SMC-TR-02-08

AEROSPACE REPORT NO.
TR-2002(8565)-2

Lead Naphthenate Additive Tribochemistry in Hydrocarbon Oils

10 December 2001

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This report was submitted by The Aerospace Corporation, El Segundo, CA 90245-4691, under Contract No. F04701-00-C-0009 with the Space and Missile Systems Center, 2430 E. El Segundo Blvd., Los Angeles Air Force Base, CA 90245. It was reviewed and approved for The Aerospace Corporation by P. D. Fleischauer, Principal Director, Space Materials Laboratory. Michael Zambrana was the project officer for the Mission-Oriented Investigation and Experimentation (MOIE) program.

This report has been reviewed by the Public Affairs Office (PAS) and is releasable to the National Technical Information Service (NTIS). At NTIS, it will be available to the general public, including foreign nationals.

This technical report has been reviewed and is approved for publication. Publication of this report does not constitute Air Force approval of the report's findings or conclusions. It is published only for the exchange and stimulation of ideas.

Michael Zambrana
SMC/AXE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE (*DD-MM-YYYY*) 10-12-2001	**2. REPORT TYPE**	**3. DATES COVERED *(From - To)***

4. TITLE AND SUBTITLE

Lead Naphthenate Additive Tribochemistry in Hydrocarbon Oils

5a. CONTRACT NUMBER
F04701-00-C-0009

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)

D. J. Carre, P. A. Bertrand, and J. R. Lince

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

The Aerospace Corporation
Laboratory Operations
El Segundo, CA 90245-4691

8. PERFORMING ORGANIZATION REPORT NUMBER

TR-2002(8565)-2

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Space and Missile Systems Center
Air Force Space Command
2430 E. El Segundo Blvd.
Los Angeles Air Force Base, CA 90245

10. SPONSOR/MONITOR'S ACRONYM(S)
SMC

11. SPONSOR/MONITOR'S REPORT NUMBER(S)
SMC-TR-02-08

12. DISTRIBUTION/AVAILABILITY STATEMENT

Approved for public release; distribution unlimited.

13. SUPPLEMENTARY NOTES

14. ABSTRACT

There is often ambiguity concerning the antiwear mechanisms of soluble lubricant additives used in bearings. For example, the common spacecraft lubricant additive lead naphthenate is thought to be effective only as long as a measurable concentration is present in the oil lubricant throughout the mechanism lifetime. Recent mechanism tests with several days of operation indicated that a hydrocarbon lubricant was depleted of lead naphthenate, even during successful operation. To elucidate this apparent contradiction, we conducted tests on 440C stainless-steel thrust bearings lubricated with Apiezon C hydrocarbon oil that was formulated with 5 wt% lead naphthenate. The remaining oil in the bearings was analyzed using Fourier Transform Infrared Spectroscopy (FTIR) after several tests with varying durations up to 336 h (2 wk). FTIR showed that lead naphthenate chemically changes within 24 h and begins to disappear in 336 h. X-ray photoelectron spectroscopy (XPS) was used to determine the chemical state of the bearing surfaces after testing. XPS spectra indicated that lead naphthenate chemisorbs onto the bearing surface with minimal bearing operation, and further reaction to elemental lead (a solid lubricant) occurs at relatively short interaction times (two weeks in our testing). Ball bearing test data indicate that, despite the early loss of additive from the oil, the lead-containing surface coatings provide continued lubrication for the ball bearing.

15. SUBJECT TERMS

Lubricants, Additives

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** **David Carre**
a. REPORT UNCLASSIFIED	**b. ABSTRACT** UNCLASSIFIED	**c. THIS PAGE** UNCLASSIFIED		15	**19b. TELEPHONE NUMBER *(include area code)*** (719)573-2449

Acknowledgments

This work was supported by the U.S. Air Force Space Division Contract No. F04701-00-C-0009. The authors thank Mr. J. J. Kirsch and Mrs. S. A. Jackson for laboratory measurements.

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1. Introduction

Lead naphthenate is a lubricant antiwear additive that is used in a number of spacecraft mechanisms. We typically consider soluble additives to be available as needed during the life of the device. This implies that a measurable concentration of the additive will be present in the oil lubricant throughout the system lifetime. However, results of analysis of oil from two recent successful mechanism tests indicate that this may not be the case with lead naphthenate. No lead naphthenate was detected using Fourier transform infrared (FTIR) spectroscopy in the oils remaining in ball bearings after a few days of testing. These oils initially contained 5% lead naphthenate. (We estimate the detection limit of this technique to be ~0.5%.) Because of these results, we undertook an experimental program to determine the fate of lead naphthenate in ball bearings. For completeness, we included static testing in air, the storage environment for one of the mechanism tests, as well as dynamic testing in vacuum of the lubricant in a wear test apparatus in our laboratories. In previous work in our laboratories, X-ray photoelectron spectroscopy (XPS) was used to understand the surface chemistry of lead naphthenate on a variety of surfaces [1,2]. In the present work, we used XPS to analyze the surfaces of our test components to compare with the results of the previous work.

