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ABSTRACT

Because tricresyl-phosphate (TCP) is a common antiwear additive in lubricants, there is great interest in its interactions with metal substrates. In this work, TCP was allowed to adsorb on polycrystalline iron and gold at room temperature. X-ray photoelectron spectroscopy (XPS) was used to analyze the adsorbed species. The substrate was then heated in steps to 330° C, and the changes in the adsorbate were analyzed after each step.

On both substrates saturation adsorption occurred at about one monolayer, but the sticking coefficient was less on gold than on iron. Comparison of the XPS spectra of TCP on each substrate with the spectrum from condensed TCP indicated non-dissociative adsorption on gold, possibly by dipole-induced dipole interaction. On iron, there was apparently additional interaction between the substrate and the tolyl groups on the TCP molecule.

TCP began to desorb molecularly from gold as soon as the gold was heated above room temperature. The desorption was complete by 200° C. However, when the iron substrate was heated, TCP did not desorb but decomposed between 150° and 250° C. An iron phosphate or organo-phosphate formed during the decomposition, and one of the tolyl groups was lost. The temperature range in which this decomposition occurred corresponds to a previously observed friction transition in the lubricating properties of TCP.

INTRODUCTION

The importance of tricresyl-phosphate (TCP) as an antiwear additive prompted the investigation of its mechanism as early as 1940 when Beeck, Givens, and Williams (ref. 1) proposed that a eutectic mixture of iron and iron phosphide creates chemical polishing on the lubricated surfaces. However, in 1965 Barcroft and Daniel (ref. 2) used P-32 labeled TCP in an operating engine, and on the basis of the film formed on the tappet surfaces, concluded that metal phosphate and/or metal organophosphates were present. In the same year, Godfrey (ref. 3) used electron diffraction to identify FePO_4 and $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ on the surface of TCP lubricated steel. Various subsequent investigations (refs. 4 to 6), including Auger electron and X-ray photoelectron spectroscopy (XPS), have confirmed the presence of phosphate on the surface of TCP lubricated steel. It is now recognized that, except for some very high temperature and severe wear conditions (ref. 7), the antiwear activity of TCP is associated with the presence of a phosphate, not a phosphide, on the worn surface.

While the final product of the TCP-metal reaction is known, the detailed chemical mechanism is still a matter of debate. There are two broad alternatives. Either the TCP adsorbs on the metal surface where it reacts directly with the metal or with other components of the lubricant solution, or the TCP first reacts or decomposes in solution producing products which then react with the metal surface. This study will be concerned with the former alternative, although it is entirely possible that both are active in an actual lubrication situation.

The first step in the adsorption-reaction mechanism is the adsorption of TCP. It is usually assumed from studies of TCP at the air-water interface (refs. 8 and 9) that the polar $P=O$ segment of the TCP molecule is responsible for the initial bond to the metal. There is, however, no data on the adsorption of TCP on metal. One purpose of this study, therefore, was to use XPS to determine the nature of the adsorption of TCP on polycrystalline iron, gold, and iron-oxide.

After adsorption, the TCP must either react with constituents of the lubricant or with the metal surface, itself. Some investigators, finding that the lubricating properties of TCP depend on the presence of air, have argued for hydrolysis or oxidation of the molecule either in solution (refs. 10 and 11) or on the surface (refs. 2 and 12). The evidence is not conclusive, however, since other investigators have found the lubricating properties of TCP to be independent of the presence of air or water and propose that the molecule undergoes thermal decomposition (ref. 13). If decomposition on the surface is, in fact, one of the relevant steps in the reaction, it is important to learn the nature of that decomposition. Accordingly, the second purpose of the present work is to use XPS to study the decomposition and reaction of TCP adsorbed on iron, gold, and iron-oxide at temperatures from 20° to 330° C.

EXPERIMENT

All the tests were performed in a stainless steel ultra-high vacuum chamber. The chamber was baked to 200° C and pumped with ion and titanium sublimation pumps. The base pressure was below 1×10^{-10} torr.

The substrate used in all experiments was a 6.35 mm diameter by 1 mm thick disk of 99.99 percent pure polycrystalline iron. It was soldered with indium to a molybdenum sample mount. The mount could be cooled to -150° C or heated to 330° C. The temperature was limited to 330° C, because above that temperature, indium migrated onto the sample surface.

The sample was cleaned by argon-ion bombardment from a 5 kV ion gun. The ion beam was rastered over the sample surface to assure that the entire analyzed area was cleaned. The beam current was approximately 5 microampere. During the sputtering process, the pressure in the vacuum chamber was raised to 5×10^{-5} torr by admitting argon through a variable leak valve.

