REPORT DOCUMENTATION PAGE

AFRL-SR-AR-TR-02-

0339

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1. REPORT DATE *(DD-MM-YYYY)*
01-08-2002

2. REPORT TYPE
Final Report

3. DATES COVERED *(From - To)*
01/03/2001-28/02/2002

4. TITLE AND SUBTITLE
High Resolution Vibrational Spectroscopy of Vapor Phase Lubrication on Ceramics

5a. CONTRACT NUMBER
AFOSR-F49620-01-1-0232

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
61103D

5d. PROJECT NUMBER
3484

5e. TASK NUMBER
US

5f. WORK UNIT NUMBER

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8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES)
AFOSR/NL
801 N. Randolph Ave.
Arlington, VA 22203-1977

10. SPONSOR/MONITOR'S ACRONYM(S)

11. SPONSOR/MONITOR'S REPORT NUMBER(S)

12. DISTRIBUTION / AVAILABILITY STATEMENT

Approve for Public Release: Distribution Unlimited

20021031 011

13. SUPPLEMENTARY NOTES

14. ABSTRACT
A High Resolution Electron Energy Loss Spectrometer (HREELS) has been purchased to allow detailed study of the surface chemistry of vapor phase lubricants on both metal and ceramic surfaces. The most commonly used types of vapor phase lubricants are the aryl-phosphates such as tricresylphosphate (TCP). These react with metal surfaces at high temperatures to form solid films that are capable of lubricating at temperatures as high as 500 – 600°C. The mechanisms by which vapor phase lubricants react to form these lubricious films are key to their success as high temperature lubricants but are not well understood. One of the reasons is that they are more complex than most of the types of compounds typically used in studies of surface chemistry. As a result there are many possible pathways by which they can react and many possible intermediates that might be formed in those reaction mechanisms. Unraveling this complex chemistry requires high resolution spectroscopy that can be used to resolve spectral features and distinguish between species on the surface during TCP reaction. The HREELS spectrometer purchased with the funding that has been provided by this DURIP grant has state-of-the-art resolution for performing vibrational spectroscopy of species on surfaces.

15. SUBJECT TERMS

16. SECURITY CLASSIFICATION OF:			17. LIMITATION OF ABSTRACT	18. NUMBER OF PAGES	19a. NAME OF RESPONSIBLE PERSON
a. REPORT	b. ABSTRACT	c. THIS PAGE			19b. TELEPHONE NUMBER *(include area code)*

AFOSR - Final Progress Report

High Resolution Vibrational Spectroscopy of Vapor Phase Lubrication on Ceramics

Grant No. AFOSR-F49620-01-1-0232
Duration - Mar. 1, 2001 to Feb. 28, 2002

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Summary

A High Resolution Electron Energy Loss Spectrometer (HREELS) has been purchased to allow detailed study of the surface chemistry of vapor phase lubricants on both metal and ceramic surfaces. The most commonly used types of vapor phase lubricants are the aryl-phosphates such as tricresylphosphate (TCP). These react with metal surfaces at high temperatures to form solid films that are capable of lubricating at temperatures as high as 500 – 600°C. The mechanisms by which vapor phase lubricants react to form these lubricious films are key to their success as high temperature lubricants but are not well understood. One of the reasons is that they are more complex than most of the types of compounds typically used in studies of surface chemistry. As a result there are many possible pathways by which they can react and many possible intermediates that might be formed in those reaction mechanisms. Unraveling this complex chemistry requires high resolution spectroscopy that can be used to resolve spectral features and distinguish between species on the surface during TCP reaction. The HREELS spectrometer purchased with the funding that has been provided by this DURIP grant has state-of-the-art resolution for performing vibrational spectroscopy of species on surfaces.

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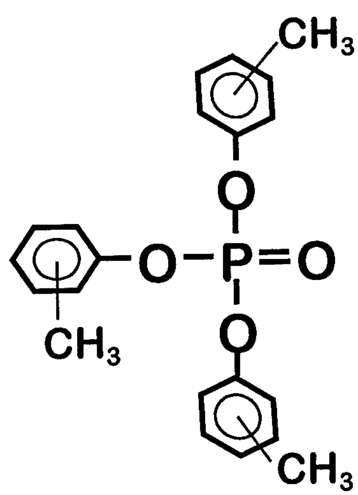
Project Objectives

The principle research efforts in the P.I.'s laboratory are focused on the study of surface chemistry and tribology. The P.I. has a developed a number of pieces of instrumentation for the study of surface chemistry related to tribology including a unique apparatus for the measurement of friction between well prepared and high characterized surfaces. These friction measurements are supported by a host of spectroscopic studies of the surface chemistry of lubricants. The High Resolution Electron Energy Loss Spectrometer (HREELS) spectrometer purchased with the funds provided by this DURIP grant will be integrated into the set of tools currently being applied to the study of lubricant surface chemistry relevant to the needs of Air Force technologies.

The primary problem for which the HREEL spectrometer has been purchased is the study of the surface chemistry of vapor phase lubricants. Vapor phase lubrication is used under extreme conditions in situations where the operating temperatures are too high to allow the use of traditional lubricant fluids. The most commonly studied VP lubricant is tricresylphosphate (TCP) shown below.