2. Experimental

2.1 Lubricants

We chose to use a petroleum-based hydrocarbon oil, Apiezon C, which we had immediately available in our laboratory. Formulated oil containing ~5% lead naphthenate was used in the tests. Unformulated Apiezon C oil was also available for use as a spectral standard.

2.2 Static Testing

440C stainless-steel coupons were used as the metal surface. The coupons were cleaned using heptane solvent. One or two drops of the test oil were placed on each of the coupons. Samples for analysis were removed by pipette at various times and were analyzed using Fourier transform infrared (FTIR) spectroscopy. The longest exposure time period was 110 h.

2.3 Dynamic Testing

Dynamic tests were performed using our in-house, eccentric bearing wear test facility, which has been described previously [3]. The tests were run with no eccentricity, using thrust ball bearings. The balls and thrust bearing raceways were composed of 440C stainless steel. The average surface roughness of raceways was ≤10 μin. The balls were ABEC grade 5, with an average surface roughness of ~2 μin. The ball retainer was the steel ribbon retainer furnished with the thrust ball bearing. The components were cleaned using heptane solvent prior to testing. The loads on the retainer are sufficiently low that reactions involving the retainer surfaces (which are not 440C) would not significantly affect the results.

The tests were run under the following conditions in a vacuum environment with pressure $<1 \times 10^{-6}$ torr: load = 1 lb per ball, speed = 1000 rpm, mean Hertzian stress = ~52 ksi, temperature = ambient, lubricant quantity = ~40 mg (2 drops). The tests were run for times that varied from 24 h to 2 wk. (One thrust bearing raceway was used in a static test to provide a control sample for XPS analysis.)

2.4 Analyses

The lubricant was removed from the ball bearings by rinsing with heptane solvent, followed by evaporation of the solvent to reduce the analysis volume and concentrate the samples. The lubricant samples were analyzed using a Nicolet Magna-IR 550 FTIR spectrometer in the internal reflectance mode. The spectra were taken with a resolution of 2 cm^{-1}.

The metal raceways were cleaned after static or dynamic testing using heptane solvent and were analyzed using XPS. The XPS data were collected using a Surface Science Instruments SSX-100 XPS system with an Al-Kα X-ray source (hν = 1486.6 eV) and a hemispherical analyzer. A 300-μm X-ray spot size and a 100-eV pass energy were used to collect the core-level spectra. These parameters result in a full-width-at-half-maximum of 0.88 eV for the Au $4f_{7/2}$ level collected from a clean Au foil. Binding energies for all spectra were referenced to the Au $4f_{7/2}$ level at 83.9 eV.

3. Results and Discussion

3.1 Ball Bearing Test Lubricant Analyses

Figure 1 shows an infrared spectrum of neat lead naphthenate over the spectral range of 1000–1800 cm^{-1}. The major absorption peaks occur at ~1400 and 1520 cm^{-1} and are due to symmetric and asymmetric carbonyl group (C=O) vibrations that are characteristic of carboxylate (metal salt) compounds. Minor peaks occur at ~1460 and 1300 cm^{-1}. These peaks will be used in the subsequent discussions.

Figure 2 shows the FTIR spectra of oil from one of the ball bearings stored for ~1 yr in air and run for ~100 h in a full-up moving mechanical assembly during the storage period. The bearings were run under vacuum at ~2000 rpm with a Hertzian stress of ~90 ksi. (The IR spectrum of the oil from the other ball bearing of the pair is identical. The spectra in this and subsequent figures are offset along the vertical axis for clarity.) In addition, the spectrum of the unused oil extracted from an unused grease is included for comparison. Note that the lead naphthenate peaks at 1400 and 1520 cm^{-1} are obvious in the spectrum of the unused oil (A) but are missing from the spectrum of the oil removed from the ball bearing.

Figure 3 shows FTIR spectra of oil extracted from the retainers of the bearings from a 6.5 yr life test. In this test, the speed was ~120 rpm, and the Hertzian stress was 80–90 ksi. It is clear that the lead naphthenate has also disappeared from the oil in the life test. XPS analysis (not shown) of the inner raceway surfaces indicated that a lead-containing film had formed on the metal surfaces.

