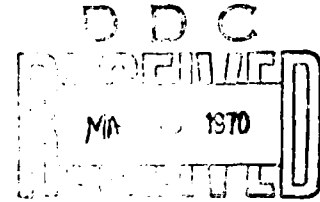# Inhibition of Iron-Catalyzed Neopentyl Polyol Ester Thermal Degradation Through Passivation of the Active Metal Surface by Tricresyl Phosphate

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To investigate the role of tricresyl phosphate (TCP) in inhibiting the iron-catalyzed thermal degradation of a neopentyl polyol ester gas turbine lubricant base stock, various TCP/ester combinations were encapsulated in mild steel tubing and heated at 500 F up to 96 hours. The relative degradation rates of the individual mixtures were measured by monitoring the effusion rate of hydrogen (a degradation byproduct) through the capsule wall. The capsule interiors were then examined by electron microscopy and diffraction to determine whether correlation existed between the features of the surface films formed and the observed degradation rates.

Distinctive films were produced in each test mixture. When ester degradation was inhibited by the addition of 2-10% TCP, a characteristic iron oxide layer was always found at the ester/steel interface. It was postulated that TCP induces the formation of this film, that the film is the agency of inhibition, and that it is similar in action and genesis to the iron oxide passive films known in aqueous systems.

INTRODUCTION

It has been shown (1), that the degradation of neopentyl polyol ester lubricants in the presence of catalytic steels at 500 F is greatly diminished by addition of 1 to 5 percent tricresyl phosphate (TCP), a widely used antiwear lubricant additive, presumably through passivation of the active metal surface. The experiments described here were undertaken in prospect of understanding more clearly the nature of the passivating effect induced by the addition of TCP.

EXPERIMENTAL

A modification of a hydrogen effusion technique originally devised to measure corrosion rates in high temperature aqueous corrosion tests (2) was chosen as a suitable technique for this investigation. In this system, the lubricant test solution is drawn up into a length of catalytically active steel (mild steel used here) tubing which is subsequently squeezed off into a series of capsules that are filled completely with liquid and contain no entrapped air. The capsules are then cut apart with a metal shear and sealed by spot welding across the ends. When these capsules are brought to temperature (500 F), degradation of the lubricant within the capsule commences and hydrogen is generated. Hydrogen diffuses readily through hot steel and the relative extent of degradation may be measured by monitoring the time-rate of hydrogen effusion from the capsule in a simple vacuum vessel as shown in Fig. 1.

When discrete surface films are formed, their composition and morphological characteristics during formation may be studied by withdrawing capsules from the oven at progressively increasing intervals and examining the films thus far developed on their interiors by electron microscopy, electron diffraction, or other appropriate techniques.

Specific Materials and Procedures.

Two different stocks of seamless mild steel tubing were used in these experiments. The tubing first used contained 0.15% C, 0.09% Si, 0.66% Mn, 0.22% Cr, 0.09% Ni, 0.026% S, 0.011% P and 0.013% N; when this stock was depleted, it was replaced by another which contained 0.14% C, 0.22% Si, 0.46% Mn, 0.24% Cr, 0.13% Ni, 0.016% S, 0.014% P and 0.009% N. The dimensions of both were the same however at 0.25" O.D. and 0.022" wall thickness.

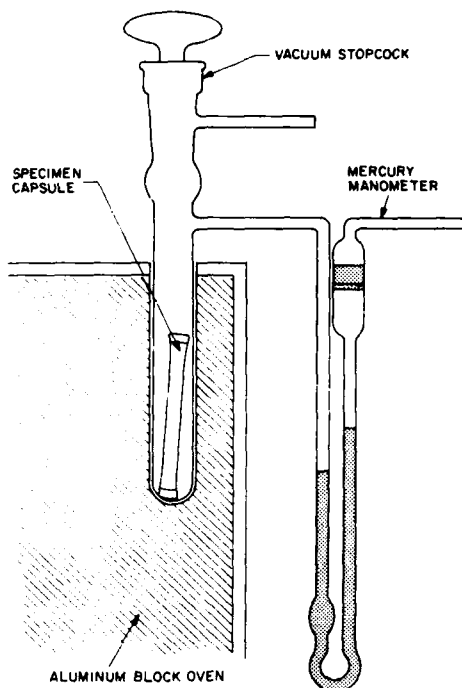Pretreatment consisted of degreasing in trichloro-

Fig. 1—Vacuum vessel and manometer used in monitoring lubricant and additive degradation by the hydrogen effusion technique.

ethylene and then trichlorotrifluoroethane, followed by vacuum annealing at 875 C and 10^{-5} torr for one hour. The annealed specimen tubing was stored in a closed container over anhydrous $CaSO_4$.

A commercial base stock was chosen from those studied by Cottington and Ravner (their PE-301 designation which consists essentially of pentaerytritol tetracaproate) as representative of the neopentyl polyol esters and suitable for this investigation. Both the PE-301 polyol ester and tricresyl phosphate were percolated through alumina and magnesia-silica gel adsorbent prior to use to remove polar impurities and any free acids present.