The iron surface was used in its cleaned condition or prepared in one of two ways. It could be oxidized to form a thin layer of Fe_2O_3 by exposing it to 1×10^{-6} torr of oxygen for 300 sec at room temperature (ref. 14). Alternatively, the surface could be coated with gold from a tungsten filament wound with gold wire. After coating the specimen with gold, the XPS spectrum revealed no iron, carbon or oxygen.

A glass tube of TCP was connected to the vacuum chamber but separated from it by a butterfly valve. With the valve open, the TCP was heated and the vapor allowed to condense in the upper part of the tube. In this way, the TCP was purified by refluxing under vacuum. Eventually, the pressure in the vacuum chamber was unaffected by this procedure. The purity of the TCP pro-

duced by this process was checked by high pressure liquid chromatography. No polar impurities could be detected. The XPS results will confirm the purity.

When the iron specimen had been prepared as desired it was positioned to face the tube of purified TCP. The butterfly valve was opened, and the stream of TCP vapor was allowed to impinge on the prepared surface for the desired time. Exposure times were shortened by heating the entire tube, up to the inlet to the vacuum chamber, to 65° C. The actual pressure of TCP to which the specimen was exposed in the vapor stream could not be measured. Therefore, the TCP exposures are not known. It was found, however, that repeated exposure of clean iron for the same time always gave the same XPS spectrum. The exposures were, therefore, quite reproducible.

XPS analysis of the sample was performed with a commercial double-pass cylindrical mirror analyzer with retarding grids. The sample was excited by Mg K-alpha X-rays. Binding energies were all referenced to the main C(1s) peak in the spectrum from TCP which was taken to be 284.6 eV. With this reference, the Au(4f7/2) peak from evaporated gold was measured to be 83.8 eV, in excellent agreement with accepted values (ref. 15). The precision of the binding energy measurements varies with the intensity of the peak being measured, its structure and the amount and slope of the background. For the C(1s) and metal peaks it is estimated to be better than ±0.2 eV, while for the P(2p) and the weaker component of doublet peaks it is perhaps twice that large.

There was a systematic decrease in the intensity of all the XPS peaks after a gold evaporation. This was due to the deposition of a small amount of gold on the window of the X-ray source. However, as will be described in the Result section, there was a reproducible maximum amount of TCP that could be adsorbed on clean iron at room temperature. Therefore, all XPS intensities were normalized to the intensity of the C(1s) peak obtained from the saturation coverage of TCP on clean iron.

To determine the effect of temperature on the adsorbed TCP, the selected substrate, with maximum coverage of TCP, was heated to the desired temperature and held at that temperature for 1/2 hour. The heater power was then turned off, and the XPS data were recorded. The substrate was then heated to a higher temperature, and the cycle repeated until the desired temperature range had been covered. Independent experiments in which the TCP covered substrate was held at temperature for periods of time up to 2 hours were performed on each substrate. These revealed that all changes in the XPS spectra occurred during the first 1/2 hour at temperature.

RESULTS

Bulk TCP Reference Spectrum

A specimen of bulk TCP was obtained by cooling the iron substrate with liquid nitrogen and exposing it to the TCP vapor. The exposure was long enough that subsequent XPS analysis did not reveal the iron substrate. The O(1s), C(1s), and P(2p) XPS features obtained from this sample are shown in figure 1. Each of these peaks was smoothed using a 9 point quadratic fit around each point (ref. 16). Then, the background was subtracted using the algorithm of Shirley (ref. 17), and peak areas were measured. The overlapping peaks in the O(1s) and C(1s) spectra were separated and their relative areas measured with an analog curve resolver. Table I shows the assignment of the various spectral features and the atomic fractions to be expected from the stoichiometry of the TCP molecule. Atomic fractions calculated from the XPS

intensities are also shown in table I. The sensitivity factors from reference 15 were used in the calculations.

In the case of the C(1s) doublet, the major peak has been taken to be due to those carbon atoms not bound to an oxygen atom. From considerations of electronegativity the atoms bound to oxygen are expected to yield electrons at higher binding energy (ref. 18). From the stoichiometry of the molecule it is to be expected that these higher binding energy electrons should have one-seventh the intensity of the others. Both expectations are borne out by the assignment of table I. The O(1s) doublet can be assigned in the same manner. In this case, too, the assignments by binding energy and intensity are consistent.

The good agreement between the measured mole fractions and the calculated mole fractions in table I gives confirmation of two important points. First, the sensitivity factors used are probably correct. Their use assumes that the analyzed volume is homogeneous. Therefore, it can be concluded that the bulk TCP specimen consists of randomly oriented molecules, since any preferred orientation would constitute an inhomogeneity in the surface layer and would lead to incorrect quantitative results. Second, the material being condensed from the vapor stream is stoichiometric TCP.