3.2 Static Testing

The results of the static testing are shown in Figure 4. Spectra of the unused oil and oil from the longest static test, 110 h, are shown. There is no detectable difference in the spectra, indicating that

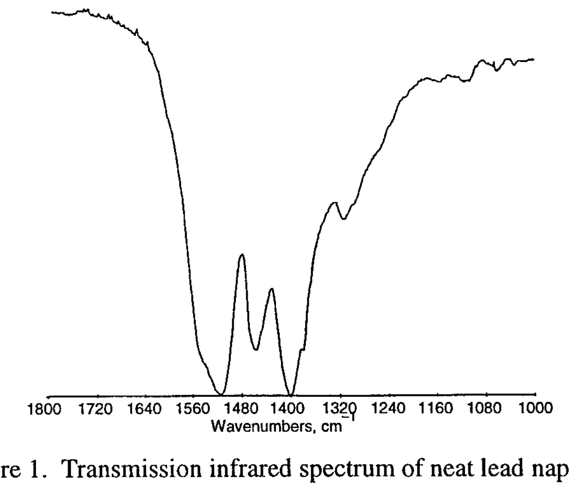

Figure 1. Transmission infrared spectrum of neat lead naphthenate.

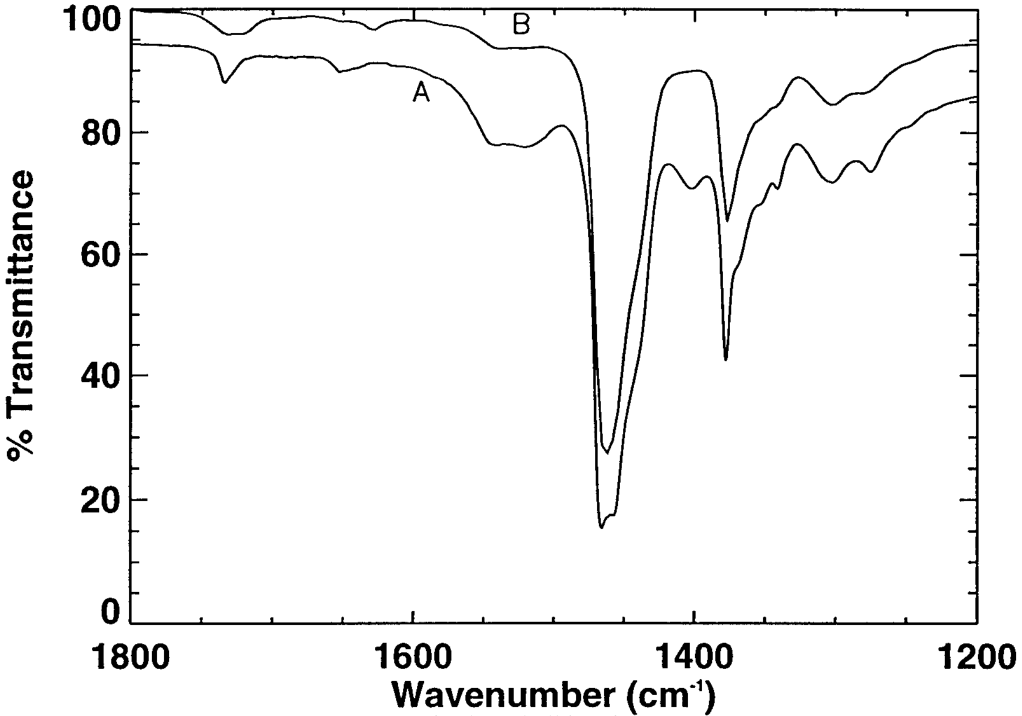

Figure 2. FTIR spectra for oils from ball bearings stored 1 yr and run 100 h in an RWA; A – unused oil, B – oil from one bearing.

