using Student's t distribution shows no systematic difference in the wear lives of the two sets of tests, even at the 10% level of significance. Thus, there is no change in the life of the bearings in this test due to pretreatment of the silicon nitride parts with TCP.

The steel raceways exhibited no differences under microscopic examination before and after the tests. This suggests that wear of the steel race probably had no influence on the failure. The silicon nitride disks had wide, visible running tracks, which appeared to consist of black deposits, probably of

Table 2. Bearing Test Results

Test	Condition	Wear Life (revolutions)
1	untreated	2.0×10^6
2	treated	2.5×10^6
3	untreated	2.2×10^6
4	treated	1.2×10^6
5	untreated	5.4×10^6
6	treated	4.4×10^6

degraded lubricant. There was no evidence of any large scoring of the disks. The profilometry showed that the overall surface roughness was not much changed during the tests. There were spikes several hundred to several thousand Ångstroms high that correspond to thick areas of the black deposits. There were no depressions in the surfaces. The collected lubricant showed no evidence of oxidation or contamination, for instance by phosphates removed from the surface coating, when examined by IR spectroscopy. No particles were seen in the oil by visual examination. The tests probably failed due to torque increases caused by lubricant degradation in the running track. Lubricant degradation can decrease the amount of oil available to the contacting surfaces and introduce particles. The particles could both prevent oil flow into the contact and cause torque increases due to driving the balls through the debris.

Previous tests in our laboratory have shown that TCP pretreatment of steel bearing parts does affect the life of bearings under conditions similar to those used in these tests. In one case,[11] tests were run at 250 ksi and 1800 r/min using 30 μL of unformulated Nye 2001. The bearings were not cooled, so the temperature of the thermocouple in the housing was 70 to 90°C during the tests. The life was 170,000 ± 50,000 revolutions without pretreatment and 290,000 ±70,000 with pretreatment, a factor of almost 2 longer. In another case,[12] tests were run at 300 ksi and 1400 r/min using 60 μL of unformulated Coray 100 (a naphthenic mineral oil). The bearings were cooled, and the temperature was 30 to 35°C. The life was $(0.6 \pm 0.3) \times 10^6$ revolutions without pretreatment and $(1.3 \pm 0.6) \times 10^6$ revolutions with pretreatment, again a factor of almost 2 longer. (The much longer lives measured in the tests with Coray 100 compared to those with Nye 2001 are probably due to the lower temperature and larger amount of lubricant.)

Based on these results, the tests reported here should be perceptive to any difference in life caused by TCP pretreatment. We saw no effect. It is interesting to note that the lives measured in our tests of hybrid bearings are much longer than those of the previous tests that used steel bearings, showing the efficacy of ceramic parts in increasing bearing life.

The lack of any difference in the test lives measured in these tests indicates that the partially decomposed film of TCP present on the surfaces of silicon nitride pretreated with TCP at 150°C is not an effective life-extending agent for contacts between silicon nitride balls and flats. These tests do not address whether TCP formulated in the lubricating oil will be a life-extending additive for silicon nitride parts, as it is for steel parts. TCP in the oil could influence the wear life of a bearing without reacting with the surface. For instance, TCP could decompose in solution under vacuum by a different mechanism to form a different product than the corresponding mechanism and product for reaction in air. The film produced by TCP formulated into the oil would be continuously replaced and might not need to adhere well to the surface. Another possibility is that TCP could alter the viscosity of the oil in the contact region, thus mitigating some of the stresses present on the lubricant molecules. On the other hand, TCP could be ineffective if surface reaction is required for life extension. Simple wear tests have indicated that oil formulated with TCP can reduce wear of silicon nitride parts.[6-8] Tests of all-silicon nitride bearings with TCP-formulated oil would indicate whether or not TCP is an effective oil additive for silicon nitride bearings.

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4. Summary and Conclusions

Si_3N_4 and SiC do not react with TCP at 110°C in air, the same conditions used in typical steel-bearing pretreatment processes. At higher temperatures, there is some reaction, but the films formed are not like those on steel. Bearing tests indicate that the reaction product is ineffective in extending the life of a lubricated, modified thrust bearing. Pretreatment of Si_3N_4 and SiC bearing parts under the same conditions as used for steel is thus unnecessary.

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