International Rolling Element Bearing Symposium

Orlando, Florida
April 28-30

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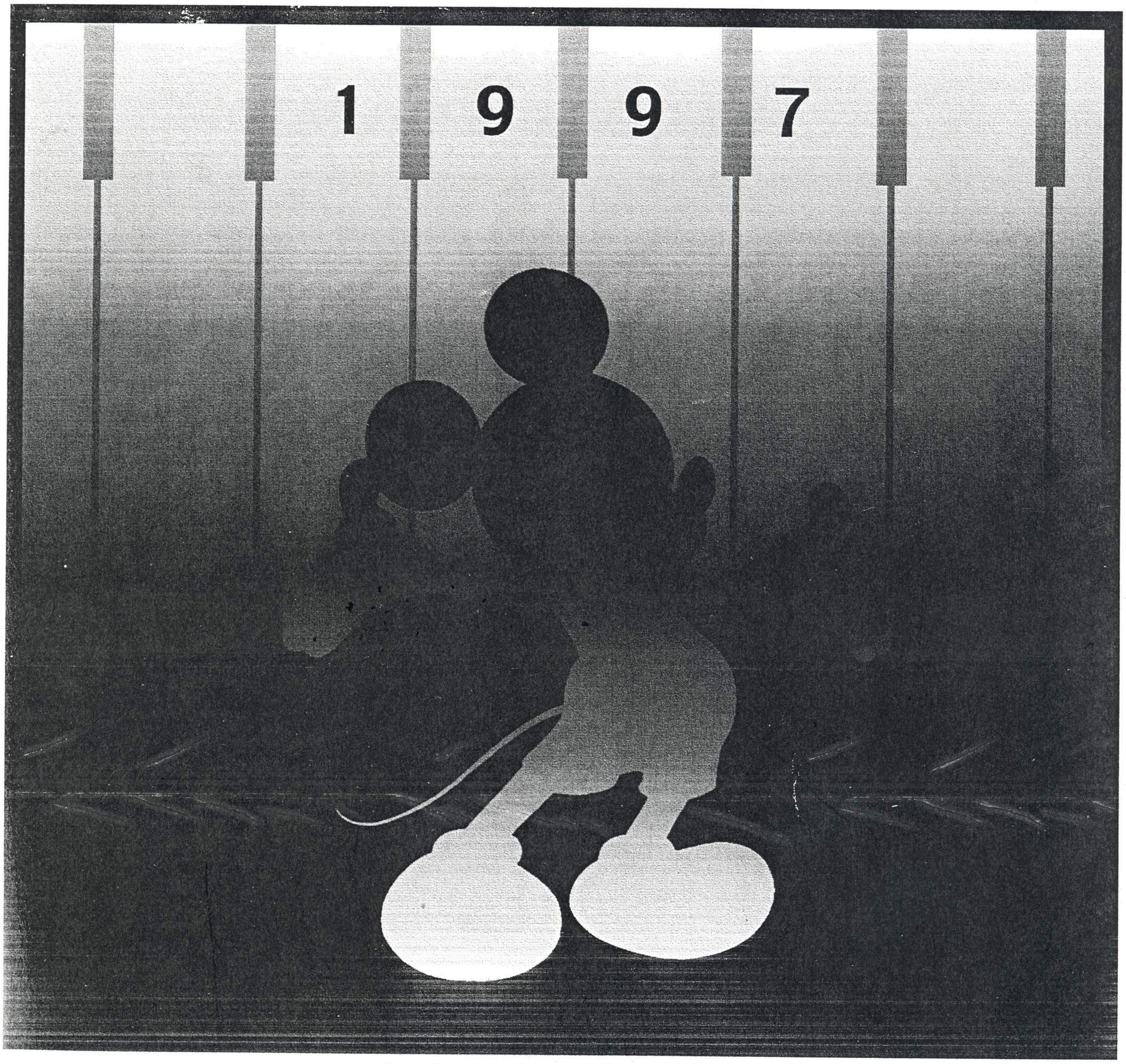

