NASA Technical Memorandum 83486

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(NASA-TM-83486) TOPOLOGICAL REACTION RATE MEASUREMENTS RELATED TO SCUFFING (NASA) 19 p HC A02/MF A01 CSCL 11F

N84-14288

Unclas
G3/26 42758

Prepared for the
Joint Lubrication Conference
cosponsored by the American Society of Lubrication Engineers and
the American Society of Mechanical Engineers
Hartford, Connecticut, October 18-20, 1983

NASA

E-1810

TOPOLOGICAL REACTION RATE MEASUREMENTS RELATED TO SCUFFING

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ABSTRACT

A ball-on-plate (both consisting of hardened M-50 steel) sliding elastohydrodynamic contact was run with trimethylolpropane triheptanoate (TMPTH) with and without tricresyl phosphate (TCP). The contact area of the plate was optically profiled with a phase-locked interference microscope (PLIM) both before and after exposure to alcoholic hydrochloric acid. As scuffing was approached, the profile within the contact region changed more rapidly after the acid treatment; after scuffing, it assumed a constant high value. A metallurgical phase found in the scuff mark was apparently responsible for the high reactivity. The microscopic profile changes (sensitivity, ±3 nm (±30 Å) in depth) involved primarily the small asperities (radius, <3 μm); the larger ones were unaffected. Soaking the steel in TCP smoothed the fine structure of the surface profile but increased its reactivity toward alcoholic hydrochloric acid before sliding was started. Thus it would appear that PLIM examination could be used for screening potentially scuff-resistant materials.

INTRODUCTION

Scuffing or scoring stainless steel bearing surfaces increases their chemical reactivity at room temperature (1). A phase-locked interference microscope (PLIM) was used to show on a microscale that the same exposure to dilute alcoholic hydrochloric acid produced much greater contour changes within than outside the score track. On the conjecture that a maximum temperature reached during scuffing or scoring was responsible for the reactivity difference, a series of stainless steel plates were briefly heated and then their reactivities toward alcoholic hydrochloric acid were measured at room temperature. Indeed, the higher the preheat temperature, the greater was the reactivity. From this result, it was assumed that the scuffing reaction depended on a critical preheat temperature but that, in contrast to the implications of the total contact temperature concept of Block (2) and others, scuffing does not have to occur at that temperature. Presumably a metallurgical change would occur on heating of the metal surfaces that could eventually affect a large enough contact area to promote the chemical changes associated with scuffing. Alternatively, or in addition, a chemical change could take place on the surface, such as a transformation of oxides or of other surface compounds (3).

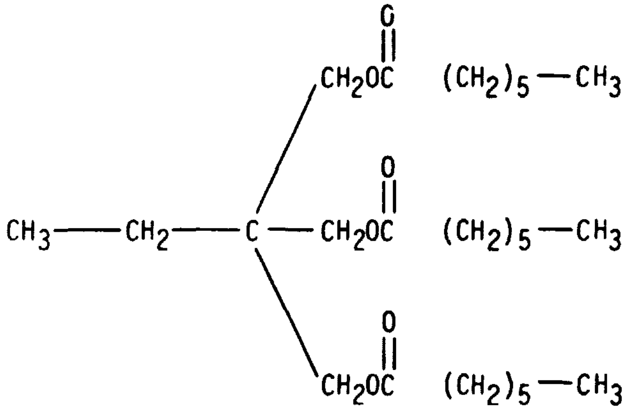
In this paper, we report on a series of experiments in which a lubricated ball-on-plate (both of hardened M-50 steel) sliding contact was run under appropriate operating conditions until scuffing occurred. The plate was removed at known intervals before scuffing and the reactivity of the contact region toward dilute hydrochloric acid was determined at room temperature. Measurements were made both with the base oil and with the base oil containing tricresyl phosphate (TCP). Soaking the bearing surfaces prior to contact operation was also investigated, originally to pursue some of the observations reported by Shafrin (4). Using Auger spectrometry, Shafrin found that exposure to TCP initially formed a phosphide on a steel surface but that this phosphide oxidized to a phosphate on prolonged exposure. This change in surface chemistry would be expected to affect bearing lubrication.

The objective of this work was to measure the reactivity of scuffed surfaces by measuring topographical changes with a phase-locked interference microscope after the surfaces had been exposed to alcoholic hydrochloric acid. Tests were performed with M-50 steel and a lubricant (trimethylolpropane triheptanoate) with and without TCP at room temperature.

MATERIALS

Lubricant

The lubricant used in this work was the base oil of a research lubricant prepared by NASA and designated as G-MIL-99. The fully formulated lubricant was designed to represent those manufactured under MIL-L-23699 specification. Specifically the base stock of G-MIL-99 is pure trimethylolpropane triheptanoate (TMPTH), which has the following structure:



Properties of this fluid are given in table I.

Ball-on-Plate Specimens

M-50 is a 4 percent Cr, 4 percent Mo, 1 percent C martensitic steel. The heat treatment procedure is given in table II. The hardness of the steel after heat treatment was 62-63 (Rockwell C).