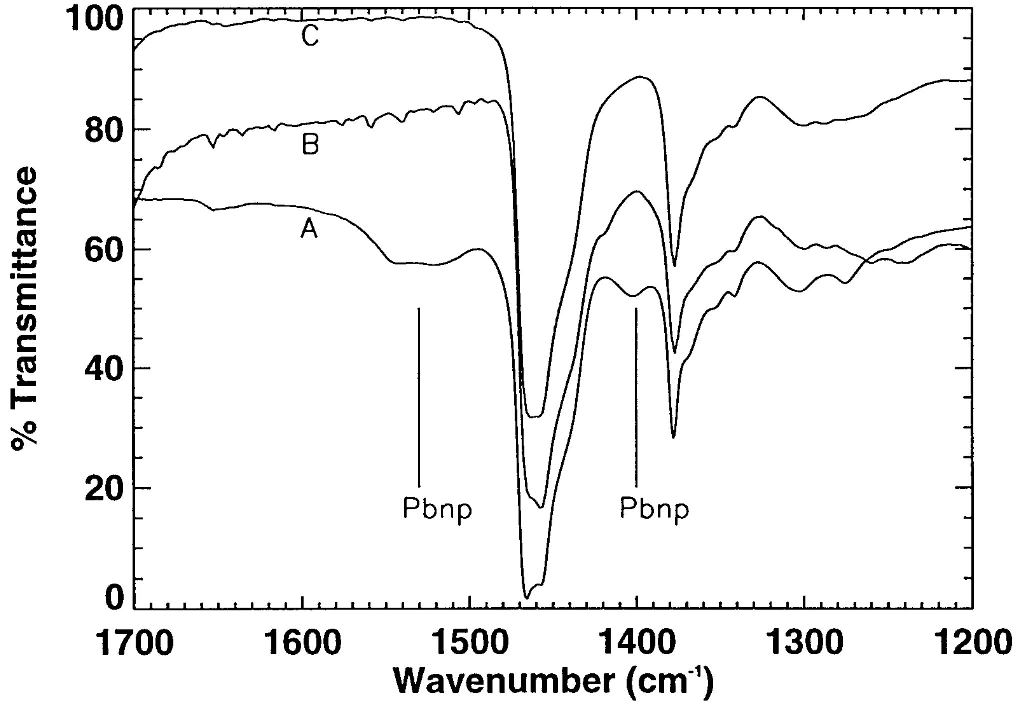

Figure 3. FTIR spectra of oil from life test bearings; A – unused oil; B – large bearing, C – small bearing.

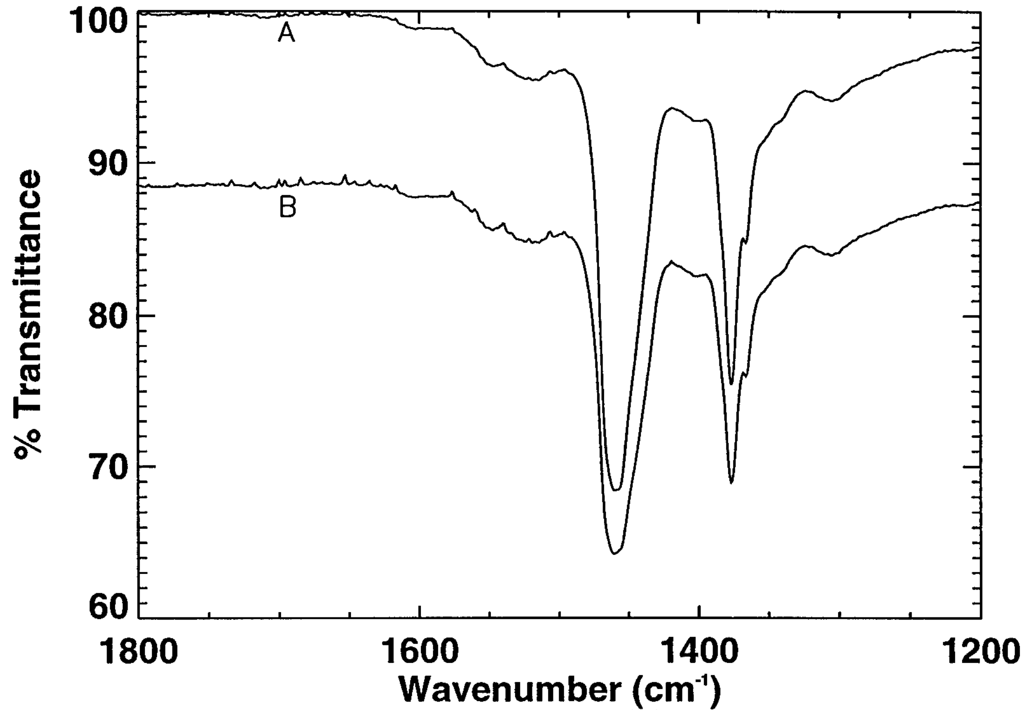

Figure 4. FTIR spectra of oil from static tests of oil on metal; A – unused oil; B – 110 h.

the lead naphthenate is not absorbed measurably during room-temperature static contact with steel surfaces. The spectrum of the unformulated oil, with no lead naphthenate, was subtracted from the two spectra given in Figure 4; the modified spectra are shown in Figure 5. [The subtraction was

