Evidence for Tribochemical Consumption of Liquid Lubricants in the Spiral Orbit Tribometer

The spiral orbit Tribometer (SOT) furnishes coefficients of friction (CoF) as a function of time, usually expressed as a function of orbit number, the number of revolutions or orbits of the ball. If the plates are clean (not lubricated) and the ball is lubricated with just a few tens of micrograms of liquid lubricant, the friction trace starts out at a low value indicative of lubrication by a liquid and then eventually transitions to a high value, gradually in the case of Pennzane 2001A as in Fig. 1a or more abruptly as in the case of one of the perfluoropolyalkyl ethers (PFPAE) such as Castrol 815Z, Fig. 1b.

The rise of the CoF to non-lubricating values has been interpreted as due to the disappearance (or consumption) of the liquid lubricant by tribochemical attack by the bearing materials with which the lubricant is in contact. In this note, five pieces of evidence for such an interpretation are presented: 1. the behavior of the friction traces; 2. the presence of debris or "friction polymer" in the track on which the ball rolls; 3. the observation of fragments of the lubricant molecules by a mass spectrometer during a test; 4. the sensitivity of the lifetime to the chemical constitution of the bearing surfaces with which the lubricant is in contact; 5. the sensitivity of the lifetime to the test environment

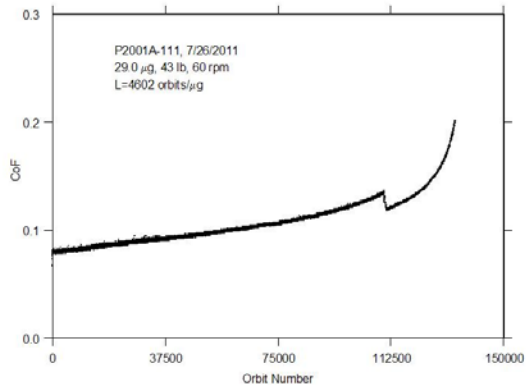

Fig 1a

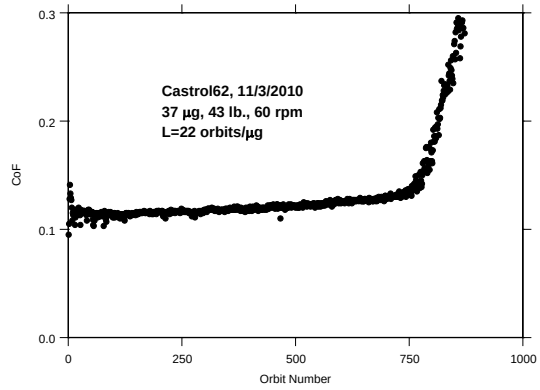

Fig. 1b

<u>Evidence for liquid lubricant consumption</u>

1. Note first that the friction traces themselves are consistent with the interpretation – if lubricant is not present then high friction is definitely expected. But where could the lubricant go? An initial consideration is simple evaporation into the vacuum ambient. However, a weighing of the lubricated specimen ball after a simple 48 hour vacuum soak indicates that the lubricant is still present on the ball. This is also consistent with the known room temperature vapor pressures of the lubricants chosen for use in devices operating in vacuum. Also, after the test is completed by transitioning to high CoF, a weighing of the ball indicates the lubricant is no longer on the

ball. A post mortem examination of the ball also indicates an absence of liquid lubricant. Again, where did the lubricant go? The lubricant could have been transferred to the plate by simple mechanical "shedding" action to the edges of the tracks where it is not available for lubrication in the ball/plate contacts. And in fact, such transferred lubricant can be observed on the edges of the track both by a metallurgical microscope and by an infrared microscope. It has not been possible thus far to quantitatively assess the amount of such shed lubricant. Although such mechanical shedding occurs and must make some contribution to the unavailability of lubricant for lubrication to take place – and thus to the eventually high friction observed – the other evidence presented in the following will show that it is not the dominant effect.

2. A micrograph of a track is shown in Fig. 2. Multicolored debris can be observed. This debris is not soluble in the fluid in which the neat lubricant dissolves. This debris is evidence of a chemical reaction of the lubricant molecules, one of whose reaction product is this solid insoluble debris. It is the second piece of evidence that chemical (really "tribochemical") activity has taken place and is contributing to the consumption of lubricant molecules that leads to high friction.