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Destruction of Fomblin Z-25 by Different Bearing Metals

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4th International Rolling Element Symposium
Orlando, Florida April 28-April 30, 1997

Abstract

The rolling contact tribometer recently developed at the NASA Lewis Research Center has been used to evaluate the severity of tribochemical attack on Fomblin Z-25 as a function of race bearing metal. The metals were 4150 steel (1% Cr), 440C steel (18% Cr), chromium plated steel and aluminum plated steel. 440C steel balls with 100 nm of the lubricant were run on the metals in vacuum until the end of effective lubrication signaled the consumption of the lubricant. The lifetimes, relative to 440C steel, were 1.7 (4150 steel), 1.0 (440C steel), .6 (Cr) and .17 (Al). Shorter lifetimes correlated with greater chamber pressure increases during rolling and more rapid buildup of friction polymer, all associated with tribochemical destruction of the lubricant. These results implicate chromium as an active element in the tribochemical attack on Fomblin Z-25, with aluminum being even more active. This lubricant/race material tribochemical interaction is thus a factor in the choice of materials in bearing design and operation.

I Introduction

Ball bearings and other moving mechanical assemblies on spacecraft frequently operate at high loads and low speeds. Under these conditions a fluid film of lubricant is not developed to separate the bearing elements and the system operates in what is called the boundary lubrication regime. The solid-solid contact experienced by the bearing elements can lead to tribochemical reactions of the lubricant with these solid elements. This tribochemistry can result in the formation of so-called friction polymer that can jam the mechanism. It can also lead to the corrosive attack of the bearing material. The absence of air in the spacecraft also prevents the formation of metal oxide scales that can furnish some protection against the development of the tribochemical process. This tribochemistry and more generally, the evolution of lubricant properties under operating conditions (of which tribochemistry is a special case), can be a factor determining the functioning of a lubricant and can be a cause for the failure of the mechanism in the spacecraft.

A new instrument for studying lubrication in vacuum has recently been described[1,2]. It is basically a retainerless thrust bearing with three balls and flat races. The analysis of this "ball on plate" rolling element tribometer demonstrates that contact motions in this instruments are similar and directly related to those in the usual angular contact ball bearing. The stresses to which a lubricant is subjected in this instrument are thus similar to those experienced in a ball bearing so that this instrument is a credible test bed with which to evaluate lubricant behavior in a ball bearing operating in the boundary lubrication regime.

This instrument's initial operation revealed two key aspects of its behavior. First, a finite lifetime for effective lubrication was observed with a limited initial supply of lubricant. That is, the friction was constant for a time related to the initial lubricant charge, after which it exhibited a sudden increase, dubbed failure here. The lubricant in the test was consumed, some of it volatilizing and some of it transforming into a semi-solid friction polymer. Second, no gross metallic wear was observed in post-test examination. The balls appeared pristine and, aside from some faint scratches, no metal removal or wear was evident on the plates. The observed finite life of the test was not due to metal spalling or wear and Hertzian sphere-on-flat elastic conditions were maintained throughout the test. These two aspects show that this instrument furnishes a test of the capability of the lubricant to survive under conditions relevant to ball bearing operation. This survival capability may be considered an important issue for long term instrument ball bearing operation.

The observation of a finite test lifetime opens up the possibility of evaluating the relative tribochemical aggressiveness of different bearing materials by comparing the lifetime to failure of a lubricant run with the different bearing materials. This paper reports a study of the relative survival capability of Fomblin Z-25 running on four different bearing materials in vacuum. Fomblin Z-25 has frequently been used to lubricate spacecraft mechanisms. The metals - 4150 steel, 440C steel, chromium and aluminum - were chosen since they are real material choices available to the bearing designer. They also present different chemical elements to the lubricant, thus providing an opportunity for tribochemical mechanisms to determine lubricant lifetime. We stress, however, that changing the materials was done here to assess the engineering result of lubricant survival and not primarily to study the tribochemistry itself. The tribochemistry should be regarded as an aspect of the study with possible explanatory power and not its primary focus.