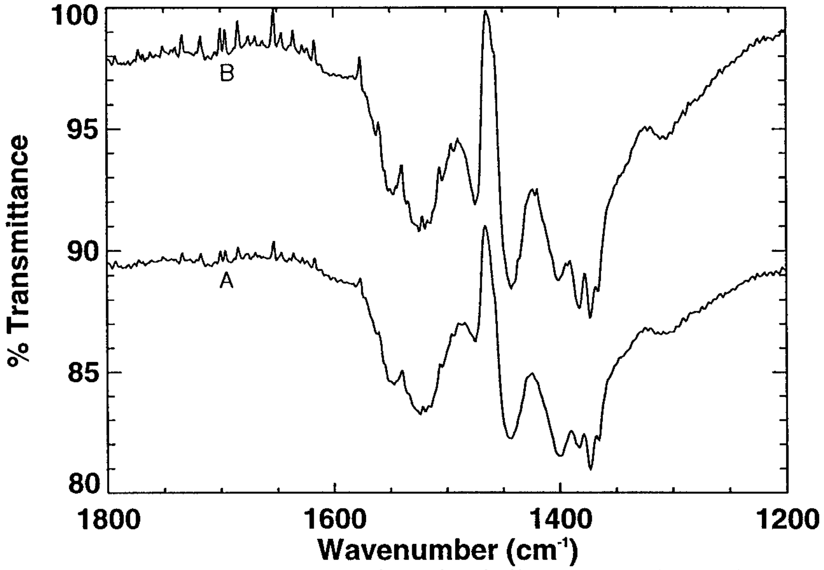

Figure 5. Difference spectra – unformulated oil spectrum subtracted from spectra in Figure 4; A – unused oil; B – 110 h.

accomplished by converting the spectra to the absorbance mode, normalizing the spectra so that the feature at 1470 cm^{-1} (carbon-hydrogen vibration) was the same size in all spectra to minimize the spectral contributions of the base oil, then subtracting. The "difference" spectra were reconverted to the % transmittance mode to emphasize the smaller features. This results in a 100% transmittance value for the 1470 cm^{-1} signal.] Note that the spectra are essentially identical, indicating that no chemical changes had occurred in the lead naphthenate. Thus, it appears that static storage does not result in measurable quantities of the additive leaving the oil or undergoing chemical changes, at least on the time scale of our experiment. Loss of lead naphthenate due to surface adsorption (see XPS section below) is insignificant. Monolayer coverage of ~4 x 10^{14} molecules-cm^{-2}, assuming an area of 25 $Å^2$/molecule of lead naphthenate, corresponds to ~7 x 10^{-10} mol. The loss of this small amount of material from the oil would be undetectable using FTIR spectroscopy.

3.3 Dynamic Testing

Figure 6 shows the spectra of oil from the dynamic tests. The spectrum of the unused oil is also included. Two noticeable effects have occurred. First, the spectrum of the additive has changed; and second, the signal at ~1400–1410 cm^{-1} is decreasing with running time. As with the static test spectra, the spectrum of the unformulated oil was subtracted from the unused oil and the 24-h oil spectra. The result is shown in Figure 7. (As before, the feature at 1470 cm^{-1} is an artifact of the subtraction procedure.) The spectra are very different, indicating that some chemical changes have taken place. The region of the IR spectrum in which the "new" absorption bands occur is still the region associated with metal carboxylate salts. However, the peaks have shifted to higher wavenumber. This could be

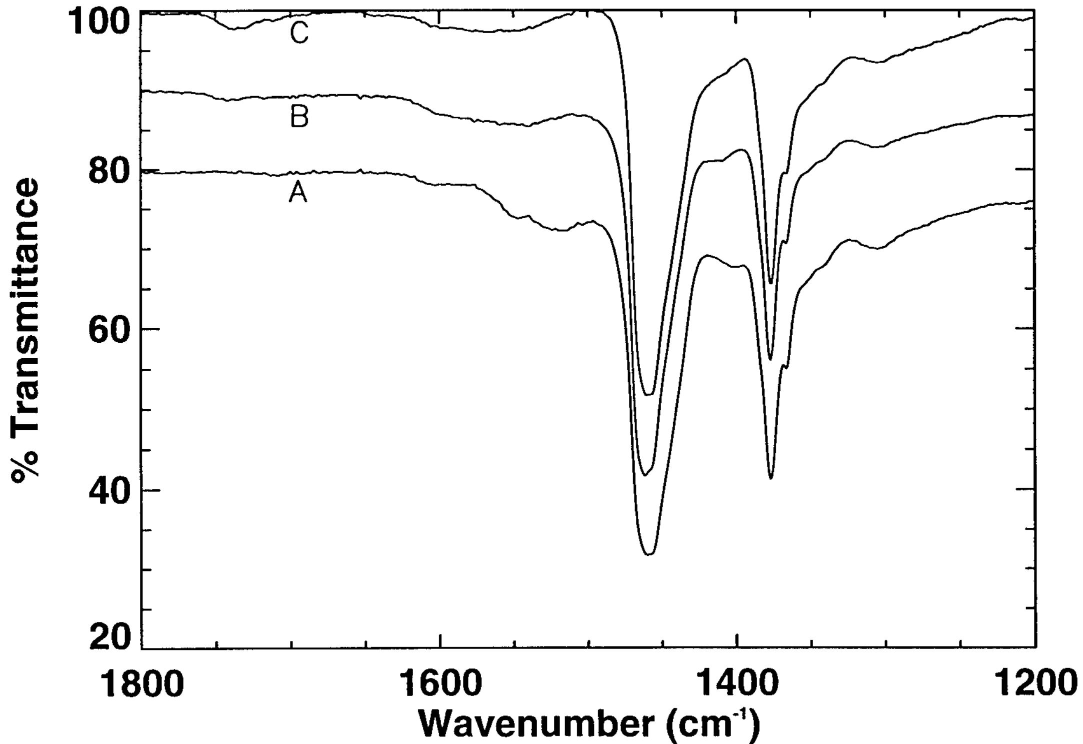

Figure 6. FTIR spectra of oils from dynamic testing; A – unused oil; B – 24 h, C – 2 wk.