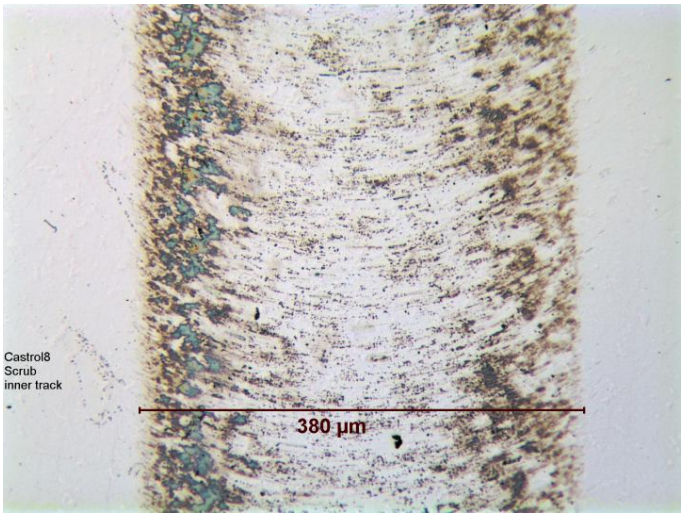

Fig.2

3. Gaseous fragments emitted into the vacuum ambient can also be the product of tribochemical reaction. An increase of the system pressure is observed during a SOT test, especially with one of the short lived PFPAEs. A quadrupole residual gas analyzer or RGA, a type of mass spectrometer, was installed on the tribology test chamber as shown in Fig. 3 and detected these gaseous fragments responsible for this pressure rise for Castrol 815Z. The mass spectrum indicated a number of fluorinated fragments in addition to both CO_2 and CO. The time plot for the intensity of one of these fragments – that of mass 69, CF_3 – is shown in Fig.4 together with the friction trace for the test. The intensity of CF_3 increases upon the onset of rolling. The sharp spikes in intensity are due to the ball in the scrub and its associated macroscopic sliding, unlike the sliding in the Hertz contact associated with pivot or spin when the ball rolls outside the

scrub. There is a significant increase in the intensities of the features associated with tribochemical destruction (fluorocarbon fragments, CO and CO_2) *before* the increase of the friction near termination of the test because of high friction. This precursor of failure with liquid lubricants is always observed. When the friction increases significantly (entering the "failure region") the spikes associated with sliding in the scrub disappear. This is consistent with the interpretation that the lubricant has been "used up" and there is no more left to decompose and emit fragments into the ambient to be sensed by the RGA *and* there is no more left to provide lubrication. The general decrease of intensities of other fragments associated with tribochemical destruction (fluorocarbon fragments, CO and CO_2) in the friction "failure region" is observed and is also consistent with the lack of lubricant – it having been already destroyed. All intensities decrease sharply at secession of rolling. The branching ratio for this tribochemical reaction, that is, the relative amounts of solid (noted above) and gaseous reaction products discussed here, is not known. This behavior of the gaseous fragments detected by the RGA is considered to be strong evidence for tribochemical reaction and consumption of lubricant molecules during the test.