A tribochemical sensitivity of this fluid to different metals may be expected based on a previous study of the decomposition rate of films of the fluid condensed onto oxide-free metal surfaces[3]. The study showed that Fomblin Z-25 decomposed at room temperatures on aluminum, decomposed only at elevated temperatures on 440C steel and evaporated intact from gold. Thus aluminum and 440C steel did in fact chemically attack the fluid, with aluminum being more aggressive than steel. The nature of these experiments, however, was of classic surface science and did not directly address the tribological/tribochemical response as is done here.

In addition to the friction coefficient and lifetime to failure, this paper also reports the vacuum chamber pressure rise and race-to-race electrical resistance during rolling operation. The chamber pressure rise is due to gas evolution from lubricant decomposing during rolling. Its magnitude is thus related to the rate of decomposition. The race-to-race electrical resistance is an indication of the buildup of electrically insulating friction polymer at the ball-race contacts. It is therefore another indicator of the progress of the evolution of the original fluid into a solid-like material.

II Experimental

General. The apparatus and its kinematic analysis has been described[1,2]. The thrust bearing, with three balls placed symmetrically on the flat races, operates with a top plate angular velocity of 4 rpm in a base vacuum pressure of $\sim 2 \times 10^{-9}$ torr. The mean Hertz stress on the contacts is 1.4 GPa, a value typical of that in a pre-loaded instrument ball bearing. The race-race bearing electrical resistance was obtained with a direct current of 1 ma and a maximum potential of a few millivolts. A typical plot of friction coefficient and chamber pressure is shown in Fig. 1. The friction is constant throughout the test until its sudden increase at ~3500 top plate revolutions. This is the lifetime to failure referred to above. The chamber pressure was also fairly constant until the friction increase, at which point it increased and then decreased to values less than those during the steady rolling. The pressure rise during rolling operation is due to the volatilization by tribological/tribochemical attack. The decrease of pressure after the friction increase is the indication that no lubricant remains to be destroyed, just as the friction rise itself indicates the absence of lubricant and end of test life.

Materials. The lubricant fluid is Fomblin Z-25, a fluid used in spacecraft mechanisms either neat or compounded with polytetrafluoroethylene to form a grease. Here only the neat fluid itself is used. The balls in all the tests were commercial grade 25 440C, .5 in. diameter bearing balls. The flat metal races, called plates in this apparatus, were a) 4150 steel, a low (~ 1%) chromium steel used in bearing applications; b) 440C steel, a high (~ 17%) chromium steel widely used for instrument ball bearings; c) chromium, frequently used to protect steel against corrosive attack; and d) aluminum. Chromium was used both as a thin (.2 μm) film sputter deposited onto a 440C steel plate and as an electrochemical layer[4] (known as "Thin Dense Chrome") deposited onto 440C steel plates. Aluminum was used as a thin (.2 μm) film sputter deposited onto a 440C steel plate. The hardness of the steels was ≥ Rc58.

Procedure. The balls and plates were ultrasonically cleaned in hexane and methanol and then subjected to UV/Ozone treatment to remove residual carbonaceous matter. No deliberate effort was made to "passivate" the surfaces by acid or other means. The importance of such procedures for improving tribological response is considered by us as still an open issue. The balls were lubricated with fluid by dipcoating from a dilute solution of the lubricant in trifluorotrichloroethylene. The same amount of fluid was used in each test. An average lubricant film thickness of ~ 100 nm on each ball was determined from the weight gain of the ball, ~ 100 μgm. No lubricant was initially applied to the plates which received lubricant only by transfer from the rolling balls. A chamber pressure of < 3 x 10^{-9} torr was attained before starting the test. Friction coefficient, chamber pressure and race-to-race electrical resistance were recorded during the test.