Samples (20.6-mm-diameter balls and 22-mm x 11-mm x 7-mm plates) were ground before heat treatment. After heat treatment, a grayish finish appeared on the surface. The plates were then mounted in epoxy and lapped. They were polished successively with 240-, 400-, and 600-grade sandpaper under water, next with 9-μm diamond-imbedded paper without water, and then with 0.3-μm aluminum oxide under water, until practically a mirror finish was attained. Under the metallurgical microscope (nital etching), the structures typical of tempered martensite were apparent (Fig. 1). Some chunks of carbide (white areas) were visible.

APPARATUS

AC Phase-Locked Interference Microscope (PLIM)

This instrument is the same as that used in a previous investigation (1) but with certain improvements. Only the improvements are described here. A major improvement was the addition of an argon ion laser, which makes it possible to use a number of different wavelengths. If a metallic surface, such as gold, or a surface coated by a transparent oxide, such as aluminum oxide (Fig. 2) is scanned, the profiles are essentially the same for different wavelengths. However, the apparent profiles of steels covered with light-absorbing oxides are different (Fig. 3). Since the oxide layers are very thin (a few hundred angstroms), the same metal surface is the source of sample reflection. The differences are therefore ascribed to phase changes on reflection, which are wavelength dependent. When a wavelength is partially absorbed by the oxide (e.g., blue light by a red oxide), the phase change depends on the thickness of the oxide layer and is significantly different from that obtained with the pure metal (not oxide coated). Therefore the "apparent depth profile" scanned by this wavelength is different from that scanned by a wavelength that is not absorbed. From this difference, the thickness of the oxide layer can be calculated if its optical parameters are known. In our reactivity studies, real and apparent profiles were mixed since only profile changes were observed. For this reason, it must be understood that the observed profile changes were not always true surface contour changes.

Distance calibration of the instrument is simple. In the horizontal plane, a reticule is used. The horizontal magnification is determined by the magnification of the objective. The larger the magnification and therefore, in general, the larger the numerical aperture (NA), the smaller is the field of view and, also, the higher is the resolution of sharp surface contours. Clearly, a steep asperity of less than 2 μm in base diameter cannot be resolved if the effective resolution of the objective is less than that. Unfortunately the higher the magnification of the objective lens, the shorter is its working distance. Depth is calibrated accurately by the phase jump in the detector plane. The separation between two successive interference fringes corresponds to a phase difference of 2π between the sample and reference beams. If there is no oxide or other dielectric layer on the sample surface, there is phase reversal at the sample surface, and this separation of fringes corresponds to a change in the depth of the sample surface profile of half a wavelength of the laser light (e.g., 0.3164 μm for the He/Ne laser).

A major improvement of the PLIM has been the substitution of two long-working-distance (18 mm) 40X objectives for the standard 40X objectives (4-mm working distance). The new objectives are Cassegrainian reflectors and should, according to theory (5), be unsuitable for this work because a small portion of the paraxial beam is cut off. However, contrary to theory and previous experience with other Cassegrainian objectives, these new objectives work. This is presumably (1) because the two objectives (i.e., one in the sample beam and one in the reference beam) are precisely matched and (2) because the blocked center portion is much smaller than the 5-cm-diameter collecting mirror. The long working distance also makes it possible to obtain profiles of surfaces through windows.

RESULTS

Effect on Surface Profile of Surface Treatment with the Lubricant Containing 4.5 Percent Tricresyl Phosphate

Fig. 3 shows the apparent profiles of the original M-50 plate surface at two different argon ion laser wavelengths. The surface was very smooth but the profiles show some differences with wavelength, which we attribute to the presence of an oxide layer since these experiments were performed in room-temperature air. For this reason, the surfaces were covered by adsorbed oxygen as well. The presence of adsorbed oxygen on M-50 steel in air was also inferred by Faut and Wheeler (3) from their experiments on the friction of TCP.

After the same M-50 plate surface had soaked in TCP-containing lubricant for 5 min, the apparent profiles (Fig. 4) at the same two wavelengths became smoother. (All profiles were obtained on dry surfaces - after exposure to lubricant the surface was thoroughly rinsed with alcohol and allowed to dry.) The smoothing is more noticeable at 0.4880 μm.

After the surface had soaked in the TCP-containing lubricant for 4 days at ambient temperatures, the profiles (Fig. 5, taken at 0.4880 μm) became even smoother. A drop of 0.01 M hydrochloric acid in alcohol was applied for about 10 sec and then washed off. The smaller asperities (base radii, 1 to 2 μm) were attacked and removed, but the larger ones were unaffected. The "steady state" situation was obtained after allowing the surface to rest for some time. It appears that chemical reactions continued even after the acid was washed off. After another acid treatment, one of the original small peaks had become a valley, but the large features of the profile remained.

To compare the TCP-treated surfaces with untreated surfaces, the series of profiles of Fig. 6 were obtained. Clearly the changes after acid treatment were small, and even an acid of ten times the original strength (0.1 M HCl) did not change the profile much. On careful examination of these profiles, a certain long-range periodicity of asperities is noticeable. This "wavelength" could correspond to an average grain size (Fig. 1). Interestingly enough therefore, the TCP-treated steel surface was much more reactive toward the acid (certainly for small asperities) than the untreated steel surface.