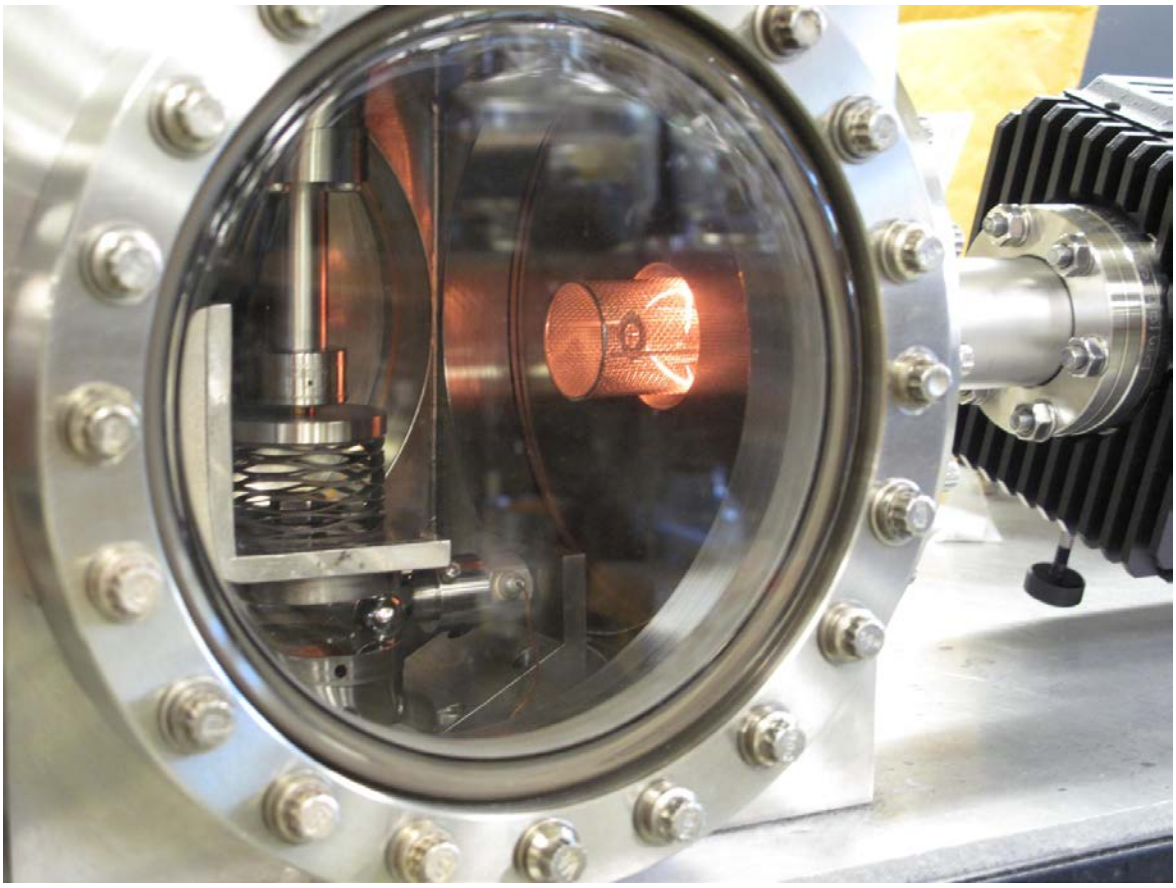

Fig. 3 Tribology test chamber. The RGA can be seen on the right

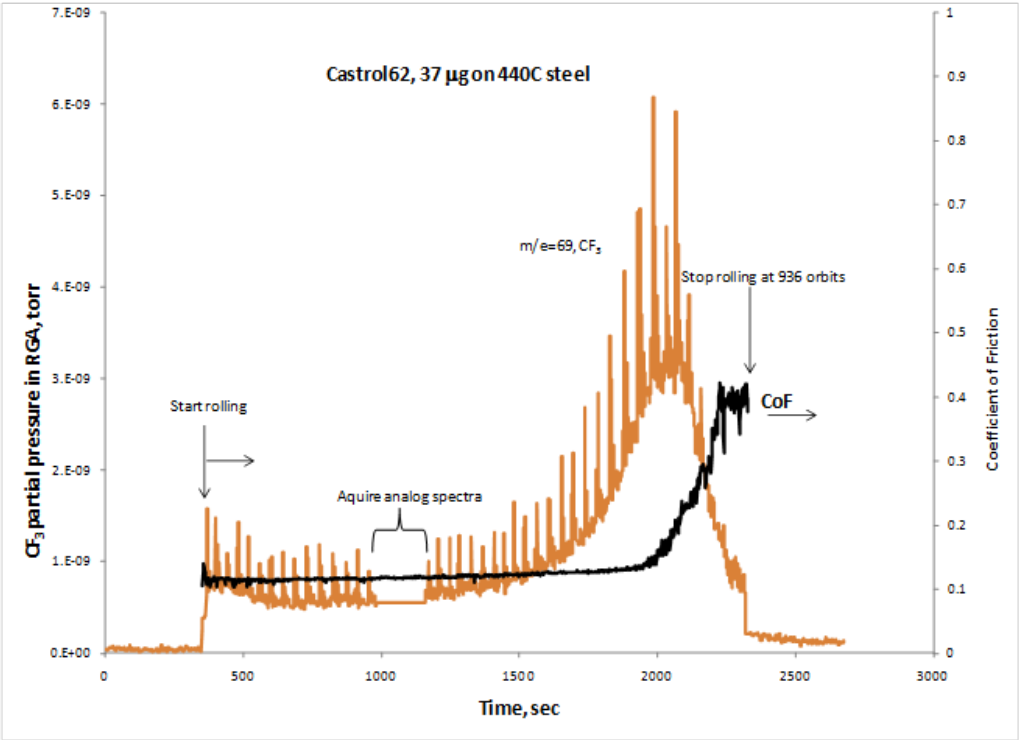

Fig. 4 Trend of the amplitude of the CF_3 feature in the RGA spectrum and the friction trace.

4. It is characteristic of a chemical reaction to be sensitive to the chemical constitution of the reactants. In the present case, it is proposed that one of the reactants is the bearing material with which the lubricant is in contact. Thus a test of the hypothesis that chemical reaction is responsible for the determination of lubricant lifetime in a SOT test would be to seek out such sensitivity to bearing material chemical constitution. This has been done for the particular test case of Pennzane 2001A lubricating a series of metals. In the tests, the plates were all 440C steel and the ball was bare 440C steel or 440C steel coated with a thin film of titanium, chromium or vanadium. The ball was lubricated as usual and then run in vacuum at 1.5 GPa Hertz pressure. In this manner the lubricant would be pressed into tribological contact with 440C, vanadium, chromium and titanium. Sensitivity of lifetime to bearing chemical constitution was found and the extreme example is that of titanium as shown in Fig. 5 below. It is seen that the system has essentially zero lifetime – in accordance with the common experience that titanium cannot be lubricated with liquid lubricants. Here, this common experience is attributed to the immediate destruction of the liquid lubricant molecules by tribochemical reaction with titanium, so that the lubricant molecules are destroyed in the contact without having a chance to perform lubrication. This high reactivity of titanium is well known and is part of the generally acknowledged trend of heightened chemical reactivity as one moves to the left from iron in Row 4 of the period table as shown in Figs. 6 and 7 below. On this “naïve” basis, therefore, the lifetimes for the cases of vanadium and chromium should be less than iron (steel) but greater

than titanium. The results in Fig. 8 show that this is in fact the case. The lifetimes of tests with both chromium and vanadium are smaller than those with iron (steel) and greater (non-zero!) than the tests with titanium as expected from such naïve reaction considerations. It is seen, however, that within statistical scatter, there is no difference between the lifetimes with chromium and vanadium, so the correlation is not perfect. In any case, the sensitivity of lifetime to chemical constitution of reactants (the bearing material) is confirmed and is taken as significant support for the interpretation of the finite lifetimes in SOT tests as due to tribochemical reaction and consumption of lubricant molecules.