III Results

The results of tests performed with Fomblin Z-25 running on the four different metal plates are displayed in Table I. The focus of interest here is the dependence of the tribological parameters on the plate material. The results are displayed in the sequence 4150 steel → 440C steel → chromium → aluminum indicated at the top of the Table.

The coefficient of friction, μ, obtained at midlife of a test is .2 - .25 and increases in the sequence

$$\mu: \text{4150 steel} < \text{440C steel} < \text{chromium} < \text{aluminum} \qquad (1)$$

These values are in the range expected for moderately effective boundary lubrication and the dependence on material is rather weak.

The lifetime to failure is the principal test of a lubricant's capability of surviving tribological stress. First, note that the four tests run with 440C steel show good reproducibility. Second, the lifetime for the two tests with thin dense chromium are very close to the lifetime of a single test run with the sputter-deposited chromium film. Thus the rougher topography of the electrolytically - deposited thin dense chromium film relative to the mirror-smooth sputter-deposited chromium film does not seem to play a major role in determining their lifetime to failure in this instrument. The major result here is the strong dependence of the lifetime to failure on the plate material. The test with 4150 steel exhibited a lifetime an order of magnitude greater than that with the test run on the aluminum film. The 440C steel and chromium surfaces exhibited intermediate lifetimes. These lifetimes, τ, are in the sequence

$$\tau: \text{ 4150 steel} > \text{440C steel} > \text{chromium} > \text{aluminum} \qquad (2)$$

The chamber pressure rise during rolling operation is indicated at a time in the middle of the life of a test. The increased chamber pressure rise at the end of a test as shown in Fig. 1 is characteristic of the severe conditions associated with the absence of lubricant and not with the processes taking place in the gradual steady state destruction of the lubricant. It was found that this chamber pressure rise, ΔP, exhibited the following sequence:

$$\Delta P: \text{ 4150 steel} < \text{440C steel} < \text{chromium} < \text{aluminum} \qquad (3)$$

The final result in Table I is the increase in plate-to-plate electrical resistance during rolling at midlife in a test. The observed resistance was not a single steady value, but exhibited fluctuations around an average value during rolling. It is thought that these fluctuations are related to the rather random making and breaking of asperity contacts within the overall elastic region of contact. In principle, these fluctuations in the resistance convey fundamental information on the micromechanics of the lubricated rolling contact. However, this analysis is not carried forward here and only the average value is presented. This provides a procedure to assess the degree of buildup of electrically insulating friction polymer on the contacting surfaces. This resistance, R_Ω, was on the order of one ohm and the following sequence of values was obtained:

R_Ω: 4150 steel < 440C < chromium < aluminum (4)

The scatter in tribological data generally demands multiple tests to establish some degree of confidence. In this data set, the lifetimes of the four tests with 440C steel are clearly distinguished from the lifetimes of the three tests with chromium films, establishing confidence in the distinction between the tribological survival capability of these different materials. However, since there was only one test with 4150 steel and one test with the aluminum film, there is a legitimate concern about the significance of these results. This concern is addressed by noting the consistency of the trends in the entire data set in terms of lubricant destruction. The primary trend is in the lifetime data, Eq. 2, indicating that 4150 steel is the least aggressive toward Fomblin Z-25 and aluminum is the most aggressive. This trend is consistent with the pressure rise during rolling, Eq. 3, in that a larger pressure rise is correlated with shorter lifetimes, a result expected if the gas evolution rate is due to the destruction of the lubricant. Consistency in the data set is also found in the plate to plate electrical resistance. A high rate of friction polymer formation, and thus higher electrical resistance across the ball/plate contacts, is expected for the higher rates of destruction of the lubricant. Thus, the trend in R in Eq. 4 is also consistent with the lifetime trend of Eq. 2. The coefficient of friction also exhibits the trend shown in Eq. 1. However, it is not clear what should be the relationship between lubricant destruction rate and coefficient of friction. Since the dependence of friction on plate material is rather weak in any case, it is not regarded as particularly relevant to the issue of overall data consistency.