TCP reacts on Fe surfaces to form a thin film of polyphosphate glass with embedded carbon. Prior work in the P.I.'s laboratory has probed the surface chemistry of this compound and other *aryl* and *alkyl* phosphates on Fe and Ni surfaces. In addition work is ongoing on the problem of vapor phase lubrication of ceramics such as SiC. The results of this work have suggested that the *aryl* phosphates decompose by the initial cleavage of

P-O bonds to form adsorbed alkoxy species. These then decompose further to give deposit carbon onto the surface. In contrast the *alkyl* phosphates such as tributylphosphate (TBP), $(CH_3(CH_2)_3O)_3P=O$, decompose by C-O bond cleavage to leave alkyl groups on the surface. These alkyl groups desorb from the surface as olefins produced by β-hydride elimination and thus deplete the surface of carbon needed to provide adequate lubrication.

The HREEL spectrometer will enable us to obtain very high resolution vibrational spectra of surface during the adsorption and decomposition of TCP. The complexity of these molecules and of the species produced during their decomposition necessitates the use of high resolution in order to be able to identify the species produced as decomposition intermediates. This ought to allow us to identify the alkoxy groups produced during P-O bond cleavage in TCP and then to identify some of the other reaction intermediates produced during the subsequent decomposition steps. Finally, the use of HREELS will allow us to characterize the nature of the films produced at high temperature that are responsible for lubrication.

A second objective of the research program is the study of a process for the vapor lubrication of ceramic surfaces such as those of SiC. TCP itself will not react to form a lubricating film on the surface of SiC, however, is one could introduce a vapor phase Fe containing compound into the vapor lubrication mixture this could decompose on the SiC surface to produce an Fe film that could then catalyze the decomposition of TCP into a lubricating film. Our work has shown that the decomposition of $Fe(CO)_5$ can be used to deposit Fe onto the surface of SiC. This does in fact then induced the decomposition of model organophosphorus compounds. At this point nothing is known about the mechanism of $Fe(CO)_5$ decomposition on the SiC surface and nothing is known about the decomposition of TCP on the Fe coated SiC surface. The use of HREELS will enable us to identify the intermediates in the decomposition of $Fe(CO)_5$ on SiC and then to unravel the more complex process of TCP decomposition on these surfaces.

Technical Progress and Accomplishments

The principle progress on this project has been the design of a new ultra-high vacuum chamber for the HREEL spectrometer. The HREEL spectrometer requires a specially designed chamber that can accommodate both the spectrometer and the other surface analysis instrumentation that we need in order to prepare the surfaces with adsorbed films of TCP and $Fe(CO)_5$. The chamber has an 18" diameter lower level which houses the HREEL spectrometer. The 14" upper level houses other instrumentation for surface analysis and for surface preparation. Much of the instrumentation for this level is in hand although there are flanges included for use with instrumentation that we will need to purchase in the future. The schematic of the chamber is shown below.

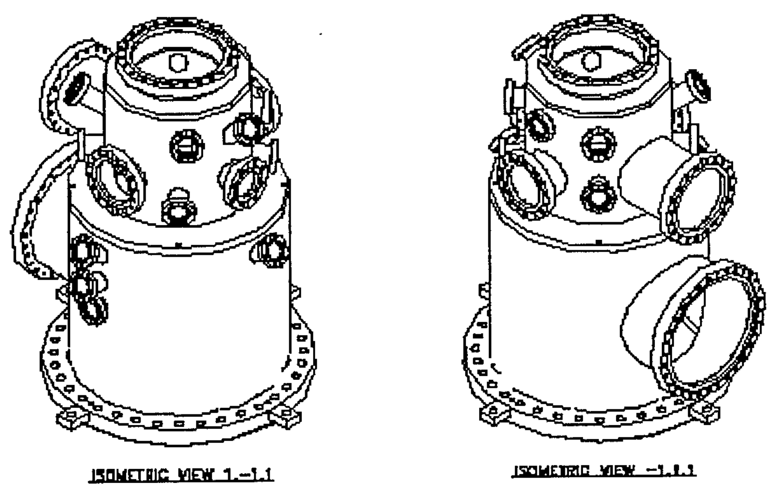


Figure 1. Schematic drawing of the UHV chamber under construction for the high resolution electron energy loss spectrometer. The chamber has two levels for sample preparation and analysis. The HREELS spectrometer is house in the large lower level. Other surface analysis and surface preparation instruments are to be housed in the upper level.

The chamber and spectrometer have been built and delivered to Carnegie Mellon. The spectrometer is currently being tested in order to determine whether it meets operating specifications. At this point we have been able to achieve a spectral resolution of less than 2 meV which is better than that specified.

During the course of the design and subsequent construction of this new apparatus we have continued the investigation of TCP vapor phase lubrication using equipment already operational in the laboratory. This has included the completion of a study of the thermal decomposition of TCP and TBP on the surface of Fe and a study of the decomposition kinetics of the three isomers of TCP (*o*-TCP, *m*-TCP, and *p*-TCP). Our study of the decomposition of the TCP and TBP has lead to the conclusions cited above concerning the difference sin the decomposition mechanism of the two. The investigation of the decomposition of the three different TCP isomers was prompted by some indication from studies done in two different laboratories that the surface reaction mechanisms may in fact differ for the three. In fact we find that when compared in the same apparatus and under the same conditions the decomposition mechanisms of the three are in fact quite similar.

Once the HREELS spectrometer is in place and functioning we will be able to bring this additional capability to bear on the study of TCP decomposition. In addition it will be used to continue our investigation of the potential for vapor phase lubrication of ceramics using vapor phase Fe containing compounds.

Equipment Purchases:

1. LK ELS-3000 HREELS spectrometer	$129,000
2. MDC z-axis translator	6,118
Total	$134,118