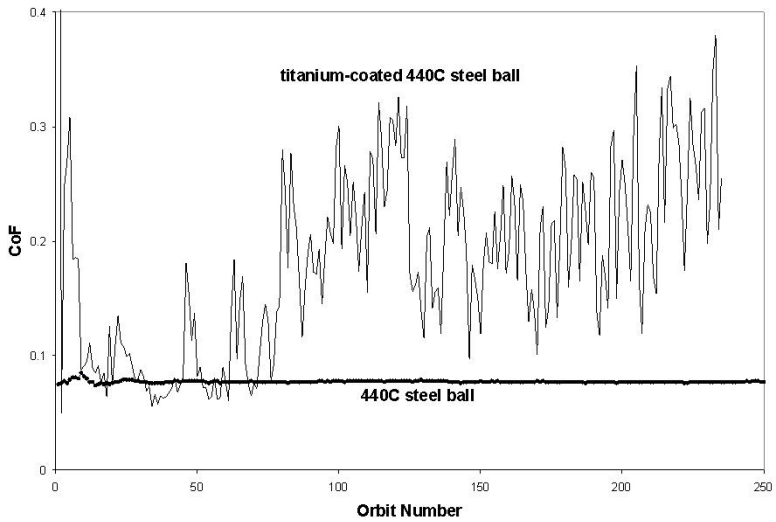

Fig. 5

Periodic Table

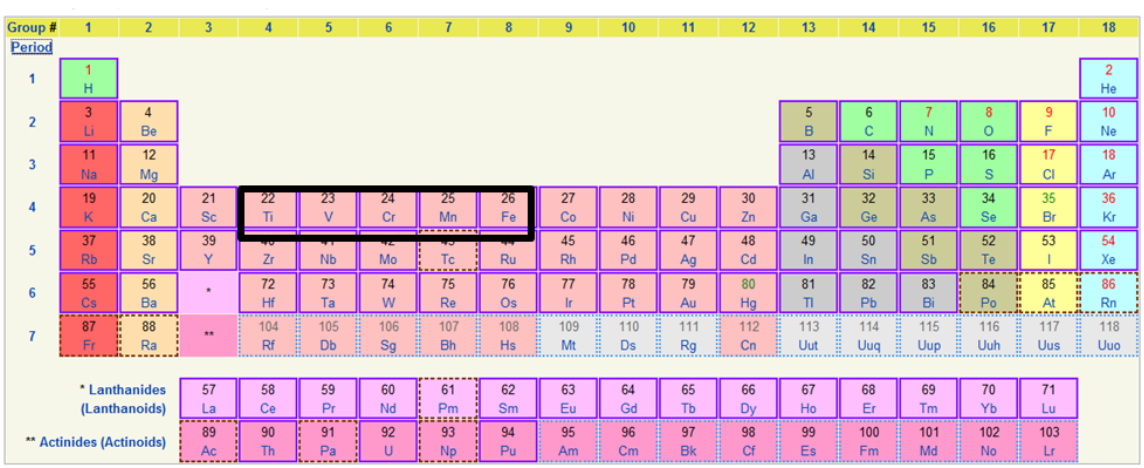

Fig. 6

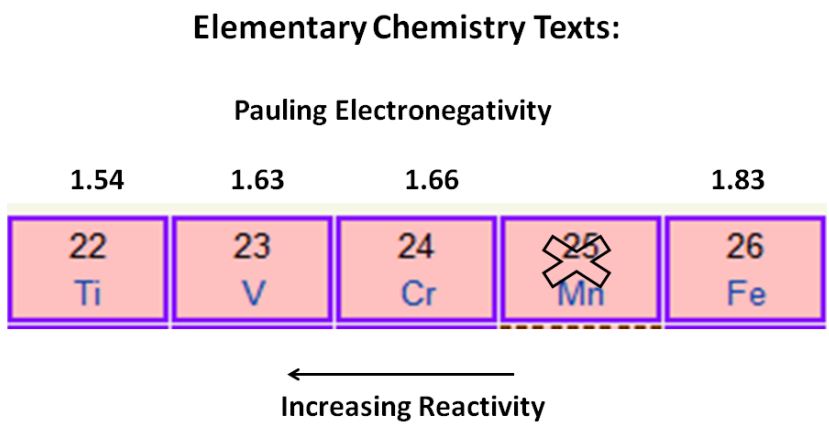

Fig. 7

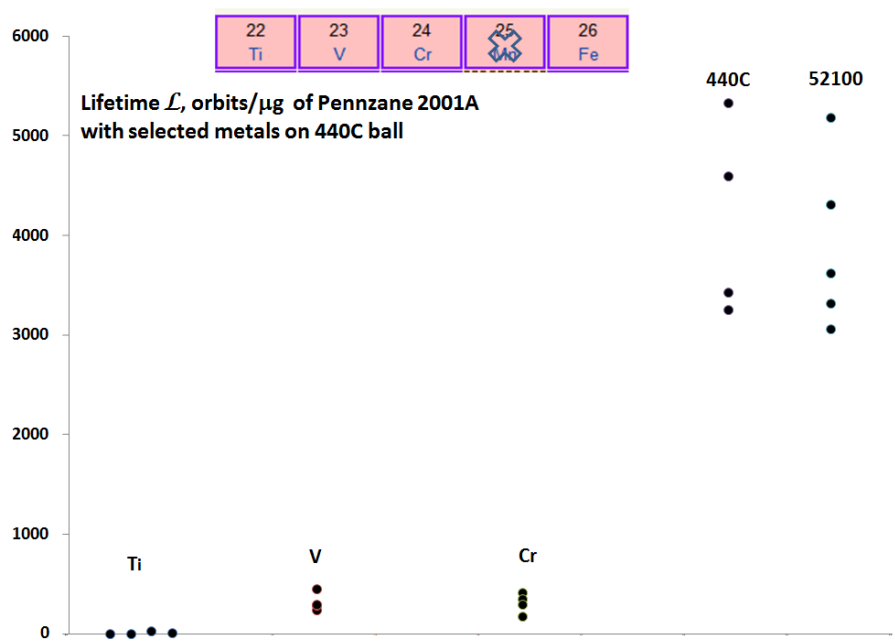

Fig. 8

- The fifth and last piece of evidence for tribochemical destruction and consumption of liquid lubricant molecules is from the dependency of test lifetime on the environment in the test chamber. All the lifetimes presented above were for running in ultrahigh vacuum, ~1×10^{-8} Torr. Tests were also performed in which the test chamber was backfilled with selected gasses to determine if there was any effect of test environment on lifetime. This, as well as the dependence on bearing chemistry, addresses the issue of whether simple mechanical shedding could be responsible in a major way for the finite test life indicated by the friction traces. The

results of these tests are found in NASA/TM—2011-217002 and only a summary is presented here. Briefly, it was found that environments of either nitrogen or oxygen up to an atmosphere of pressure had no effect on lifetime of Pennzane 2001A or Krytox 143AC. However, the presence of small partial pressures of water vapor lengthened the life of both of these lubricants. Fig. 9 shows the effect for Krytox and Fig. 10 shows the effect for Pennzane. This observed dependence on the presence of water vapor is not understood at present. What