The consistency and correlation of the data noted above provide a degree of confidence in the trends. That is, in terms of the tribological attack rate on Fomblin Z-25, the overall result is

Reactivity: 4150 steel < 440C steel < chromium < aluminum (5)

The final result presented here is the micrograph, Fig.2, of the track on a plate, taken after the test with Fomblin Z-25 on 440C steel. Post-test chemical analysis with infrared microspectroscopy showed very little lubricant in the track. Some neat fluid was found on the edge of the track, deposited there by transfer during rolling and no longer available to lubricate the system. The salient feature in the micrograph is the dark-colored material in the track. This material was insoluble in trichlorotrifluoroethylene, the fluid in which the lubricant was dissolved for the dipcoating deposition process and is clearly not the original lubricant. Chemical analysis indicates that it does contain C-F bonds, so that it derives , at least in part, from the lubricant. However, it also contains other chemical moieties that are not found in the lubricant. The chemical analysis of this debris will be described in a future publication. Here it is simply pointed out that the dark material is the friction polymer referred to in the introduction and is one of the products of the tribochemical attack on Fomblin Z-25, the other being the volatile species that contribute to the pressure rise in the chamber during rolling operation.

IV Discussion

The first topic in this discussion is to consider the statement in the introduction that the lubricant is consumed or destroyed during operation in this instrument. The interpretation of different lifetimes to failure as different rates of lubricant destruction is really the basis for this instrument's claim to engineering relevance: tribologists have an obvious interest in knowing if the lubricant is, in fact, disappearing, and, if so, the relative rates of its disappearance. The primary evidence for lubricant destruction as the mechanism responsible for the rise in friction is, at least for this case of Fomblin Z-25, the presence of friction polymer seen in Fig.2 and the pressure rise during rolling operation indicated in Table I. The lubricant has been both volatilized into the ambient and evolved into a semi-solid friction polymer. An additional piece of evidence is the virtual absence of lubricant remaining on the ball at test conclusion. There is, however, some neat fluid that had been transferred to the plates and was found after the test to be at the edges of the tracks. Although the amount of this fluid has not been quantified and compared to the original lubricant charge, no large differences in this quantity has been noticed between the tests with the different metals. The simplest approach to dealing with this transferred fluid is that it is present as a result of simple mechanical transfer in all tests in about the same quantity and plays no particular role in lifetime determination beyond reducing the amount of lubricant actually available to be consumed.

The second topic in this discussion is the role that the observed friction polymer may play other than as a passive spectator. It can certainly be expected to play *some* role because *anything* that intervenes at a contact may affect friction and wear. However, since the friction coefficient is observed to rise to very large values at some definite point, designated here as the lifetime or failure point, the friction polymer itself evidently cannot lubricate the contact as well as the neat fluid itself. It also does not seem to play a major role in determining the friction coefficient throughout the steady state portion of the test since the friction coefficient is about the same at the beginning of the test, when friction polymer is absent, as it is near the end of the test when friction polymer is more well developed (Fig. 1). There is, however, a gradual increase in friction through the life of the test that may involve the friction polymer in some way as yet to be determined. Although no clearly beneficial role of the friction polymer is evident here, it may yet be shown to be the "lubricant of last resort". Its presence in the contact in the absence of any of the original lubricant at all may in practice prevent metallic wear and seizure of the bearing elements. Such a possibility, however, is presently speculative.