Reactivity of M-50 Surfaces as a Function of Running Time Toward Scuffing

The ball-on-plate sliding contact apparatus described in an earlier publication (6) was modified to accommodate a 20.6-mm-diameter ball and a steel plate instead of a sapphire window. Both ball and plate were of the same hardened M-50 steel described earlier. The lubricant was fed into the contact region by a peristaltic pump. Traction was monitored with a strain gage. Loading (∿15 kg) took place from the top to produce an average Hertzian pressure of 2 GPa (Hertzian radius, ∿75 μm).

Fig. 7 shows plots of traction as a function of time under these conditions. The curves in Fig. 7(a) correspond to the ester-containing TCP; and the curves in Fig. 7(b), to the base oil alone. Both sets of plots also compare the effect of soaking the M-50 surface for 3 hr in the ester at room temperature. In the case of the base oil, prior soaking (curve 3) merely extended the time to scuffing from 120 sec to 400 sec if scuffing is identified by the first steep rise of traction. (Subsequent examination of the wear track was consistent with this identification.) The traction was somewhat reduced by prior soaking. In the case of the TCP-containing oil, prior soaking (curve 1) yielded traction values similar to those obtained with the base oil; however, the traction was almost halved when soaking was eliminated. On the other hand, without soaking the traction was erratic, exhibiting steep rises as well as drops. It was difficult to obtain reproducible scuffing times in that case.

Comparing the traction curves of Fig. 7 shows a sharp increase at approximately 400 sec (repeatability, ±10 percent) for all cases except the base oil without soaking (curve 4). As this increase apparently corresponds to scuffing, it appears that TCP does not delay scuffing.

Fig. 8 shows a series of profiles inside the wear track of the M-50 plate contact before and after acid treatment for zero, 20, 40, and 60 sec (after scuffing in this particular experiment). It is clear that the reactivity of the plate contact changed continuously with time and became particularly large after scuffing. For example, the asperity of the next-to-the-last profile (after scuffing) became a valley on acid treatment.

The profiles of Fig. 8 were obtained with the base oil without soaking. When the profiles before acid treatment are examined as a function of time, a slight increase of roughness can be seen up to the scuffing transition, which is accompanied by a large increase of roughness. In general the acid produced a profile of changed roughness, the increase nearly corresponding to the running time.

To evaluate the profile changes produced by the acid reaction and thus get a measure of the surface reactivity, the centerline average method was used. That is, a centerline parallel to the horizontal axis was drawn so that areas bounded by the profile and the centerline were equal above and below. These areas were used as a measure of reactivity. In other words, the change of roughness so defined is a function of the action of the acid with respect to the surface. Fig. 9 shows plots of these roughness changes produced by the acid as a function of time for three of the conditions of Fig. 8. The test with the ester base oil without soaking (curve 4 in Fig. 7) showed the reactivity to increase rapidly, corresponding to the early scuffing (∿120 sec). With soaking, the reactivities prior to scuffing were greater when TCP was present, but the sharp increase of surface reactivity subsequent to scuffing occurred at about the same time for both the TCP-containing oil and the base oil near 400 sec of operating time. Four hundred seconds was also the time at which traction sharply increased in these cases (Fig. 7). As a matter of fact, for the base lubricant the profiles became smoothed (or hardly changed) as a result of the acid soak prior to scuffing.

Fig. 8 also shows the high reactivity toward the acid of the TCP-soaked surface before startup. It is higher than any reactivity noted after running.

To confirm that the reaction inside the scuff mark was much greater than that outside, a profile was obtained at the edge of the scar before and after acid treatment (Fig. 10). The scar was "filled in" after acid treatment. There was little change outside the mark.

To investigate the nature of the material in the scuff mark, the plate was barely polished and then etched with nital. Fig. 11 shows that material within the mark did not etch. The half-circular appearance of the mark would seem to indicate that the normal to the plate made a slight angle with the direction of the load. When the plate was polished more, the unetched material disappeared, even though some of the grooves still remained.

DISCUSSION

It appears that a reactive phase is produced at the scuffing transition and perhaps even earlier - though to a much smaller extent. This phase is long lasting and may be responsible for changes of surface profiles on treatment with dilute alcoholic hydrochloric acid. It should be emphasized again that our measurements were made on a microscopic scale. The more macroscopic (microscopic in a plane but not depth sensitive) metallurgical etching tests showed the presence of a thin layer of a different, and apparently inactive, nonetching phase. It appears that the phase of Fig. 11, which was resistant to etching, was similar to that reported by Rogers (7) for diesel piston rings.

The reactive phase has not been positively identified. Metallurgists have identified some highly corrosive material when tempered martensite is heated to about 400° C and have associated it with exceedingly small granular masses. Calculations based on Archard's procedure (8) show that we probably exceeded this temperature in our ball-on-plate device.