TCP Adsorbed at Room Temperature

TCP was adsorbed on clean iron, oxidized iron and gold. In each case the substrate was exposed to the TCP vapor stream for varying lengths of time. After each exposure, the C(1s) XPS feature was recorded. The area under this peak was used as a measure of the amount of adsorbed TCP. The uptake curve is shown for all three substrates in figure 2.

Within the accuracy of the measurements, the uptake of TCP is identical on the sputter cleaned and the oxidized iron substrates. On the other hand, the initial adsorption of TCP on the gold substrate is slower than on the other two substrates. On all three substrates there is a maximum coverage - the saturation coverage - of TCP. It is achieved after about 40 min on both iron substrates but requires about 60 min for the gold substrate.

The thickness of the TCP layer can be calculated from the attenuation of the substrate peak intensity, if the electron exit angle and inelastic mean free path (IMFP) are known (ref. 19). On the iron substrate, the ratio of the Fe(2p_{3/2}) peak area after a 60 min exposure to the intensity before exposure, I/I' , was 0.62. For the CMA used in these experiments, the take-off angle was 43 ± 10 degrees. The IMFP of electrons in organic materials is not well established. However, Clark (ref. 20) summarizes a series of measurements of the IMFP in polyparaxylene that cover a range of electron energies including the energy of the Fe(2p_{3/2}) electron - 546 eV. From his data, it can be concluded that the IMFP is 17 Å. Other estimates of the IMFP for organic materials at this energy (refs. 21 and 22) range up to 46 Å. This range of IMFP yields values for the TCP thickness of 6 to 16 Å. The calculation was repeated for TCP adsorbed on gold. For that system, $I/I' = 0.82$, and values of the IMFP range from 22 to 70 Å. The calculated value of the TCP thickness thus ranges from 3 to 14 Å. The thickness of a monolayer of TCP adsorbed at the air-water interface is known from pressure-area isotherms (ref. 8). At zero pressure, it is 5.5 Å. This is well within the range of the calculations from the XPS data. Therefore, saturation coverage is taken as one monolayer.

Gold and sputter cleaned iron were exposed to the TCP vapor stream long enough to reach the saturation coverage of TCP. The C(1s) and O(1s) spectra

obtained from these two surfaces are shown in figures 3 and 4, respectively. The spectra from the bulk material condensed on iron at -150°C are included for comparison. In figure 4, the spectra have been smoothed. After stripping the background from each peak, an analog curve resolver was used to resolve the doublet structures, and the areas of each feature were measured. The results are summarized in table II. In all cases, the binding energies are consistent with those for the bulk TCP (table I), and the peak assignments have been made accordingly. The relative peak intensities and shapes, however are not the same as those from bulk TCP.

The C(1s) peak from TCP on iron was broader than that from TCP on gold or from bulk TCP. No asymmetry could be detected with the analog curve resolver. Any high energy shoulder present was less than about 5 percent of the total peak intensity. In the case of the gold substrate, the high energy C(1s) shoulder was about 14 ± 5 percent of the total peak intensity. That is the same as the ratio of C(1s) peak areas found for the bulk TCP (table I).

The O(1s) doublet, by contrast, was well defined in all cases, and the relative intensities of its components can be measured to about 10 percent. These relative intensities are best appreciated from the graphical presentation in figure 5. Compared to the bulk TCP, there is an apparent excess of double bonded oxygen (low binding energy) on the iron substrate and a deficiency of double bonded oxygen on the gold substrate. The converse is the case for the bridging oxygen (high binding energy).

Thermal Effects on Adsorbed TCP

Substrates of clean iron, oxidized iron and gold were exposed to the stream of TCP vapor long enough to produce saturation coverage on each substrate. Then, in the manner described in the Experiment section, they were heated to successively higher temperatures and the XPS features were recorded. The heights of the C(1s) and P(2p) peaks obtained in this way are presented as a function of heating temperature in figure 6.

There was no distinction between the iron and iron oxide substrates. Between 150° and 250°C the C(1s) intensity dropped to about 2/3 of its initial value, while there was an accompanying increase in the P(2p) intensity. In the iron oxide case, it was possible to continue heating to 370°C , before indium was detected on the substrate. There was no significant change in the XPS spectrum from 330° to 370°C . As the P(2p) peak area increased there was a proportional increase in the area of the O(1s) peak, so that the O:P ratio remained constant. Clearly a transition of some sort occurred on the iron and iron oxide surfaces at temperatures around 200°C . If that transition involved chemical changes in the adsorbate as well as changes in the coverage, there should be changes in the binding energies in the XPS spectrum.