Before discussing the tribochemistry that has been referred to in both the Introduction and Results, it is important to note that the mechanical properties, as well as the chemical properties, can differ for the materials used here. It is not at all clear how these different properties, whether it is hardness or ductility or some other property, will manifest themselves in terms of determining the rankings of Section III. There are, however, aspects that tend to discount strong effects of material differences. First, three of the four materials were either 440C steel or thin films on 440C steel. This steel has about the same hardness as the 4150 steel, so at least the bulk material properties do not differ greatly. The films of chromium and aluminum may have very different mechanical properties in their bulk form than do their steel substrates. However, the thickness of the sputter - deposited chromium and aluminum films are only .2 μm and this is a very small fraction of the 368 μm diameter of the elastic contact area. The overall mechanical properties of the contact must then be determined by the mechanical properties of the substrate and only to a minor extent by the mechanical properties of the film.

Having given these arguments against the rankings being strongly influenced by mechanical property differences, these tribological results are considered to be determined by the rate of tribochemical attack on the lubricant by the metallic bearing materials. In other words, the shortest lifetime, greatest chamber pressure rise and greatest production of friction polymer is associated with the highest rate of lubricant-substrate chemical reaction. There are two aspects of the data that can be regarded from a chemical point of view. First, note that the ranking in Eq.5 correlates with the chromium content of the materials-more chromium is associated with higher reactivity or shorter lifetimes. Thus the chromium in the steel alloys is implicated as a more active element than the iron. The second aspect of the data is the high reactivity of aluminum relative to the other bearing materials.

Some concepts are offered here to provide a framework within which these results may be considered, even though a complete and convincing chemical explanation is not yet at hand. Many workers have contributed ideas or scenarios[5]. A scenario consists of i. Chain scission ii. Substrate reaction iii. Attack on the lubricant. These will be discussed in turn.

i. Scission. The chemical events start with the mechanical scission or tearing apart of the long chain Fomblin Z-25 polymer molecules by shearing forces in the ball - plate contact. Mechanical scission has long been considered a method by which polymers degrade in a mechanical contact[6,7]. The severed chains would then have active end groups or radicals. These chemically active moieties can then react with their neighbors and this might be the route for the formation of the observed cross - linked friction polymer.

ii. Reaction with bearing materials. The active moieties react with the metals which they are in contact to form metal oxides and metal fluorides. Metal oxides and fluorides have been found on bearing elements lubricated by

Fomblin Z-25 by all investigators who have used surface analytic techniques such as x-ray photoelectron spectroscopy (XPS)[8]. These metal compounds have also been found on our specimens by XPS..

iii. Attack on Fomblin Z-25. The initial observations of Sianesi et al[8] showed that perflouropolyethers, such as the closely related Fomblin Y-25, reacted with metal oxides. The direct reaction of the lubricant with the metal fluorides has been suggested by Carre'[9] and studied in some detail by Zehe and Faut[10] and Kasai[11] and coworkers. In addition to the reaction of the lubricant with the metal oxides and fluorides on the surface, oxide - free metals have also been observed[3] to attack Fomblin Z-25. In the present study, nascent metal may be exposed by the shear stresses at the contacts.

The ranking of the tribochemical activities of the different bearing metals, as expressed in Eq. 5, may be considered in terms of the above ideas. The above discussion of the mechanical properties of the metals suggests that the contact conditions are the same for all the metals so that the scission rates would not be expected to differ greatly. Thus the first step of the above scenario is probably not the reason for the ranking. Part iii is a candidate to explain the observed ranking. There is certainly evidence that Lewis acids, in the form of both metal oxides and halides, attack Fomblin Z-25 and their aggressiveness may be different according to whether they are compounds of iron, chromium, or aluminum. However, with the exception of the study of Sianesi et al[8], the studies have not ranked their reaction rates in terms of the identity of the metal atom. Sianesi et al[8] showed that the reactivity of metal oxides with Fomblin Y-25 does depend on the cation of the oxide and that CrO_3 and Al_2O_3 were more reactive than Fe_2O_3. Although this is in line with the rankings found here, it is emphasized that the metallic fluorides present here also play a reactive role and their relative reactivities have not been studied to date. Thus, not enough independent chemical evidence related to the issue of relative reactivity of metal compounds is presently available to allow tribochemical mechanisms to be assigned with any assurance. On the other hand, it *has* been found that *clean* aluminum metal (not its compounds) is much more reactive toward Fomblin Z-25 than clean 440C steel[3]. Thus, there is some prior evidence for the higher reactivity of aluminum metal. Although the experiment did not directly compare pure oxide - free iron, chromium and aluminum, it suggests that the rankings may also be understood on the basis of nascent metal reactions with Fomblin Z-25.