Reagent grade 85% phosphoric acid was used to prepare the two special PE-301/H_3PO_4 and TCP/H_3PO_4 test mixtures. The acid was difficultly soluble in both TCP and PE-301 polyol ester and ultrasonic dispersion was used to hasten solution. No phase separation occurred in either solution over a period of several months however and the H_3PO_4 concentration is considered to be 0.5% by volume, whether actually present in true solution or not.

The individual capsules all contained the same volume of lubricant (approximately 0.6 ml). Although Fig. 1 indicates only one capsule, the test runs were generally made using two capsules in a vessel to provide the most appropriate range for pressure measurement. The capsules were made up in groups of six and frequently some capsules would be subjected to heat-

ing after standing overnight whereas others of the group would remain several days at room temperature before being used. In these instances, the time of standing did not influence the subsequent behavior of the capsule on heating, the implication being that low temperature effects such as physical adsorption, etc. do not play a determining role in the degradation process at 500 F.

The capsules were heated in a block oven (Fig. 1) which was held to within ±2 of 500 F during the course of a 96-hour run.

At the completion of a run, the capsules were opened and the lubricants collected into glass vials for further examination. Following this, the capsules were rinsed thoroughly in boiling trichloroethylene and then boiling methanol and bisected transversely so that the interior might be inspected visually. When possible, sections of the surface film were detached from the capsule wall by the iodine-methanol technique (3) and characterized by electron microscopy and diffraction.

RESULTS

Figure 2 shows the course of hydrogen evolution during the degradation of five pertinent PE-301/TCP/H_3PO_4 solutions as they were heated, while encapsulated in mild steel, at 500 F. That the evolved gas is in fact hydrogen was verified by mass spectrometry. It probably results from reaction of free acids, which both TCP and PE-301 are capable of forming, with the capsule wall, but until the mechanism of degradation is better understood, the data in Fig. 2 must be regarded as only indicative of the relative degradation rates of the solutions under test.
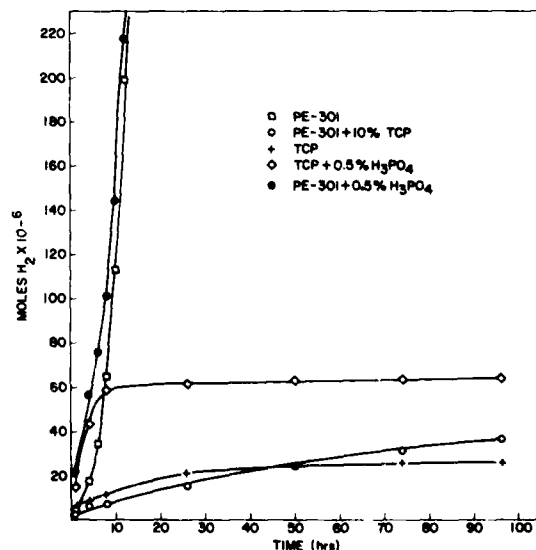

Fig. 2—Release of hydrogen as a function of time for various lubricant and additive combinations encapsulated in mild steel tubing (1.2 ml volume) and heated at 500 F.

PE-301

The hydrogen evolution curve in Fig. 2 for the PE-301 polyol ester base stock, with relatively low initial evolution rates being soon succeeded by increasingly higher ones as the capsule remains at temperature, indicates that its degradation is probably autocatalytic in nature. Appreciable quantities of hydrogen are liberated in the degradation process; hydrogen was still being evolved from the two 0.6 ml specimens at 35×10^{-6} moles per hour after 24 hours, and at about 10×10^{-6} moles per hour even after 48 hours.

The relative rates of hydrogen evolution reflect stages in the breakdown of the ester within the capsule. At one and four hours, where the hydrogen evolution rates are low, the fluid comes from the capsule little changed, being still colorless after one hour and only moderately red-tinged after four. At 24 hours, however, after the period of highest hydrogen evolution, the interior is completely filled with a dark brown, slightly tacky, resinous-appearing solid polymerization product of PE-301. This polymerization reaction is evidently only an intermediate step in the degradation of PE-301, for inspection of capsules heated 96 hours reveals that there has been further breakdown and that instead of the brown solid described above the capsules now contain a small amount of a nearly black viscous liquid, residual gases under considerable pressure, and a fine-grained, black, carbonaceous material deposited as a coating on the capsule wall. Size limitations make an analysis of the gases contained in these capsules impractical, but mass spectrometry of the breakdown products of PE-301 in tests using Cottington and Ravner's experimental arrangement (1) has indicated the presence of some CO_2 and CO. It is presumably these gases along with other low molecular weight ester degradation products which cause the pressure build up observed within the capsule at 96 hours.

Although there were indications of an incomplete surface film in the one and four hour capsules, there were in general no discrete surface films as are observed when TCP is employed as an additive (see section below). This was particularly true at 24 and 96 hours where the capsule interiors took on an etched appearance which strongly suggests the loss of metal to the liquid phase. This would be in agreement with the findings of Cottington and Ravner where coupon weight losses of up to 10% were measured in degrading neopentyl polyol esters.