Figure 7 shows the P(2p) binding energy as a function of the temperature to which the substrate was heated. The binding energy was that of bulk TCP at low temperature, but decreased as the temperature was raised, dropping a total of 0.5 to 0.7 eV at the highest temperature used. This decrease in binding energy followed closely the change in intensity shown in figure 6. In figure 8 the O(1s) peak is shown after heating the iron substrate to 330°C . There is no longer a doublet structure. All the O(1s) intensity is concentrated in the low binding energy component of the peak. There was clearly a chemical change occurring as the iron is heated.

The behavior of the TCP on the gold substrate was distinctly different from its behavior on the other two substrates. The C(1s) intensity began to decrease immediately on heating. At 260°C it was essentially gone. The

point plotted at that temperature in figure 6 represents a peak that could not be distinguished from the background noise in the spectrum. Because of the high background intensity, it was tedious to record the P(2p) peak after every heating of the gold substrate. However, after the final temperature of 260° C, there was no detectable P(2p) peak. The O(1s) peak had also disappeared. Apparently, the C, O, and P atoms left the surface simultaneously. Figure 8 shows the O(1s) feature after heating to 100° C on gold. (Above 100° C the O(1s) peak became too weak to measure reliably.) Comparison of figure 8 with figure 4 shows that, although the O(1s) intensity was decreasing, the shape of the peak remained unchanged on the gold substrate. Apparently, as the gold was heated the TCP did not undergo any detectable chemical change.

DISCUSSION

The similarity of the results on the iron and iron oxide substrates was the motivation for the measurements on the gold substrate. They confirmed that differences in the adsorption and thermal behavior of TCP on different substrates could be observed, and that the identical results on iron and iron oxide were not an artifact of the experiment. However, besides offering this confirmation, the gold results are interesting in themselves and, by comparison, shed some light on the results on iron. For this reason and since they have the simplest interpretation, they will be discussed first.

TCP on Gold

The TCP-gold interaction is weaker than the TCP-iron interaction. Figure 2 shows that the initial uptake of TCP is much slower on gold than on iron or iron oxide, which implies that the sticking coefficient is smaller on gold. Likewise, the rapid desorption at low temperatures evident in figure 6 shows that the energy of desorption is lower on gold than on iron or iron oxide.

A possible mechanism for this weak but measurable interaction between gold and TCP is the dipole-induced dipole attraction. The dipole associated with the TCP molecule will induce an image dipole in the conducting gold surface. There will be an attraction between these dipoles. This is similar to the orientation energy between polar molecules (ref. 23), but will be larger in this case because of the exact correlation between the molecular and image dipoles. The orientation energy is the major interaction, between molecules like water with large dipole moments. The dipole moment of TCP can be calculated from its dielectric constant (ref. 24) using the Onsager equation. It is 2.5D, whereas the dipole moment of water is only 1.8 D. The actual binding energy of TCP on a conducting surface due to this interaction depends critically on the distance of the molecule from the surface, and that is unknown. However, the comparison with the intermolecular interaction in water indicates that the dipole-image dipole interaction is a reasonable mechanism for binding TCP to gold at room temperature.

The fact that the XPS intensities from carbon, oxygen and phosphorous decreased together when the gold substrate was heated, implies that the molecule desorbed without dissociation. The similarity of the O(1s) peak before and during heating also argues that there was no decomposition of the molecule. Therefore, it is presumed that TCP adsorbs and desorbs nondissociatively on the gold substrate.

Figure 5 shows a comparison of the relative intensities of the two components of the O(1s) doublet from bulk TCP and TCP adsorbed on gold. If the adsorbed molecule did not dissociate, the difference between the two cases

must be due to differences in the shielding of the oxygen atoms. The molecules in the bulk material were randomly oriented, as was pointed out above. Thus the relatively greater shielding of the double bonded oxygen atom evident in figure 5 implies that it was located closer to the gold surface, on the average, than the bridging oxygen. That is consistent with the dipole-image dipole interaction mechanism, since the electric dipole of the TCP molecule is due primarily to the double bonded oxygen (ref. 8).

To summarize, the data are consistent with a model of nondissociative adsorption of TCP on gold. The molecule is oriented with its polar oxygen toward the substrate. Upon heating the TCP desorbs nondissociatively. The TCP-gold bond is weaker than the TCP-iron or the TCP-iron oxide bond.

TCP on Iron and Iron Oxide

In every case, the data reported here are identical for TCP on iron and TCP on iron oxide. There is, therefore, no reason to distinguish between them in discussing the results. It must be borne in mind, however, that it was not possible to get results from the iron oxide substrate that were as detailed as those from the iron substrate, because the O(1s) peak from the TCP was obscured by the same peak from the oxide substrate. Thus, differences between the two cases may, in fact, exist.