As a final comment on the rankings, we note that all tests were carried out with 440C steel bearing balls. Since the rankings indicate that 440C steel is tribochemically active toward Fomblin Z-25, this activity of the balls must also contribute to the destruction of the lubricant. Passivation of this activity by either appropriate coatings or a different choice of a ball material thus offers the opportunity of extending lubricant life by a reduced destruction rate.

V Conclusions

Fomblin Z-25 has been run on four different bearing materials in an instrument that simulates ball bearing operation in vacuum under boundary conditions. The different lifetimes observed for effective lubrication of the different metals can be considered as due to different rates of destruction of the lubricant by tribochemical attack. This is probably the clearest demonstration of the limitation of lubrication effectiveness by tribochemistry yet to be shown in an instrument with engineering credibility. The capability of the instrument to rank tribochemical activity of the bearing materials provides a valuable method to explore this subject in a way closely aligned to engineering practice.

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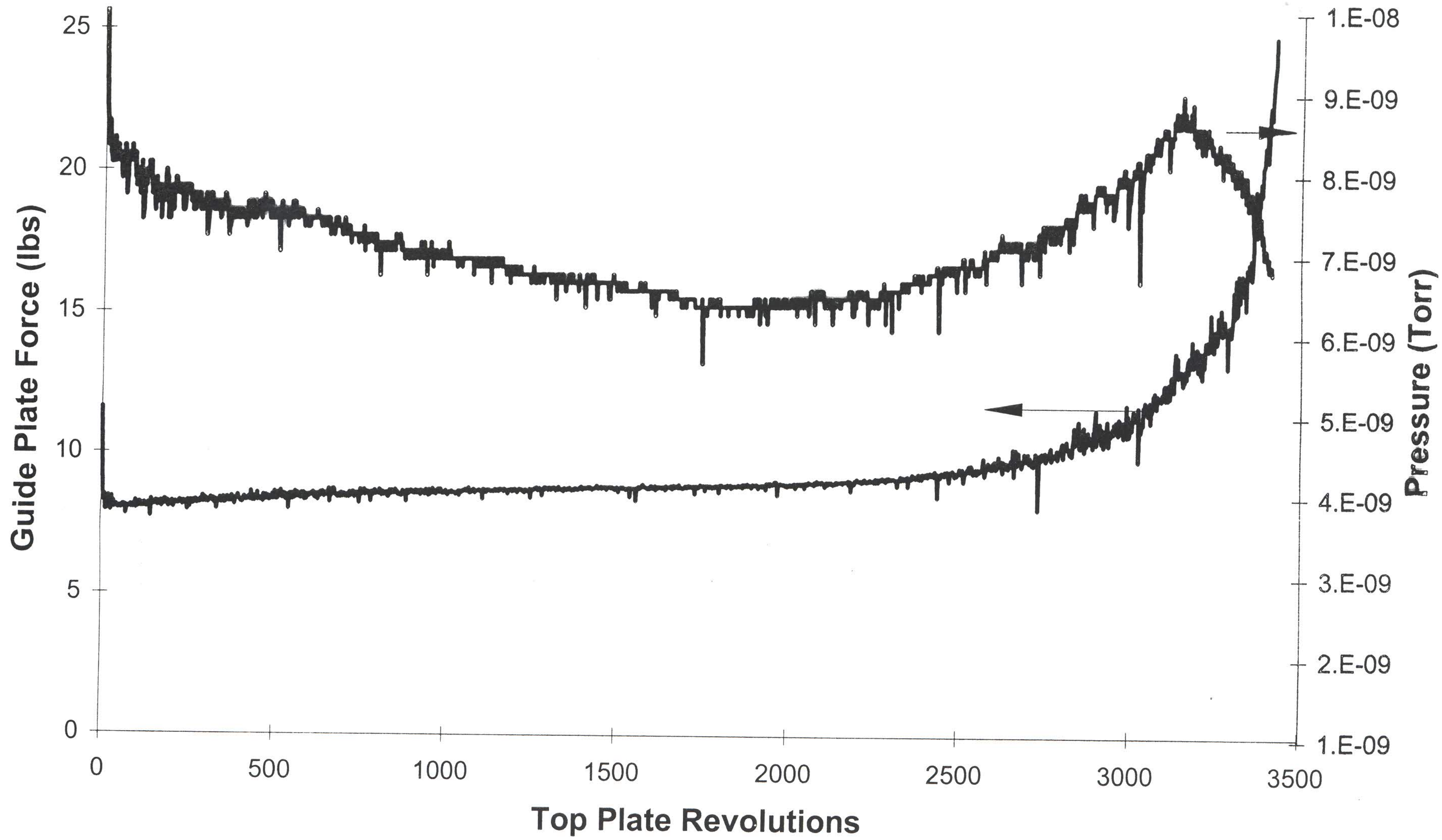
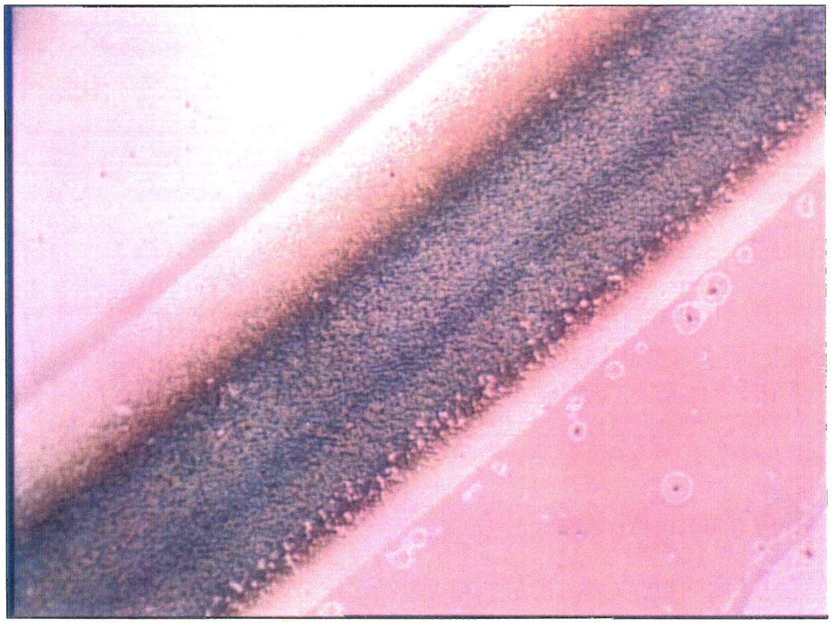


Fig 1. Guide Plate Force and Chamber Pressure



.1 mm

Fig. 2 Micrograph of track on bottom plate

Table 1
Response of Fomblin Z-25: Dependence on Plate Material

Plate Material:	4150 (1% Cr)	440C (17% Cr)	Chromium	Aluminum
friction coefficient	.2	.22	.23	.25
life time, revolutions	8000	~4600	2800	800
pressure rise during rolling at midlife, $\times 10^{-9}$ torr	.3	.5	1.2	5
electrical resistance at midlife, ohms	.2	1	2	10