PE-301 + 10% TCP

The curves in Fig. 2 for PE-301 with and without TCP illustrate how drastically the thermal stability of encapsulated PE-301 is improved by the addition of TCP. The PE-301/TCP lubricant mixture was little degraded and remained liquid throughout the test although it did undergo some color change, being still water-white after 1 and 4 hours heating, very slightly
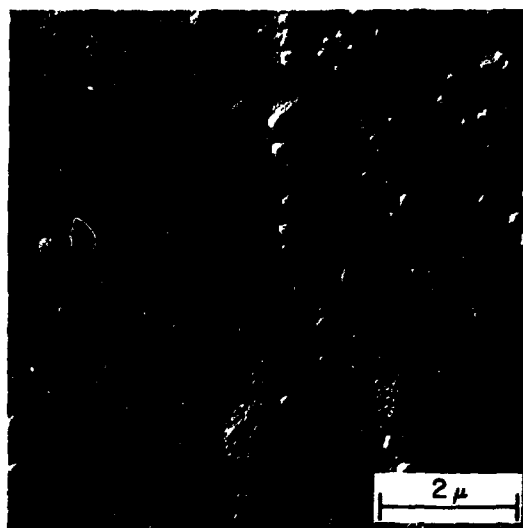

Fig. 3—Replica of the oxide film produced on the interior of a mild steel capsule containing PE-301 + 2% TCP after 68 hours at 500 F.

yellow after 24 hours, and light brown at the completion of the run (96 hours).

This change in degradation behavior is likely a result of the presence of a surface film which develops on the capsule interior here, but not with PE-301 alone. The film in question is uniform and apparently continuous both to the eye and to the electron microscope and appears, moreover, in the electron microscope to be made up of very tiny crystallites (Fig. 3). It strips from the capsule easily and gives quite good transmission electron diffraction patterns which indicate that the film has a spinel crystal structure, and is most probably predominantly Fe_3O_4 (Table 1).

Chemical analyses of the stripped films show, however, that they do contain some phosphorous, two tests with 96-hour films giving Fe:P atomic ratios of 5.7:1 and 4.9:1, respectively.

A noteworthy aspect of this film is that it grows in thickness with time, passing through the interference colors silver to gold to blue at the 1, 4 and 24-hour stages of heating. (The hydrogen evolution curve for PE-301 + 10% TCP has a slight positive slope even at 96 hours and it may be that the two phenomena are related, the reaction which leads to thickening of the surface film also generating hydrogen.) That the surface oxide continues to thicken over an extended interval is evidence that the oxygen necessary for the growth process may come in some way from the neopentyl polyol ester base stock itself. Dissolved or entrapped oxygen, even if present in sufficient quantity (and this is almost certainly not true, considering the experimental technique employed), would be quickly used up at 500 F and the development of the oxide surface film, in such a case, would be curtailed shortly after the capsules came to temperature.

Table 1

A comparison between the electron diffraction pattern from the film generated on the interior of a mild steel capsule by PE-301 + 10% TCP after 24 hours at 500 F and the ASTM standard X-ray diffraction pattern for Fe_3O_4.

Electron Diffraction Pattern From Film Produced In PE-301 + 10% TCP		X-Ray Diffraction Pattern for Fe_3O_4 (ASTM 11-614)	
$d(A)$	I(est.)	$d(A)$	$I(I/I_1)$
4.85	MW	4.85	40
2.96	S	2.966	70
2.53	VS	2.530	100
2.43	W	2.419	10
1.92	VW	—	—
1.87	VW	—	—
1.72	MW	1.712	60
1.61	M	1.614	85
1.49	S	1.483	85
1.42	W	—	—
1.33	MW	1.327	20
1.28	M	1.279	30
1.27	VW	1.264	10
1.21	MW	1.2112	20
1.17	W	—	—
1.12	MW	1.1214	30
1.09	M	1.0922	60

TCP

The TCP molecule contains a sizeable percentage of oxygen, and the possibility exists that this oxygen may be made available through some mechanism for the formation of the iron oxide film observed above. On the other hand, there is evidence that the presence of TCP could lead to the formation of an iron phosphate barrier film (4). It became a matter of some interest then to determine the nature of the surface film formed in a capsule filled with 100% TCP.

When encapsulated TCP was heated, the amount of hydrogen evolved was low, particularly after 24 hours when the rate dropped to almost zero (Fig. 2). Some degeneration of TCP evidently continues to occur however, for although the TCP comes from the capsule essentially colorless even after 96 hours at temperature, it takes on a reddish cast after standing in air with the final degree of coloration being related to the time of exposure at 500 F.

The film formed on the capsule wall was blue after 1 hour heating and remained blue and essentially unchanged in appearance from that time onward. This surface film is shown by electron microscopy to be more complex than those produced in PE-301 + 10% TCP. Replica studies indicate that the uppermost layer has a polymeric character, and although it is essentially continuous, there are occasionally "holes" (Fig. 4) whose appearance serves to emphasize the lacquer-like nature of this coating. When the stripped
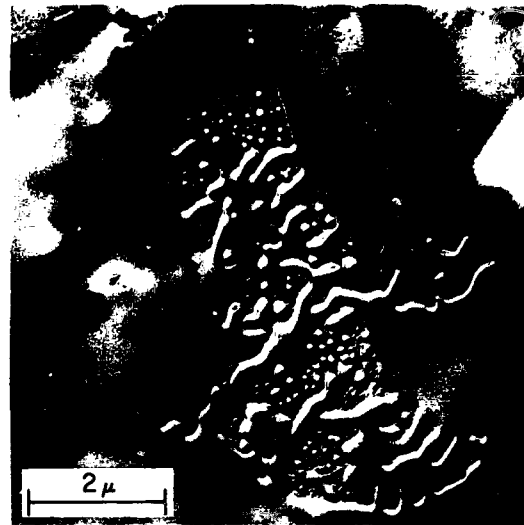