It was found that upon adsorption of TCP on iron, the XPS spectrum showed an apparent increase in the signal from the double bonded oxygen and a decrease in the signal from the bridging oxygens as compared to both the bulk TCP and TCP adsorbed on gold (fig. 5). The intensity of the total oxygen signal, the phosphorous signal and the carbon signal were about the same as they were for TCP adsorbed on gold.

Two alternative configurations consistent with these results are shown in figures 9(a) and (b). Increased shielding of the bridging oxygen atoms located near the substrate combined with greater exposure of the double bonded oxygen accounts for the change in the O(1s) doublet. Greater intensity in the low binding energy part of the doublet could also be due to the proximity of the bridging oxygens to the conducting substrate, since actual charge transfer from the substrate and image charge screening by the conduction electrons could lower the binding energy of electrons emitted by the oxygen atoms. The observed breadth of the C(1s) peak may also be the result of screening in the carbon atoms located near the substrate. In figure 9, an adsorption bond is shown between the substrate and the bridging oxygen atoms. It is likely, however, that pi-electron transfer from the tolyl group also contributes to the bond.

Upon heating the iron substrate to 300° C, several changes were observed in the TCP spectrum. The C(1s) intensity decreased by about one-third. There was a corresponding increase in the P(2p) and O(1s) intensities, while the ratio of oxygen to phosphorous on the surface remained the same. The O(1s) peak, after heating, was a single peak at low binding energy. The P(2p) binding energy decreased by 0.5 to 0.7 eV during heating. These changes are all consistent with the changes in configuration from figures 9(a) to (c) or from figures 9(b) to (d).

In figure 9(c), the loss of one aromatic ring from the TCP molecule causes the reduction in C(1s) intensity, and the consequent decrease in the shielding of the P and O atoms is responsible for the increase in intensity of the P(2p) and O(1s) peaks. The change of the O(1s) peak from a doublet to a singlet suggests that a single oxidation state of oxygen is present after heating. Consequently, figure 9(c) shows the remaining two aromatic rings

detached from the phosphate group. Although no good binding energy standard for iron phosphate was available, the reduction in the P(2p) binding energy is in the same range as the difference between TCP and certain other phosphates that has been reported (ref. 15).

The configuration of figure 9(d) also shows the loss of one aromatic ring. In this case, that does not decrease the shielding of the P and O atoms markedly. However, a change in conformation of the remaining aromatic groups could account for the decrease in shielding. In this configuration, the four oxygen atoms are not identical, but the bond orders are more nearly the same than they are in configuration 9(b) so narrowing of the O(1s) doublet is to be expected.

The XPS data presented here is insufficient to permit a choice between the two reaction sequences 9(a) to (c) and 9(b) to (d). There may, in fact, be others that suit the data as well. It is clear, however, that adsorption is different on gold and iron, and that the reaction of adsorbed TCP on iron heated above 200° C involves loss of one aromatic ring and a change in the oxygen and phosphorus bonding.

Comparison with Friction Tests

Previously (ref. 6), we reported the results of friction tests as a function of temperature on steel specimens lubricated with TCP and run at increasing temperatures. There was a decrease in the friction at a temperature of about 215° C, and above that transition temperature a thick phosphate layer formed on the surface. The present results are similar.

First, a transition temperature is also seen in the present experiment. While not precisely defined, the transition takes place around 200° C, in good agreement with the friction results. Furthermore, at the transition there is a chemical change in the TCP which is consistent with the formation of iron phosphate or an iron organo-phosphate on the iron surface. Thus, it seems likely that the same transition is being observed in both the friction and adsorption experiments. If so, it indicates a mechanism for TCP lubrication that is very like that usually assumed for e.p. additives (ref. 25). At low temperatures, adsorbed TCP effectively prevents metal-metal contact. It is generally known that adsorbed hydrocarbons are effective boundary lubricants, so this is not surprising. As the temperature increases, rapid desorption, such as that observed here from gold, will destroy the interfacial layer, unless something happens to prevent it.

On iron another type of layer is formed before the desorption can expose the surfaces: The adsorbed TCP breaks down to form a reaction film containing phosphate and carbon. That film is stable to much higher temperatures. It cannot be determined from the present results whether the phosphate or carbonaceous material is the effective component of the film, above the transition, or whether any tenacious film would do. The experiments of reference 6 showed that the presence of oxygen was important to the protective properties of TCP, but in the present experiments, the iron and iron oxide substrates were indistinguishable. It may be that it is in the effectiveness of the reaction layer rather than in its formation that oxygen is important.