The behavior of the TCP-containing lubricant and presumably the TCP-coated surfaces resulting from it was somewhat different. Indeed scuffed steel surfaces after soaking were also more reactive than the just-soaked surfaces. In fact, the original M-50 surface was almost inert toward the acid but after exposure to TCP it became very reactive. A possible explanation is a surface layer of phosphide or phosphate as shown by Shafrin (4) that changes rapidly during wear. Faut and Wheeler (3) showed that TCP-coated surfaces of M-50 steel exhibit less friction when heated beyond a characteristic transition temperature of 218° C. This is consistent with our observations of decreases in traction for the TCP-containing lubricant, which were not observed with the base oil, and a large reactivity for the TCP-soaked steel but not for the rubbed steel. Their results were also explained in terms of chemically different surface layers. Work now in progress is aimed at the chemical analysis of these layers.

It also appears that M-50 steel surfaces approaching or after scuffing, having been exposed to high temperatures, are also much more reactive at ambient temperature toward dilute hydrochloric acid. Conversely then, such an acid reaction may be useful in predicting scuffing tendencies for different solid materials and lubricant combinations.

SUMMARY OF RESULTS

An M-50 steel, ball-on-plate sliding elastohydrodynamic apparatus was run with an ester lubricant (trimethylolpropane triheptanoate) with and without a tricresyl phosphate (TCP) additive. The contact area of the plate was then optically profiled with a phase-locked interference microscope before and after exposure to dilute alcoholic hydrochloric acid. The following results were obtained:

1. M-50 surfaces were relatively inert toward alcoholic hydrochloric acid but became very reactive after exposure to the ester containing TCP.
2. M-50 surfaces approaching the scuffing transition and after the transition showed a greater reactivity toward alcoholic hydrochloric acid than did unrun surfaces.
3. Presoaking of the M-50 specimens in the ester base oil reduced traction, but presoaking in the ester plus 4.5 weight percent TCP increased traction.
4. It appears that a reactive metallurgical phase is produced at the scuffing transition and is responsible for the profile changes on exposure to alcoholic hydrochloric acid.

ACKNOWLEDGMENT

This work was funded by grants from the Air Force Office of Scientific Research, Grant AFOSR-81-0005, and from the National Aeronautics and Space Administration, Grant NSG-3180-12-81.

We also thank Dr. Lavern D. Wedeven of NASA Lewis Research Center, Cleveland, Ohio, for his help in obtaining the materials used in this research and for many helpful discussions. Dr. Eric Bamberger of the General Electric Company, Cincinnati, Ohio, supplied us with the information for the heat treatment of the steel.

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TABLE I. - PROPERTIES OF TEST FLUID (G-MIL-99)

Kinematic viscosity, m^2/sec (cS)	
At 98.9° C	3.5×10^{-6} (3.5)
At 37.8° C	1.52×10^{-5} (15.2)
At -17.8° C	2.87×10^{-4} (287)
At -40° C	2.4×10^{-3} (2400)
Pour point, °C	-68
Specific gravity, 25° C	0.963
Moisture content, percent	0.02

TABLE II. - HEAT TREATMENT SCHEDULE FOR M-50 STEEL SPECIMENS

Preheat, °C	816
Harden, °C	1100
Quench (in molten salt), °C	552
Air cool	Room temperature
Temper[a] (2 hr), °C	538
Air cool	Room temperature
Temper (2 hr), °C	538
Air cool	Room temperature
Three more tempers at 524° C	

[a] Tempering was started as soon as room temperature was reached to avoid cracking.

Figure 1. - Photomicrograph of M-50 steel as used. (Surface etched with nital.)

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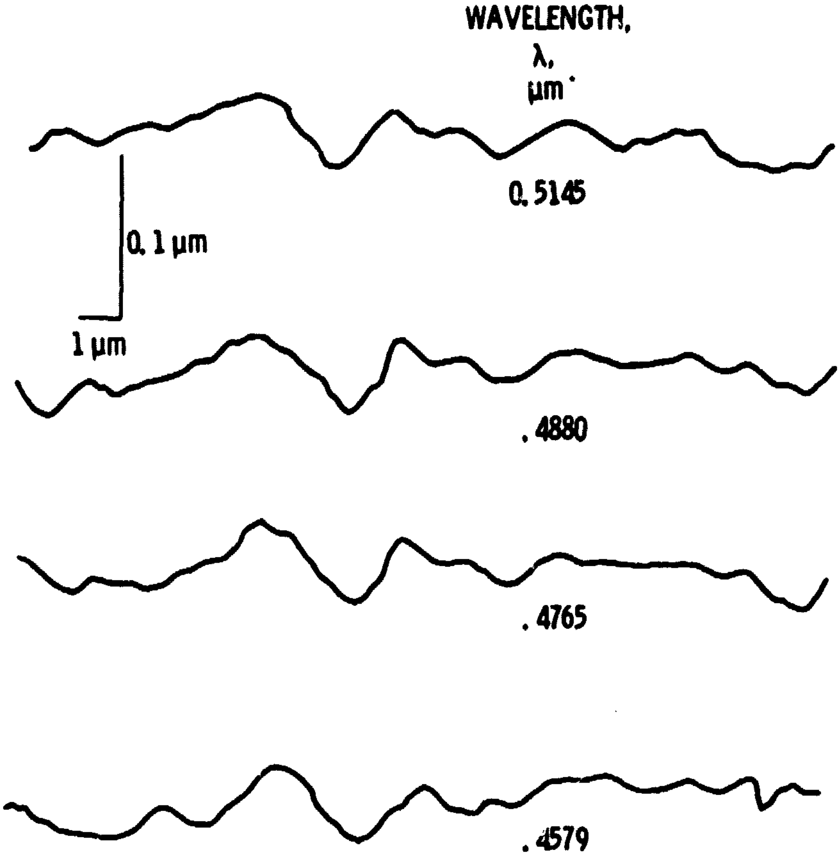