Fig. 4—Replica of surface film produced on the interior of a mild steel capsule containing 100% TCP after 1 hour at 500 F. The film is lacquer-like and essentially continuous, but "holes" such as this do exist.

films are viewed directly, however, it becomes apparent that they also have a crystalline sublayer (Fig. 5). Selected area diffraction from uncoated areas (lower right hand corner of Fig. 5) shows this sublayer to be an iron oxide giving essentially the spinel pattern listed in Table 1. Moving the specimen then so that diffraction is from both layers obscures this spinel pat-

Fig. 5—Transmission electron micrograph of the surface film generated on the interior of a mild steel capsule containing 100% TCP after 68 hours at 500 F. The light area is the site of a "hole" as shown by replica in Fig. 4. Note that an iron oxide film underlies the amorphous upper layer.

tern by the superposition of a diffuse "amorphous" diffraction pattern, thus providing further evidence for the noncrystallinity of the upper coating.

The extent of the oxide sublayer, as well as its degree of perfection, seems to vary from specimen to specimen. Since this inner oxide layer likely derives from the oxide film which existed on the tubing at the time the TCP was encapsulated, its existence might be expected to depend on the initial thickness of the air-formed film (which will vary somewhat depending upon the specimen and its history), and on whether the film is augmented (by capsule wall reaction with trace O_2 or H_2O, or with H_2O from possible minor degradation reactions within the TCP) or depleted (through dissolution by H_3PO_4 formed by the breakdown of TCP) during the course of heating. These possibilities can not be verified readily in the experimental system employed here. It was established however that the iron content of the stripped films did fluctuate widely; for example, the chemical analysis of one 96-hour film indicated an Fe:P atomic ratio of 0.9:1 whereas analysis of a second film (different specimen, different run) gave the same ratio as 3.4:1.

Of perhaps more significance for present interests are the surface crystals which appear as isolated clusters (Fig. 6) on the capsule surface with extended heating. They grow in greater or lesser number, apparently depending somewhat on the TCP batch and tubing stock used. The selected area electron diffraction patterns which can be obtained from these crystals are not adequate to allow identification of the species, but scanning electron microprobe analysis has indicated that these crystals are phosphorous-rich. On this basis, it is hypothesized that they are iron phosphate crystals

formed by reaction between the capsule wall (perhaps at a weak point in the surface film) and free phosphoric acid generated by the slight degradation of encapsulated TCP that occurs with time at 500 F.

TCP + 0.5% H_3PO_4

To test the idea that the "iron phosphate" crystals described in the preceding section resulted from attack by free phosphoric acid produced by the breakdown of tricresyl phosphate, a small percentage of the free acid was specifically added to the TCP stock prior to the makeup of the test capsules. This caused, as shown in Fig. 2, an early, rapid evolution of hydrogen at the commencement of heating, presumably from reaction of the free acid. Once this acid is depleted, however, there appears to be little further attack by the TCP itself.

During the interval of high hydrogen production, surface crystals exhibiting an unusual morphology (shown by replica in Fig. 7 and more graphically by scanning electron microscopy in Fig. 8) developed on the capsule interior, growing as "islands" which gave an almost complete covering of the substrate surface. Similarities between the morphology of the individual crystals here and those appearing with 100% TCP lead to the conclusion that they are probably the same species.

Even though the crystals are now larger and present in much greater quantity, they still represent difficult subjects for both electron diffraction and x-ray diffraction. An incomplete x-ray diffraction pattern containing a few weak lines (Table 2) was obtained however, and comparison with the ASTM patterns available for iron phosphorus compounds shows that the best fit (albeit
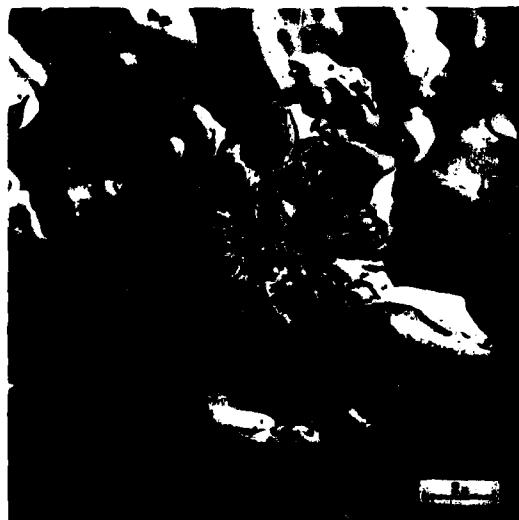

Fig. 6—Replica showing a type of surface crystal which tends to develop on the walls of capsules containing 100% TCP with longer periods of heating at 500 F.