can be said, however, is that this dependence on a specific chemical constituent in the test environment (H_2O) is consistent with the interpretation of the finite test lifetimes being due to specific (tribo)chemical reactions. Simply put, chemical reactions are influenced by chemical environments. In this case, in some way, water vapor in the test environment protects both the Krytox and Pennzane lubricant molecule from reacting with the bearing material. Such small pressures should play no role in any simple mechanical shedding that may be taking place.

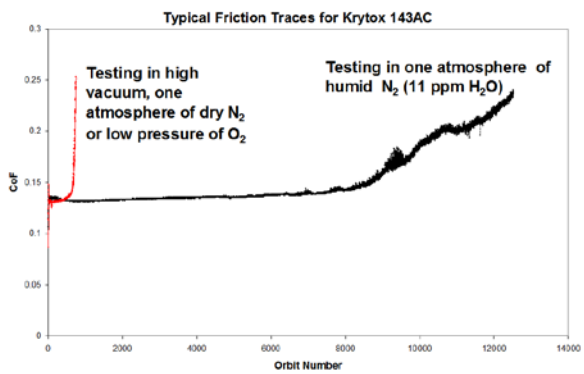

Fig. 9

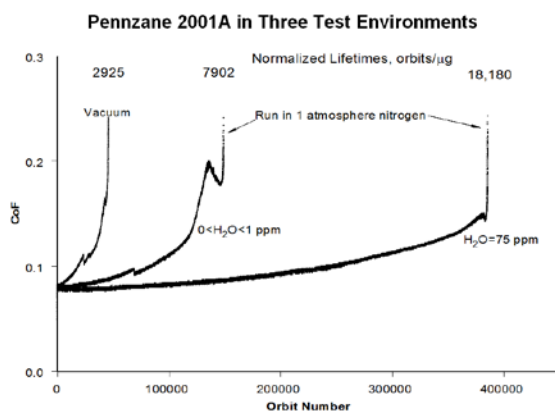

Fig. 10

Conclusion. Arguments have been advanced here to make the case that tribochemical reactions are responsible for consuming the lubricant and that they determine the finite lifetime of tests with tens of micrograms of liquid lubricant in the spiral orbit tribometer. It must be admitted, however, that the evidence is indirect and rather circumstantial. More direct evidence for this hypothesis is needed to confirm or possibly even to disprove it. However, any other explanation to account for the finite lifetimes observed must account for the other observations presented here. Assuming that the hypothesis is confirmed, this tribochemical reaction and lubricant consumption deserves consideration as a fundamental tribological phenomenon.