Figure 2. - Apparent surface profiles of an aluminum plate obtained with different wavelengths of an argon ion laser.

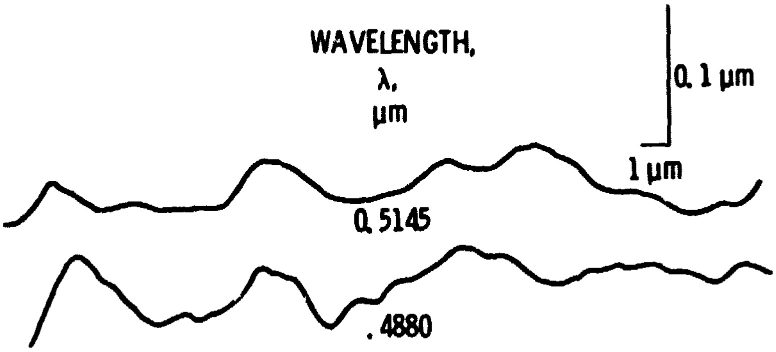
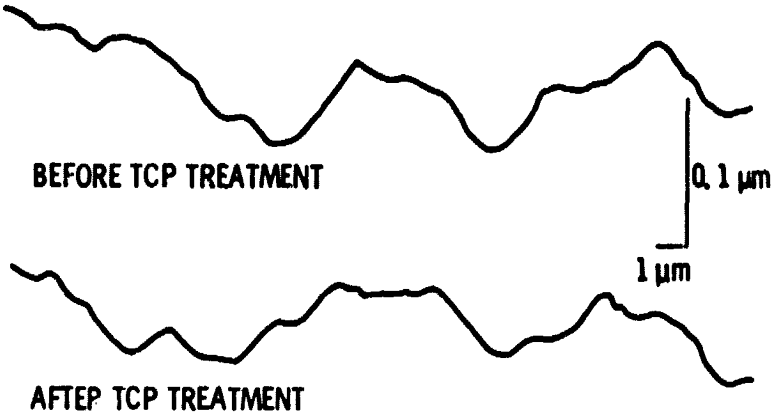
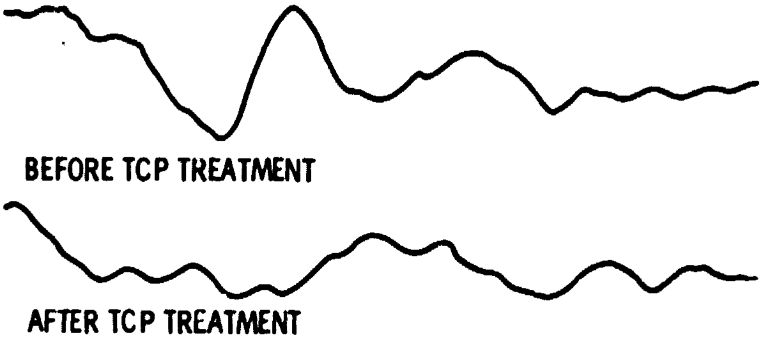


Figure 3. - M-50 plate profile before tests, showing profile difference with wavelength.



(a) λ = 0.5145 µm.



(b) λ = 0.4880 µm.

Figure 4. - M-50 plate profiles after soaking for 5 min in a formulated ester (4.5 weight percent TCP) for two wavelengths λ.