Fig. 7—Replica showing the morphology of iron phosphate crystals formed in mild steel capsules containing TCP + 0.5% H_3PO_4 after 1 hour at 500 F.
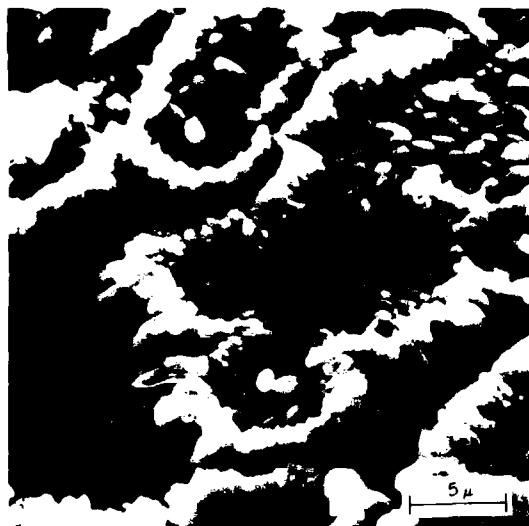
Fig. 8—Scanning electron micrograph of iron phosphate crystals showing crystal morphology in perspective (same specimen as Fig. 7).

not a particularly good one) is with the $Fe_3(PO_4)_2$ pattern. Doubt as to the correctness of this identification was raised when analysis of the stripped film gave an Fe:P atomic ratio, 0.92:1, which might indicate that the iron exists in the ferric rather than the ferrous state where the iron to phosphorus ratio would be 1.5:1. On the other hand, the capsules contain about 1.1×10^{-4} moles of H_3PO_4 and simple reaction of this

TABLE 2

A comparison between the X-ray diffraction pattern from the film generated on the interior of a mild steel capsule by TCP + 0.5% H_3PO_4 after 96 hours at 500 F and the ASTM X-ray diffraction pattern for $Fe_3(PO_4)_2$

X-RAY DIFFRACTION PATTERN FROM FILM PRODUCED IN TCP + 0.5% H_3PO_4	X-RAY DIFFRACTION PATTERN FOR $Fe_3(PO_4)_2$ (ASTM 14-337)	
$d(A)$	$d(A)$	$I(I/I_1)$
8.18		
7.07	no lines	
6.17	reported	
4.62		
4.25	4.28	(14)
	3.64	(8)
3.41	3.42	(90)
3.21	3.168	(14)
	3.070	(6)
3.015	3.013	(45)
no lines discernible	many lines, including	
beyond this	2.910	(55)
	2.838	(100)

amount of acid with iron to give the tribasic salt would result in the generation of 1.6×10^{-4} moles of H_2 (3/2 moles of H_2 per mole H_3PO_4). But the total quantity of hydrogen collected up to 26 hours, a point at which, according to Fig. 2, all of the acid would have been reacted, was only 0.6×10^{-4} moles, i.e., only 1/3 to 1/2 the amount of hydrogen expected. This might argue that the phosphate occurs in the crystal as the monobasic or dibasic anion. And so, these surface crystals can only be identified presently as iron-phosphate compounds of unknown stoichiometry having a crystal structure somewhat similar to $Fe_3(PO_4)_2$.

The influence of the free phosphoric acid upon the thermal stability of TCP itself under these conditions is not known, although there is evidently some effect, for the TCP/H_3PO_4 mixture is nearly black after 96 hours heating, and as discolored (red) at 24 hours as pure TCP is at 96 hours.

PE-301 + 0.5% H_3PO_4

The pertinent question now becomes whether or not the addition of H_3PO_4 to PE-301 will also bring the formation of an iron phosphate film, and if so, whether or not this film will prove passivating against attack by PE-301 at 500 F. (This is by way of testing the applicability of the theory developed in lubrication studies by Godfrey (4) that the role of TCP is to yield free H_3PO_4, this acid then forming a phosphate film on the metal surface which is the active agency in wear reduction or presumably, in this case, degradation inhibition.) And the answer, at least to the latter question, is given by the hydrogen evolution curve for PE-301 + 0.5% H_3PO_4 in Fig. 2 which shows clearly that it does not. There is a high hydrogen evolution at 1 and 4 hours heating as with TCP/H_3PO_4, but subsequent to this the rates, rather than dropping to a low level, become increasingly rapid and the hydrogen evolution curve then almost exactly parallels that for PE-301 alone. Moreover, upon opening the capsules, the neopentyl polyol ester is found to have been transformed to a brown, polymeric solid by 24 hours heating, indicating that the course of degradation for PE-301/H_3PO_4 is the same here as when H_3PO_4 is not present.

Although the early high evolution rates might be expected to reflect the buildup of a discrete film here also, electron microscopy of the 1 and 4-hour specimens shows definitely that there is no film of the type pictured in Figs. 7 and 8 on the capsule surface. Furthermore, the rates at 1 and 4 hours for PE-301 + 0.5% H_3PO_4 are approximately the sum of the rates for PE-301 alone and TCP + 0.5% H_3PO_4 at the same times; that is, it appears that the reactions of PE-301 and H_3PO_4 are essentially independent of one another. This may not be strictly true, however, since strong acids are known to catalyze the decomposition of neopentyl polyol esters. In any event, this last experiment would seem to indicate that the presence of H_3PO_4, either as added deliberately or (presumably) as a by-product of TCP, is not sufficient to prevent the degradation of encapsulated PE-301.