The mechanism proposed here is concerned with the transition from the low temperature adsorbed layer to the high temperature reaction film. It postulates that a material will be effective if that material adsorbs strongly enough and reacts readily enough on the substrate being used, so that the reaction occurs before desorption can remove the material from the substrate. Whether or not this will be the case will depend on both the adsorbate and the

substrate. In the present case, for example, TCP desorbs from gold before decomposing. On iron, however, the additional interaction with the bridging oxygen atoms or with the aromatic rings holds the molecule on the surface, until temperatures are reached at which TCP can decompose and react with the iron. The decomposition temperature is lower than expected from bulk data, and that too may be because of the interaction with the iron substrate (ref. 26).

These results suggest that further studies comparing friction-temperature data with adsorption-desorption data for a variety of adsorbate and substrate combinations are now desirable. These experiments would test the model proposed here and determine what properties of the molecule and substrate give the desired adsorption-reaction behavior.

CONCLUSIONS

Analysis of the XPS spectrum of TCP during adsorption on gold and iron at room temperature leads to the following conclusions:

1. TCP is adsorbed nondissociatively on gold with the polar P=O part of the molecule near the metal surface. A dipole-induced dipole interaction is proposed.

2. On iron, adsorption is more rapid than on gold indicating a stronger TCP-metal interaction on iron.

3. The XPS spectrum of TCP on iron shows less shielding of the P=O group and greater shielding of the bridging oxygen atoms. An interaction between the bridging oxygen and/or the tolyl groups and the iron is proposed to account for this tilted configuration and the stronger TCP-metal interaction.

When TCP, adsorbed on gold and iron, was heated to 320° C, the changes in the XPS spectrum lead to the following conclusions.

4. TCP desorbs nondissociatively from gold. The desorption is essentially complete by 200° C.

5. On iron TCP reacts with the substrate rather than desorbing. The reaction occurs at about 200° C. It is proposed that the decrease in friction of steel lubricated with TCP at 215° C is related to the reaction of adsorbed TCP observed here.

6. Upon reacting, TCP loses at least one of its tolyl groups and forms iron phosphate or an organo phosphate.

Similar experiments were performed with TCP on an iron-oxide substrate. In that case, the oxygen XPS peak from TCP was obscured by the oxygen XPS peak from the substrate so that only the adsorption and decomposition kinetics could be observed. These are identical to those on the clean iron substrate.

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TABLE I. - XPS ANALYSIS OF BULK TCP

Spectral feature	Binding energy	Peak area, A	Sensitivity factor, S	A/S	Calculated mole fraction	Assignment	Stoichiometric mole fraction
O(1s)	533.7	352	0.63	559	0.11	(C ₆ H ₇ CO) ₃ P _O	0.12
O(1s)	531.5	159	.63	252	.05	(C ₆ H ₇ CO) ₃ P _O	.038
C(1s)	^a 284.6	700	0.205	3415	0.69	(C ₆ H ₇ CO) ₃ P _O	0.69
C(1s)	285.6	114	.205	556	.12	(C ₆ H ₇ CO) ₃ P _O	.12
P(2p)	134.4	50	0.25	200	0.04	(C ₆ H ₇ CO) ₃ P _O	0.038

^a284.6 by definition.

TABLE II. - XPS ANALYSIS OF TCP ADSORBED ON IRON AND GOLD AT ROOM TEMPERATURE

Energy level	Iron		Gold		Assignment
	Binding energy	Peak area	Binding energy	Peak area	
O(1s)	533.6	85	533.7	102	(C ₆ H ₇ CO) ₃ P _O
O(1s)	531.5	75	531.7	31	(C ₆ H ₇ CO) ₃ P _O
C(1s)	^a 284.6	238	^a 284.6	194	(C ₆ H ₇ CO) ₃ P _O
C(1s)	(b)		285.8	31	(C ₆ H ₇ CO) ₃ P _O
P(2p)	134.2	19	134.3	15	(C ₆ H ₇ CO) ₃ P _O

^a284.6 by definition.

^bdoublet could not be resolved.

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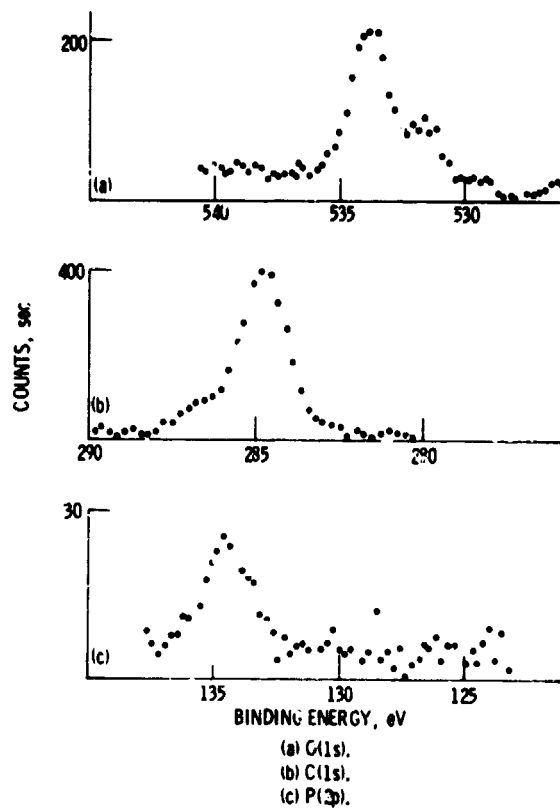


Figure 1. - XPS spectra from TCP condensed on iron at -150°C.