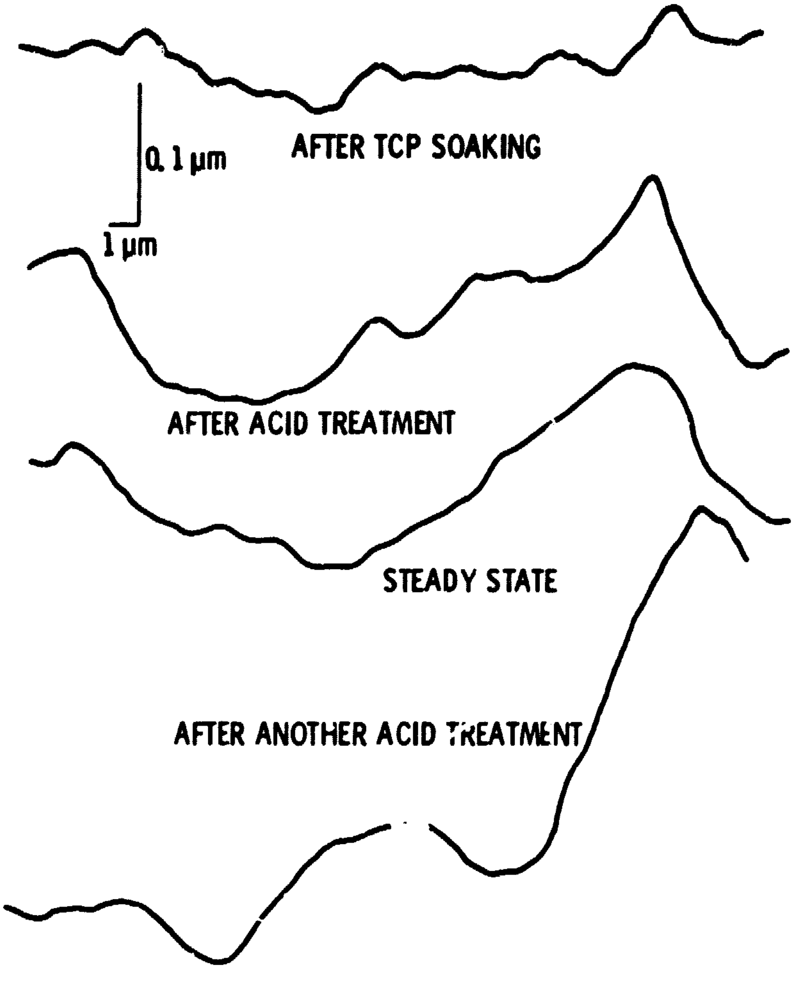


Figure 5. - Apparent M-50 plate profiles after soaking for 4 days in a formulated ester (4.5 weight percent TCP). Wavelength, λ, 0.4880 µm.

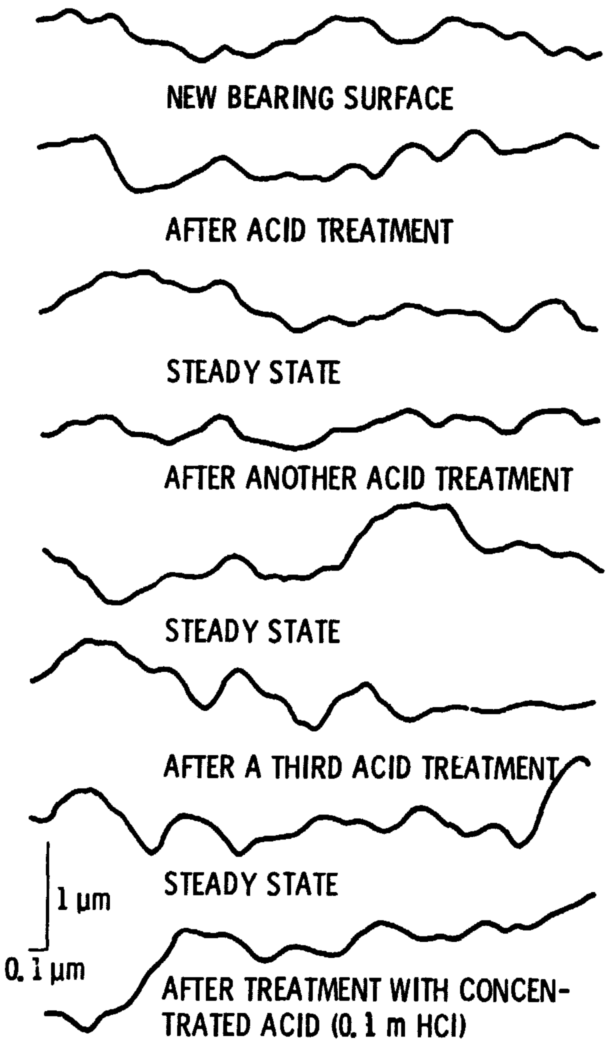
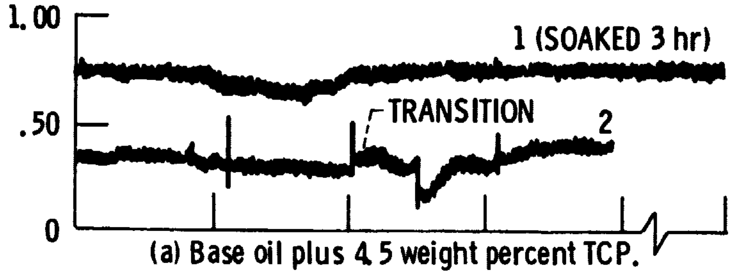
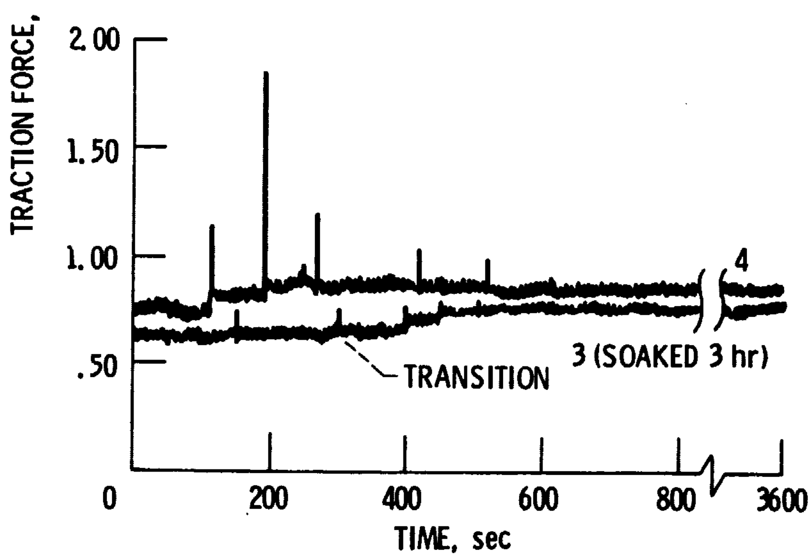