DISCUSSION

Results in these experiments are in qualitative but perhaps not quantitative agreement with the earlier findings of Cottington and Ravner where the catalytic effect of metals in the thermal degradation of lubricants was measured by heating the lubricant and test metal coupon together in an evacuated and sealed glass cell (1). Direct comparison tests with PE-301 and mild steel (the coupons in the Cottington-Ravner cells were cut from the same specimen of tubing from which the capsules were made) show, for instance, that the degradation tendency is stronger in the capsule system. And, with capsules, a somewhat larger percentage of TCP (in the range 5–10%) is required, particularly with the last tubing stock used, for effective inhibition. Conversely, when surface films are formed, the films on the capsule interiors are better developed and more amenable to examination than those appearing on the Cottington-Ravner coupons. The same definitive inhibition behavior was always observed in both systems however: PE-301 alone degraded; PE-301 plus a few percent TCP did not. It is believed therefore that TCP serves the same function in both systems and that this function may be explained according to the following hypothesis.

The hydrogen evolution curve for PE-301 in Fig. 2 suggests an autocatalytic reaction for the pyrolysis of the encapsulated neopentyl polyol ester. It appears therefore that PE-301 *per se* does not react with mild steel, but that its breakdown, once initiated, leads to the production of corrosive species which do attack the capsule wall. The net effect of this attack is 1) the release of soluble iron salts of the corrosive species into the as yet undegraded PE-301 and 2) the removal of surface layers of iron from the capsule itself. Either effect could instigate an autocatalytic reaction depending whether the thermal decomposition of PE-301 is stimulated by the presence of soluble iron ion species (e.g., an iron ion-catalyzed polymerization reaction) or by exposure to "active" iron surfaces. In the latter case, the capsule wall would presumably become more active with time as a result of the corrosive attack, perhaps through dissolution of the oxide film preexisting on the capsule at the time of fabrication. This film is very thin (100-200 A) however and should be removed early in the run at a time when the reaction rate has yet to increase by orders of magnitude. And so the first mechanism seems the more likely. On the other hand, it may be that soluble iron salts and iron metal surfaces act synergistically to induce the thermal breakdown of neopentyl polyol esters since glass cell experiments have shown esters containing TCP to be stable at 500 F in the presence of steel but not both steel and dissolved ferric toluate.

In any event, the chain of reaction is broken when TCP is present because TCP promotes the formation of a passivating oxide film which acts as a barrier against further corrosion. This has the effect, depending on the viewpoint above, of either closing off the source of iron ions or forming a shield between the active (elemental) iron and PE-301.

An interesting and perhaps significant sidelight here is that when FeO and α-Fe$_2$O$_3$ powders were tested, using the evacuated glass cell system, to determine their effect in accelerating the degradation of PE-301, both were found to be much less active than mild steel, but with FeO, the less oxidized species, being consistently slightly more active than α-Fe$_2$O$_3$, both in terms of induced acidity (23 versus 10 neutralization number) and dissolved iron content (approximately 1% versus 0.1%).

The role of passivating oxide films on iron and steel in aqueous corrosion has long been recognized, and the structure of passive films, as well as the phenomenon of passivity in general, has been the subject of extensive study in this field. And, although some contention still exists, the majority opinion seems to be that the passive oxide film is a nonstoichiometric oxide layer which is essentially Fe$_3$O$_4$ at the metal/oxide interface and γ-Fe$_2$O$_3$ at the oxide/solution interface (5).

It has been found that certain anions facilitate the formation of the passive oxide film (6, 7) and thus inhibit corrosion. One of the first demonstrations of this came when it was shown that sodium phosphate in the presence of oxygen produced a passivating film on iron under conditions where the oxygen alone (or sodium phosphate, as later experiments using carefully deaerated solutions proved (9)) was not sufficient to bring about passivation (8). The film itself was shown by electron diffraction to be an iron oxide and not some form of iron phosphate as might have been expected, the oxide being described at that time as a "cubic oxide" which might be Fe$_3$O$_4$, γ-Fe$_2$O$_3$ or possibly some partially oxidized intermediate.

The so-called inhibitive anions influence the passivation process by complex means which even now remain little understood. It is known, however, from recent radiotracer experiments by Thomas (10) on the anodic passivation of iron at room temperature in near neutral solutions containing phosphate anions, that phosphate ions are incorporated into the three-dimensional film which develops on the iron surface once the specimen is brought into the "passive" potential region. Thomas suggests that the phosphate is taken into the passive film as ferric phosphate inclusions or through ion exchange (with the passive film presumably remaining primarily an iron oxide film as found by previous researchers, although he does not discuss this point explicitly).

Incorporation of the inhibitive anion also occurs in the anodic passivation of iron in the presence of molybdate ions as shown by Cartledge (7). In this instance, the passivating film is postulated to consist of a Fe(II)—Fe(III)—MoO$_4$$^{2-}$ complex, analogous to the Fe(II)—Fe(III)—O^{2-} iron oxides, with the stoichiometries and iron oxidation states varying according to the electrode potential. Moreover, Cartledge points out that the molybdate anions must facilitate the oxidation of iron ions here through a chemical rather than

electrochemical mechanism since the films are produced at potentials too noble for the reduction of Mo(VI).