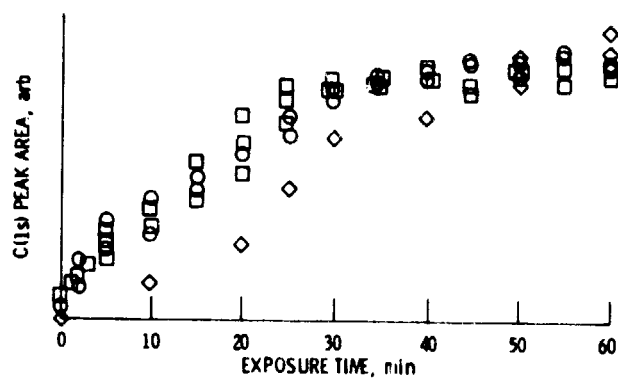


Figure 2. - Adsorption of TCP on three substrates at room temperature, circles-sputtered iron substrate, squares-oxidized iron substrate, diamonds-gold substrate.

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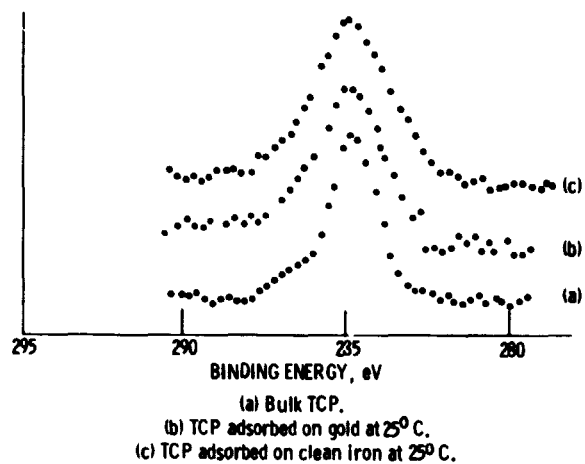


Figure 3. - C(1s) XPS feature from three specimens of TCP.

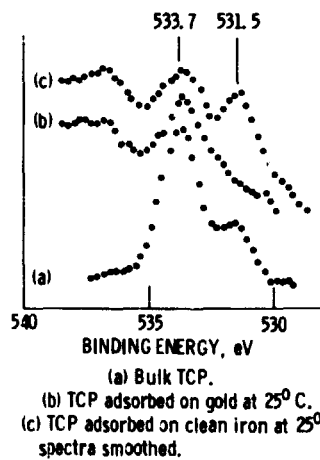


Figure 4. - O(1s) XPS feature from
three specimens of TCP.

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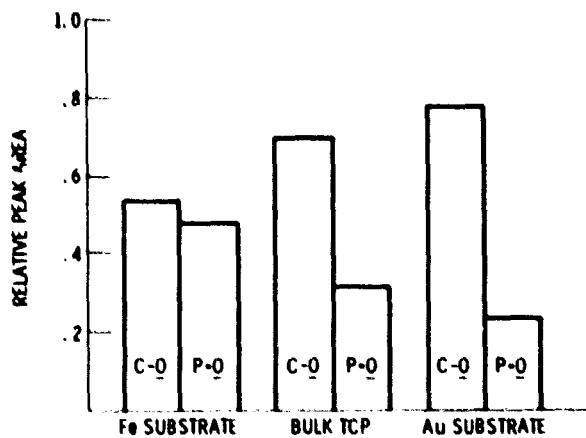


Figure 5. - Relative intensity of the components of the O(1s) XPS doublet from three different specimens of TCP.