Figure 6. - Series of apparent profiles of untreated M-50 plate. Wavelength, λ, 0.5145 µm.



(a) Base oil plus 4.5 weight percent TCP.



(b) Ester base oil.

Figure 7. - Traction as a function of time for ball-on-plate contact operation. (These are recorder traces of independent experiments. The inversion of the numbers of the two pairs and the upward step at 400 sec of all traces but 4 should be noted.)

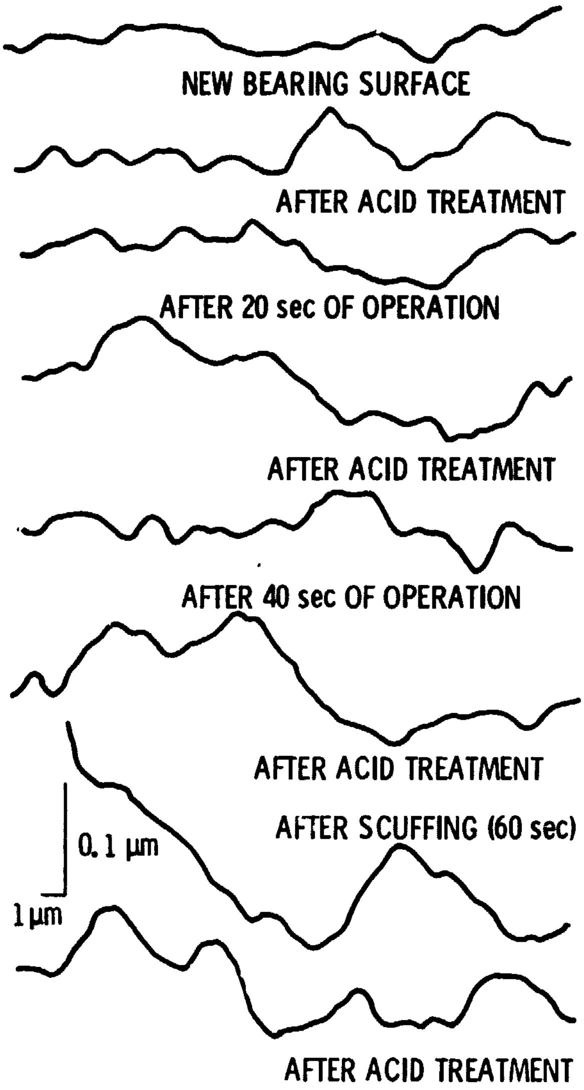


Figure 8. - Apparent surface profiles inside wear track of M-50 plate as scuffing conditions were approached. Wavelength, λ, 0.4880 µm.