Viewed against this background, our findings would appear to suggest that althu gh "classical" passivation has been mostly observed and studied in aqueous environments, it is in fact a general phenomenon and may occur under certain circumstances in organic media as well. (This does not necessarily imply a water-free environment however, since H_2O may be introduced as a product from reactions taking place between the organic species.) If the oxide films here are actually true passive oxide films, then the extra diffraction lines in Table 1 beyond the standard Fe_3O_4 pattern may signify the presence of $\gamma\text{-}Fe_2O_3$ or some other film component more highly oxidized than Fe_3O_4 (11). There are sufficient difficulties in distinguishing $\gamma\text{-}Fe_2O_3$ from Fe_3O_4 in high temperature corrosion films by electron diffraction (12), however, that these extra lines must be considered only as consistent with the surface oxide being a passive oxide film, not as proving it. In somewhat the same vein, the preceding discussion of Thomas' work would indicate that the discovery of phosphorus within our films does not argue against their being passive oxide films, but might indeed be quite in keeping with the idea. The classic criterion for passivity lies in the behavior of the metal under anodic polarization, but unfortunately electrochemical measurements of this sort are infeasible in the system at hand and a more quantitative definition of the role of TCP in film formation is precluded for the present. The experimental evidence is, however, that TCP interacts with iron under these conditions, possibly through complex formation (i.e., TCP may exert an inhibitive influence here essentially chemical rather than electrochemical in nature, in analogy with the findings above for the molybdate anion), to bring it to a state from which it is readily oxidized and converted to an adherent, protective iron oxide film by the PE-301 neopentyl polyol ester or one of its degradation products.

SUMMARY

Neopentyl polyol ester based lubricants thermally degrade in contact with mild steel at 500 F. The process can be inhibited by the addition of small percentages of tricresyl phosphate (TCP) (1). The present work shows that the effect of TCP is to promote the formation of a passivating surface film. This film is not an iron phosphate film however, as might be anticipated from earlier dynamic lubrication studies with TCP (4), but rather an iron *oxide* passivating film, probably related in structure and mechanism of generation to the iron oxide passive films known from aqueous media corrosion investigations.

ACKNOWLEDGEMENTS

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DISCUSSION

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This paper presents a well conceived and detailed laboratory investigation to analyze the real field problem of turbo-jet engine lubricant thermal instability and resultant corrosion.

It was noted that the effect of metal catalysis was recognized and data developed for polyol esters in other than all glass thermal stability apparatus. Thus the data was in reasonable agreement with that obtained in similar studies performed several years ago at the Petroleum Refining Laboratory of Pennsylvania State University under Air Force Materials Laboratory contract. This work was accomplished at temperatures of 100 F to 200 F more than the NRL experiments. One area of agreement was in the amounts of free monocarboxylic acids generated by pyrolysis of polyl esters. Both investigations showed they were proportional to the amounts of corresponding groups in the parent esters. In the presence

of metal catalysts and higher temperatures, the Air Force sponsored work determined that the activity of these acids extended to the formation of metallic salts present in an amount directly related to the amount of hydrogen generated by the acid-metal reaction. The more volatile mono-basic acids formed with the polyol esters were more corrosive or reacted more readily with the metal catalysts. It was assumed that increased pressures in the test apparatus would tend to keep these volatile acids in the liquid phase where increased corrosion and degradation would produce an autocatalytic effect. This is alluded to in the second phase of this NRL experimental study. In the Air Force study it was also observed that the major products of decomposition and combination appeared to be soluble in the original esters while this was not true for dibasic acid esters.

The mechanistic study of the inhibiting action of the passive film formed by the interaction of pentaerythritol ester and TCP forms a second natural division of this paper. The analogy of the formation of an effective lubricative surface film composed of iron oxide with the classical passivation mostly observed and studied in aqueous environments is in sharp disagreement with other published work in this area. For example, Godfrey (4) in his investigation of the lubrication mechanism of TCP on steel sliding on steel showed the formation of a mixture of iron phosphate and the hydrate of iron phosphate. Phosphate formation was substantiated by other friction and wear experiments. Electron diffraction analysis of the deposition material formed in the wear surfaces of test specimens confirmed the presence of iron phosphate complexes. These compared favorably with accepted ASTM standards.

Further work performed at Pennsylvania State University under Air Force contract utilizing radiation techniques has contributed additional evidence to the presence of phosphorus in TCP lubricated wear surfaces. These studies showed that substantial quantities of polar P-32 impurities in typical TCP-32 appear to be responsible for all of the P-32 adsorbed on metal surfaces. This physically adsorbed material then furnished a sufficient supply of phosphorus containing chemical reactants at the wear surfaces to provide effective lubrication. This was confirmed by the presence of P-32 in the wear scars of dynamic test specimens.

This, then, gives rise to a certain amount of conjecture with respect to the conclusions reached in this paper. Possibly the answers to the following questions will help clarify certain points of disagreement: 1. Are there several ways to interpret the patterns obtained by electron and X-ray diffraction? 2. Does a double layer of deposit from the test capsule actually exist? 3. Would the instrumental analyses used have the capability of discerning between deposits formed by dynamic testing and those formed statically?

Perhaps the answers to these questions giving a more detailed explanation of the techniques and interpretations of electron and X-ray diffraction analysis might shed greater light on the conclusions reached in this investigation.