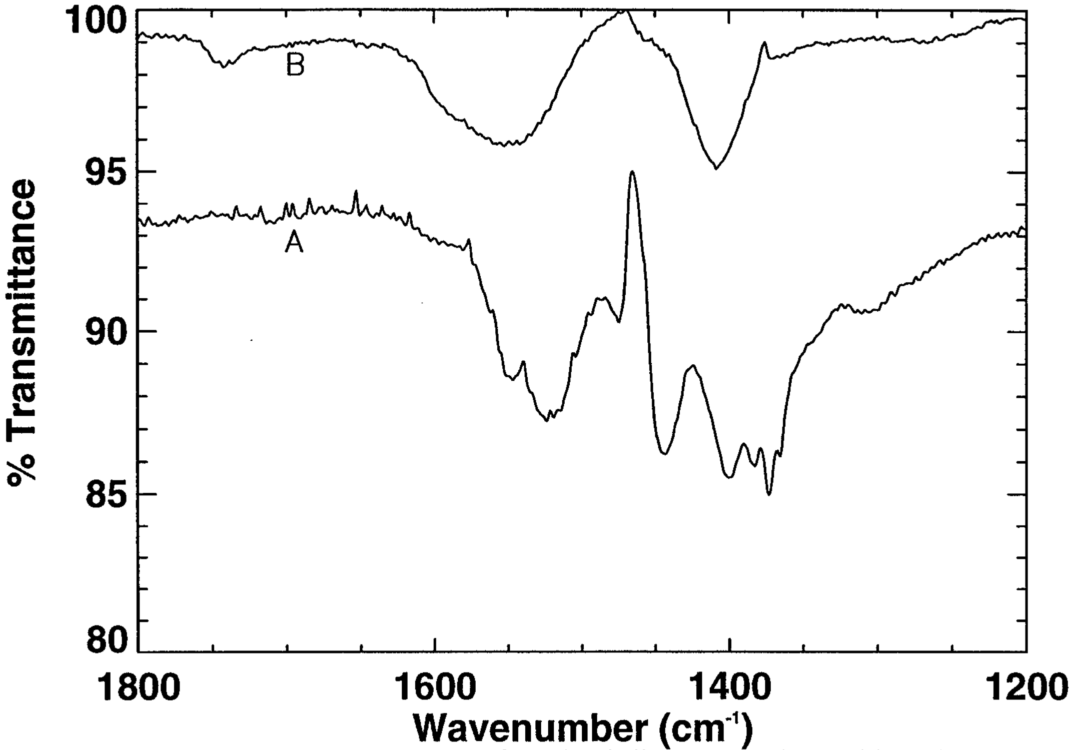

Figure 7. Difference spectra – unformulated oil spectrum subtracted from the spectra in Figure 6; A – unused oil, B – 24 h.

due to reaction with the surface atoms with substitution of iron or chromium for lead as metal naphthenates dissolved in the oil. Iron naphthenate has absorptions at 1410 and 1550 cm^{-1}, similar to those seen in Figure 7b [5]. Since the metal surfaces in the dynamic testing were 440C stainless steel, it is possible that chromium naphthenate might also form. Another possibility is that displacement of one of the carboxylate groups of lead naphthenate occurs, producing some other carboxylate species in the oil and leaving lead and some naphthenate on the surface. We have been unable to find spectra in the literature that would support this conclusion, but nothing would indicate that the conclusion was not reasonable. Other studies of lead naphthenate on 440C surfaces have concluded that both lead- and carboxyl-containing species are left on the surface [2,4].

The disappearance of the "carboxylate" signal at 1400 cm^{-1} with time in our dynamic tests, Figure 6, is consistent with our observations of the oil from test ball bearings. Our experimental tests were run at lower Hertzian stress than the mechanisms, and this might result in a retardation of the deposition rate; depositing lead more slowly than the lead naphthenate loss from the oil in the mechanisms.

3.4 XPS Analysis

The metal raceways from the 24-h and 336-h dynamic tests were analyzed using XPS. Figure 8 shows wide energy range scans obtained inside the wear tracks of these samples, and are compared to a sample subjected to a static test for 48 h.