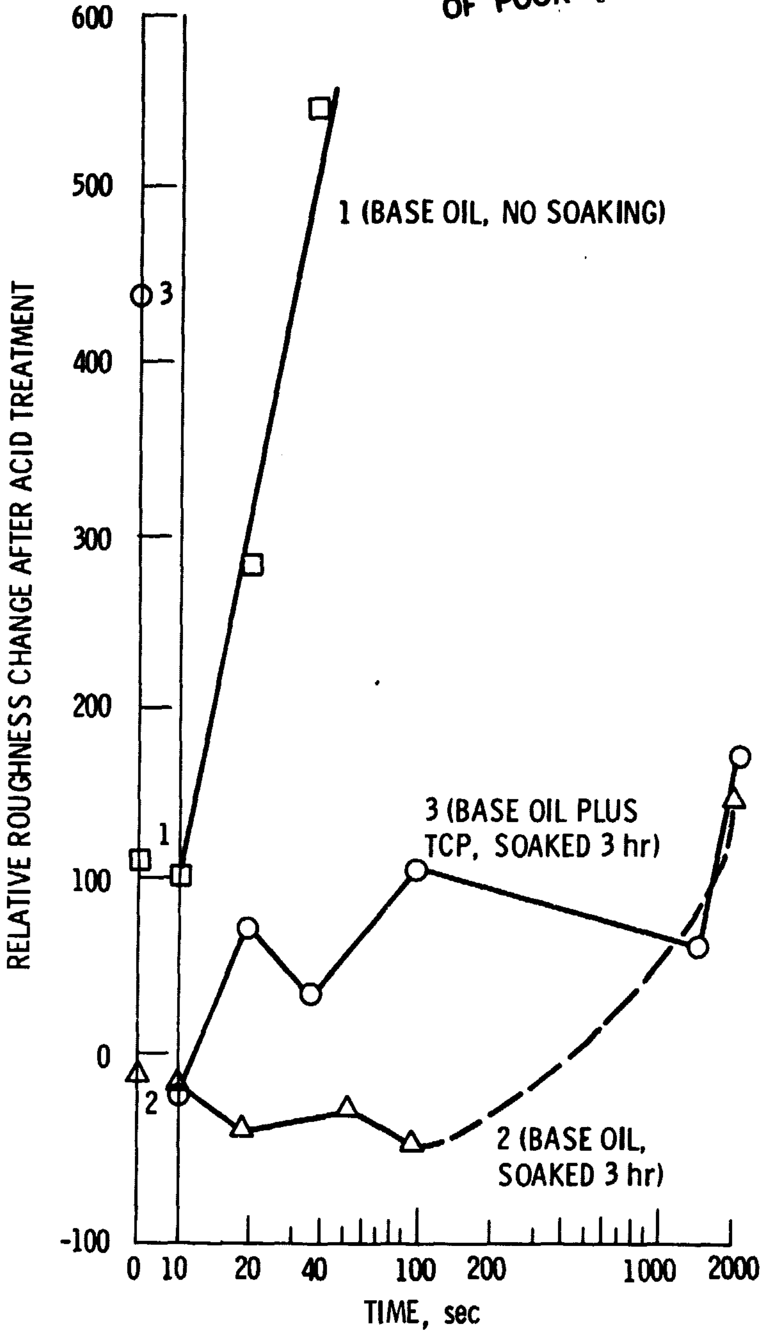


Figure 9. - Effect of acid on contact region roughness as scuffing conditions were approached. (Roughness is defined as the area under the trace of the surface profile, which is bounded by the horizontal line representing the "centerline average.")

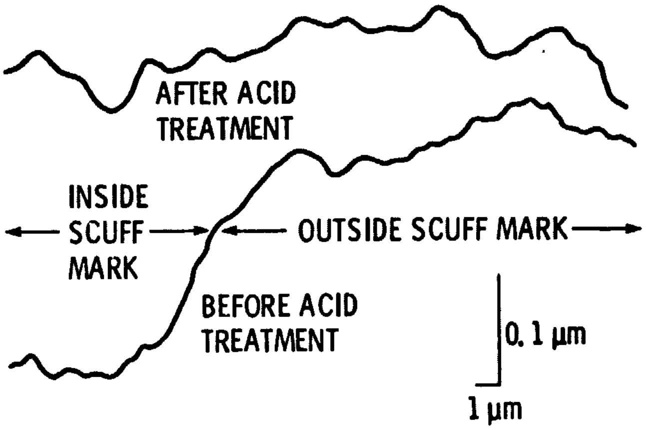


Figure 10. - Apparent surface profile near edge of scuff mark on M-50 plate. Wavelength, λ, 0.4880 µm.

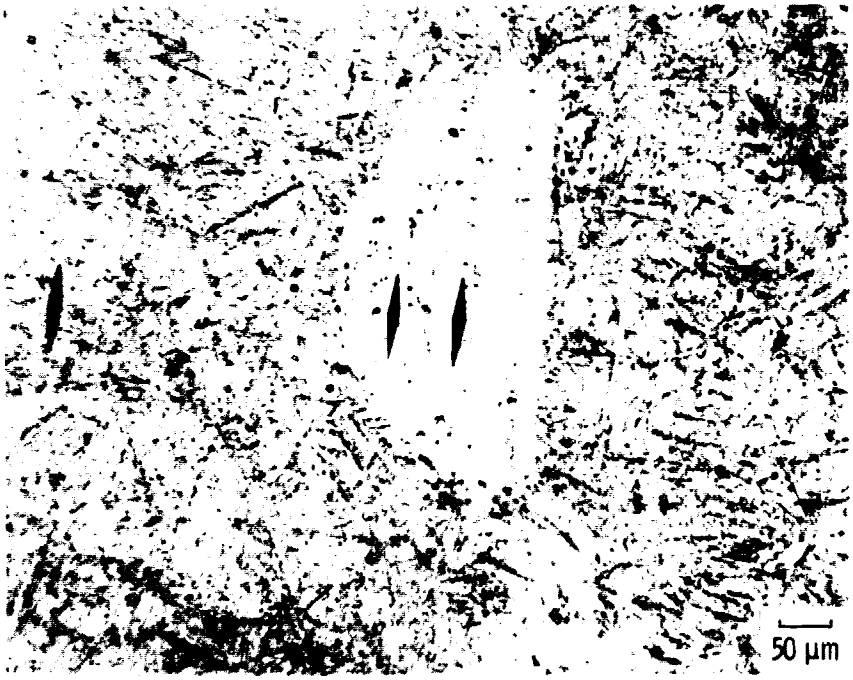


Figure 11. - Photomicrograph of scuff mark after nital etching.