DISCUSSION

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The authors are to be commended for their "in depth" experimental approach and detailed evidence in explaining the role of tricresyl phosphate (TCP) in inhibiting the iron-catalyzed thermal degradation of neopentyl polyol esters by promoting the formation of passivating oxide film. This study is of much interest at this time since neopentyl polyol esters typify lubricant base stock extensively used by the military.

Since it is generally known that chlorine containing compounds may initiate incipient corrosion on mild steel, the advisability of using trichloroethylene and trichlorotrifluoroethane as pretreatment compounds is questionable. Can the authors provide any experimental evidence that the use of chlorinated solvent did not affect the formation of the passivating oxide film?

In the experimental section, it is stated that the capsules were completely filled with liquid and contain no entrapped air. Were precautions taken to insure that the dissolved air and water were also removed since it is known that the thermal stability of esters are affected due to hydrolysis or oxidation caused by the presence of small quantities of oxygen or moisture. Such precautions (removal of oxygen and moisture) were stipulated in the previous paper but are not mentioned here. While the role of the possible presence of dissolved oxygen is described in the section of the paper covering the formation of the surface oxide film (PE-301 + 10% TCP at 96 hours), nevertheless, would not small quantities of oxygen or moisture alter the initial degradation reactions?

AUTHORS' CLOSURE

The authors are indebted to Mr. Morris and Mr. Messina for pointing out several areas in this paper in need of clarification and further discussion. The specific questions raised by Mr. Morris will be considered first. Identification by electron diffraction involves essentially just a comparison of the "unknown" pattern (line spacings and intensities) with a standard pattern from the pure compound. The better the agreement, the more certain the identification. In the present case, the fit is quite good (Table 1), and the authors are therefore confident of the identification.

The authors assume the "double layer of deposit" referred to in Question 2 is the double layer formed with 100% TCP (Figs. 4 and 5). The amorphous, lacquer-like upper layer does exist here and it is not an artifact of specimen preparation, etc. It is probably similar to the resinous films which have been found previously on steel in TCP (Albertson Discussion of Godfrey's paper (4)).

As concerns diffraction technique, the films formed in our PE301/TCP (Fig. 3) and 100% TCP (Figs. 4 and 5) runs were uniform and sufficiently thin that they could be stripped from the capsule surface and examined by *transmission* electron diffraction, i.e., where the electron beam passes directly through the film from top to bottom. With thicker films, as the authors found with

TCP/H_3PO_4 and as presumably might be found in dynamic lubrication tests, one must resort to *reflection* electron diffraction where the electron beam is reflected from the specimen film while it is still in place on the substrate surface. If the film is uniform and not layered, the same diffraction pattern is obtained with either method. If this is not the case, as for example in Fig. 8, then there may be a difference, for reflection electron diffraction will tend to give a pattern from the upper crystals, and transmission electron diffraction one from the thin "base film" (the upper crystals will not contribute appreciably because they are too thick for direct electron transmission).

It seems to the authors, however, that the disagreement between this work and dynamic studies, e.g. Godfrey's, does not result only from the use of different diffraction techniques, but also from the fact that two different behavioral phenomena may be involved. When 2–10% TCP is added to the pentaerytritol ester (PE-301), it is observed that the formation of a surface oxide occurs and it is concluded that it inhibits decomposition of the ester by passivating the active metal surface. Godfrey finds good load-carrying properties with 100% TCP and identifies iron phosphate crystals on the sliding surface. It is not necessary, or even likely, that the surface film is the same in both instances. The authors note, for example, that Godfrey could not detect iron phosphate crystals on sliding surfaces lubricated with 1–2% TCP in white oil (open air experiments), even though wear resistance was definitely improved by the TCP addition (his Fig. 5). On the other hand, when 100% TCP was substituted for PE-301/10% TCP in the authors' capsules, a distinctly different surface film was formed in which iron phosphate

crystals were found (Fig. 6). The authors' results then are essentially in accord with Godfrey's for 100% TCP, the difference being only in degree, with more iron phosphate being generated in his rubbing experiments as might be expected. Whether they are or not for the low percentage TCP solutions is uncertain. There seems to be, however, no direct evidence to contradict the possibility that low percentages of TCP in lubricants can, in the presence of oxygen or water, produce "passive" iron oxide films (which may have some lubricating effectiveness), while 100% TCP yields an iron phosphate film (TCP→phosphoric acid→iron phosphate) which contributes good antiwear properties, but is not necessarily an effective inhibitor against corrosive attack.

In answer to Mr. Messina's question, the reagents here were taken from the same lot and purified in the same manner as those in the preceding paper by Cottington and Ravner. No precautions beyond those mentioned were taken to reduce the oxygen and/or water content within the specimen capsules. It is not, however, believed that this, or the fact that chlorinated solvents were used in specimen cleaning, affected the results. First, the experiments were "comparative", i.e., all capsules were cleaned the same way, and the oxygen and water impurity level would presumably have been the same, yet only those capsules containing TCP (as little as 2%) showed the particular inhibitive effect reported here. And, secondly, the same qualitative results were obtained by Cottington and Ravner who did not use chlorinated cleaning compounds, and who did take the precaution of evacuating their test chambers while the contents were heated and thoroughly shaken to reduce the oxygen and water levels to very low values.