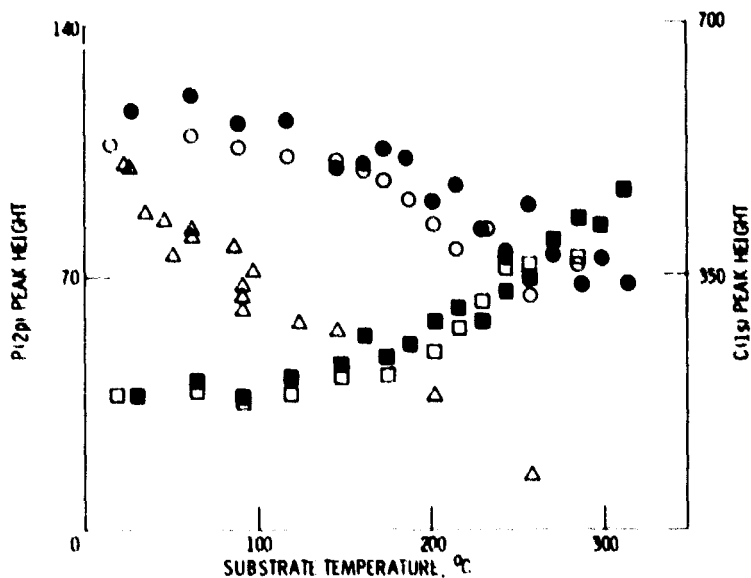


Figure 6. - C(1s) and P(2p) XPS peak heights for TCP adsorbed on several substrates and heated, circles-C(1s) peak, iron substrate, squares-P(2p) peak, iron substrate, triangles-C(1s) peak on gold, filled symbols indicate oxidized substrate, open symbols clean substrate.

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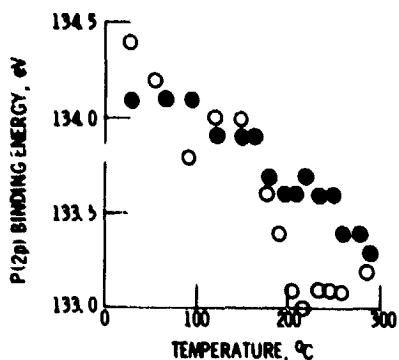


Figure 7. - Change in P(2p) binding energy from TCP on iron, when the substrate is heated, open symbols indicate clean iron, filled symbols oxidized iron.

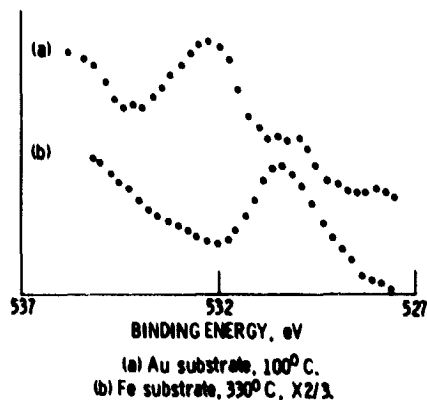


Figure 8. - O(1s) XPS peaks from TCP on gold and iron substrates after heating to 100°C and 330°C, respectively.

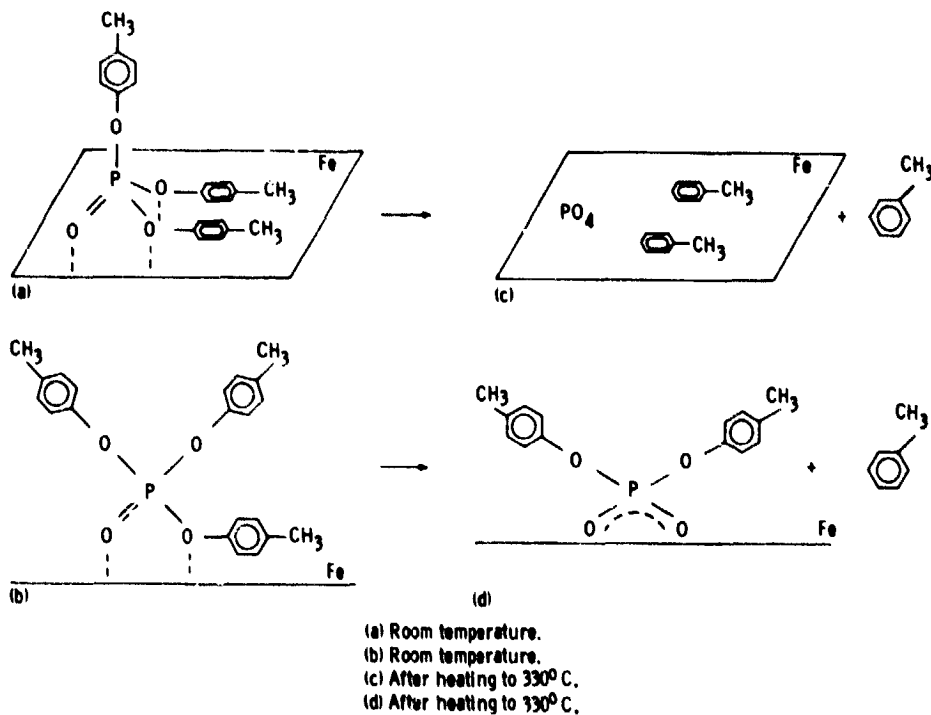


Figure 9. - Alternative models of TCP adsorption on iron.