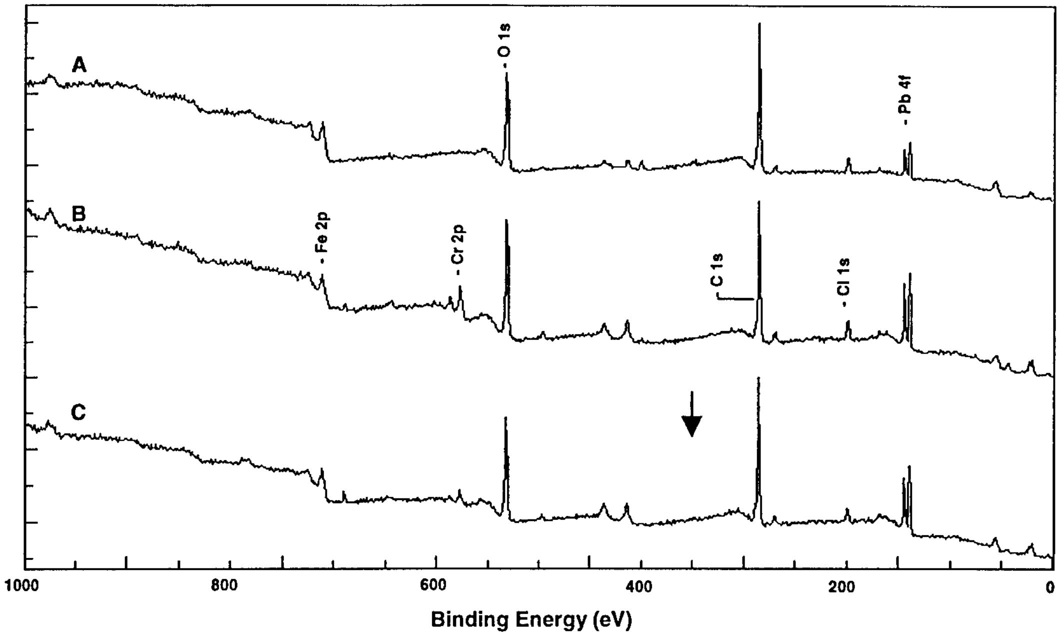

Figure 8. XPS wide energy range scans obtained from inside the wear track on (A) raceways exposed to the formulated oil for 48 h in a static test, and raceways that underwent dynamic tests for (B) 24 h and (C) 336 h.

The relative atomic concentrations of the various species were calculated. The lead:(iron+chromium) atomic ratios for the static test sample and the 24-h and 336-h dynamic test samples were 0.26, 0.35, and 0.51, respectively. A higher value is consistent with a thicker lead-containing film, which blocks the substrate species (iron and chromium) from detection by XPS. As such, these data indicate that there is a thicker lead-containing surface film for the dynamic tests compared to the static test, and that the 336-h test has a greater quantity of lead on the surface than the 24-h test.

Higher energy resolution XPS data for the lead $4f_{7/2}$ region are shown in Figure 9. The peak maxima occur at a position that is consistent with chemisorbed (i.e., partially decomposed) lead naphthenate [2]. The shoulder that is marked with "PbO" is consistent with lead oxide. It is likely that the lead in the lead naphthenate was reduced to elemental lead by iron and/or chromium that was exposed during the wear process in vacuum. In fact, elemental lead has been observed following the interaction of lead naphthenate with scratched 440C metal surfaces [2]. In our study, the elemental lead was then oxidized to PbO during storage of the test parts prior to XPS analysis. (In Ref. 2, lead oxides were not seen because the samples were analyzed within 10 min of testing.) The decomposition of lead naphthenate to elemental lead is consistent with the presence of transition metal naphthenates in the oil solution detected by FTIR, formed from the interaction of naphthenates with iron and chromium from the steel surface.

Higher energy resolution XPS spectra in the carbon 1s region for the three samples are shown in Figure 10.

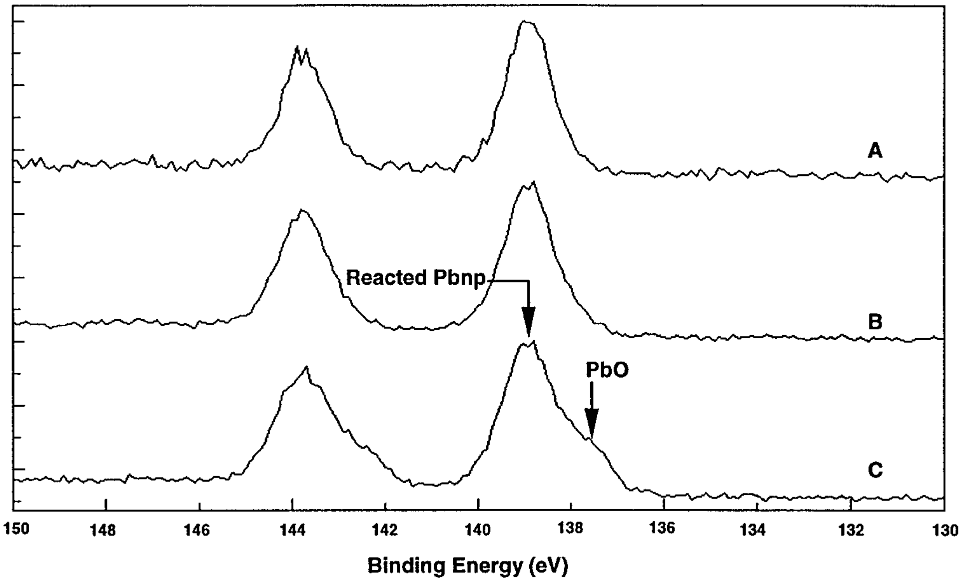

Figure 9. XPS scans in the Pb 4f$_{7/2}$ region obtained from inside the wear track on (A) raceways exposed to the formulated oil for 48 h in a static test, and raceways that underwent dynamic tests for (B) 24 h and (C) 336 h.

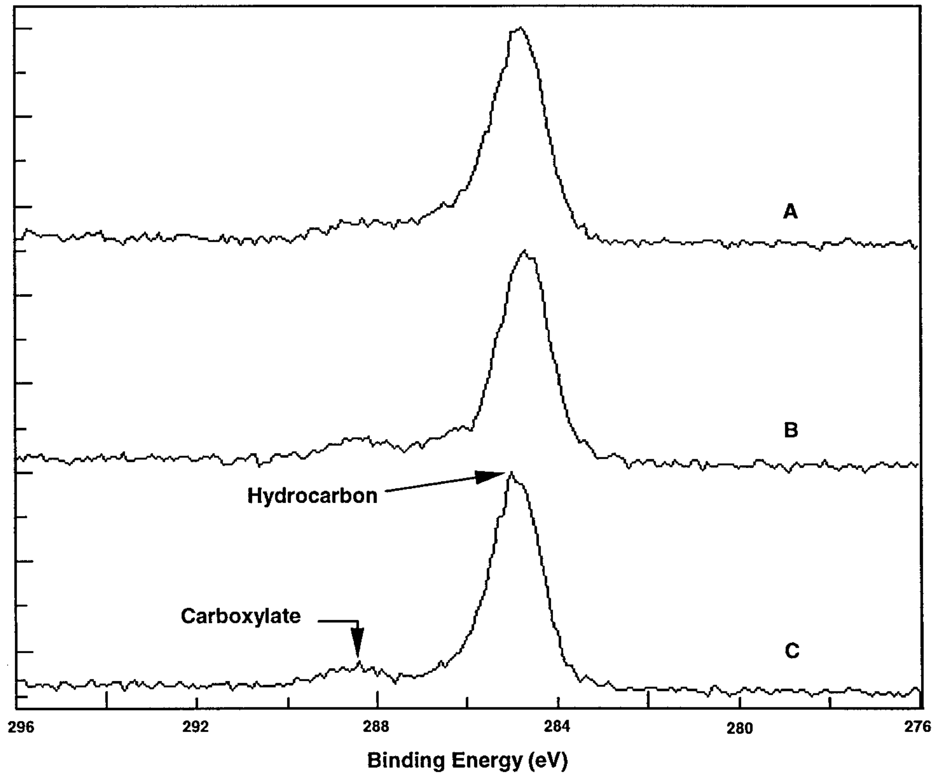

Figure 10. XPS scans in the C 1s region obtained from inside the wear track on (A) raceways exposed to the formulated oil for 48 h in a static test, and raceways that underwent dynamic tests for (B) 24 h and (C) 336 h.

The spectra are normalized to the same maximum peak height, which corresponds to the binding energy of saturated (C-H) carbon. The intensities of the carboxylate regions relative to the hydrocarbon peaks for all three samples are similar to that expected for chemisorbed lead naphthenate, and are significantly lower than that expected for unreacted (physisorbed) lead naphthenate [2]. This is consistent with the binding energy of the main component in the Pb $4f_{7/2}$ spectrum for all three samples, indicating some reaction of the lead naphthenate with displacement or reaction of the naphthenate portion of the molecule.

4. Conclusions

The results of our experiments indicate that lead naphthenate does disappear from oil in a relatively short time on the time scale of a ball bearing spacecraft application. The disappearance is characterized by a change in the FTIR spectrum of the lead naphthenate, indicating chemical reaction of the lead naphthenate in the oil. XPS spectra indicate that reaction of the lead naphthenate occurs at relatively short interaction times (two weeks in our testing) to form elemental lead via reaction of the lead naphthenate with metal exposed through the wear process. The change occurs under dynamic bearing operating conditions and not under static conditions. Ball bearing test data indicate that, despite the early loss of additive from the oil, the lead-containing surface coatings provide continued lubrication for the ball bearing.

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