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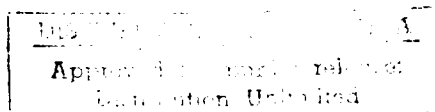
**THERMAL AND CHEMICAL EFFECTS IN HIGH  
PRESSURE ROLLING/SLIDING CONTACTS**

**FINAL REPORT  
TO  
THE OFFICE OF NAVAL RESEARCH**

**Contract No. N00014-79-C-0241**

**J. W. Brasch  
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| <p>This program involved both thermomechanical and chemical effects. The former involved analysis and experimentation relating to thermal effects in two important systems: elastohydrodynamically (EHD) lubricated bearings or gears, and high-current-density electrical brushes.</p> <p>A thermodynamic heat balance has been applied to an EHD contact utilizing experimental values for surface pressure and temperature distributions. The results showed that the magnitude of compressive and shear heating in the lubricant were higher than that due to convection to the fluid.</p> |                       |                                                             |

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## 20. Abstract

Experimental measurements of axial film thickness profiles for rolling/sliding disks were made using an x-ray shadow technique. The objective was to determine if the profile under load will vary due to nonuniform heating and thermal expansion at the disk contact leading to scuffing failure. No significant changes in profile were measured, but a limited range of experimental conditions were studied.

A high-current-density electrical slip ring apparatus was constructed and used to study the effect of material properties on the contact between the stationary brush and the copper slip ring. The results showed that above a particular threshold speed, the brushes exhibited a sparking phenomenon which consisted of periodic motion of a cluster of small sparks at the brush/slip ring interface. The peak temperature and the period of the spark motion was shown to be a function of the thermal and mechanical properties of the brush. A theoretical model shows good agreement with the experiments for the electrographitic brush.

Surface chemical reactions were studied in a simulated (static) lubricant/bearing surface system consisting of a lauric acid/dodecane solution in a high pressure diamond anvil cell having thinly metallized windows. Fourier Transform Infrared Spectroscopy was used to follow the rates of reactions at various temperatures and pressures. The rate of reaction was found to increase dramatically at a temperature of about 100 C. No measurable reaction was found at pressures high enough to solidify the solutions.

FINAL REPORT

on

THERMAL AND CHEMICAL EFFECTS IN HIGH  
PRESSURE ROLLING/SLIDING CONTACTS

to

OFFICE OF NAVAL RESEARCH

September 14, 1981

by

J. W. Brasch, E. Drauglis, R. J. Jakobsen,  
T. A. Dow, R. D. Stockwell and J. W. Kannel

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## EXECUTIVE SUMMARY AND CONCLUSIONS

The program discussed in this final report involves both thermal aspects of tribiology and chemical effects at high pressures. The work on thermal aspects is described in detail in a Summary Report.\* For the convenience of the reader the principal conclusions of these phases of the program are summarized below along with a summary of the results of the chemical studies.

The first section of the Summary Report deals with the heat generated in an elastohydrodynamic (EHD) contact. The second and third sections involve an interaction of heating and thermal expansion on contacting surfaces. Section 2 deals with an EHD contact and Section 3 deals with an electrical brush. The results presented are in some ways preliminary and future work is planned in each of these areas.

### Section 1. Heat Balance in EHD Contact

A thermodynamic heat balance has been applied to an EHD contact utilizing experimental values for surface pressure and temperature distributions. The relative magnitudes of the main heating terms (shear and compression) have been evaluated as well as the main heat transfer mechanisms. The heating due to compression is as significant as that due to shear and it adds to the heating in the inlet region and subtracts from it past the peak pressure region. The heat loss due to conduction is significantly larger than that due to convection.

The heat balance has been used to explain the origin of an anomalous secondary peak in the measured distribution for pure rolling conditions. This peak is caused by the combination of rapid expansive cooling followed by shear heating.

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\* Dow, T. A., Stockwell, R. D. and Kannel, J. W., "Thermal and Thermomechanical Effects in Rolling/Sliding Contacts", Summary Report to The Office of Naval Research, Contract No. N00014-79-C-0241, May, 1981.

## Section 2. Thermoelastic Effects in Rolling/Sliding EHD Contacts

Experimental measurements of film thickness profiles for rolling/sliding disks has been performed in a twin-disk machine. The lower disk is cylindrical with a 36 mm diameter; the upper disk is also 36 mm in diameter, but it also has a crown radius of 140 mm. These disks were run under conditions ranging from pure rolling to pure sliding.

A technique was developed for measuring the film thickness profile axially along the crowned surface under loaded conditions using the X-ray film measurement technique. The objective was to determine if this profile will significantly change as a result of non-uniform heating and thermal expansion of the mating disks, leading to scuffing failure. No significant changes in profile were measured in the experiments, but only a limited range of conditions was studied.

## Section 3. Thermomechanical Effects in High-Current-Density Electrical Slip Rings

An experimental apparatus has been constructed to study the contact of electrical brushes passing high currents. This apparatus consists of a 100-mm copper slip ring and a brush holder which can be loaded against it. The surface temperature of the brush, the extent of contact, and friction can be measured with this apparatus. Four brush types were studied: one electrographitic brush and three silver-filled graphite brushes.

The results of the experiments showed that above a particular threshold speed, the brushes exhibited a sparking phenomenon which consisted of periodic motion of a cluster of small sparks on the brush surface. The peak temperature and the periodicity of the sparking was shown to be a function of the properties of the brush material.

A theoretical model of the sparking phenomenon has been developed which shows good agreement with the sparking motion observed using the electrographitic brush.

### High Pressure Chemistry at Interfaces

Experimental studies of chemical reaction occurring between model lubricant additives and iron surfaces were performed at high pressures in a diamond-anvil-high-pressure cell. Both optical microscopy and Fourier Transform infrared spectroscopy were employed in studying the phenomena of interest. In these experiments one or both faces of the anvils were coated with a layer of sputtered iron thin enough to allow transmission of an infrared beam. The system lauric acid (dodecanoic) and dodecane was studied. Rates of reaction were studied at many different pressures and temperatures. It was found that rates of reaction of lauric acid in a dodecane solution increase dramatically at 100 C. Also, no measurable reaction occurs if the pressure is sufficiently high to maintain the solid phase. In the course of the work it was necessary to design and construct new apparatus for the accurate measurement of pressure by means of a fluorescence technique.

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THE OFFICE OF NAVAL RESEARCH  
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by

J. W. Brasch, E. Drauglis, R. J. Jakobsen, T. A. Dow,  
R. D. Stockwell, and J. W. Kannel

from

BATTELLE  
Columbus Laboratories

September 9, 1981

INTRODUCTION

In a previous report to the Office of Naval Research, several thermal and thermomechanical aspects of tribology pertinent to rolling/sliding contacts were described in some detail. In this final report there is presented an account of related work on surface chemical reactions occurring at high pressures. A model lubricant system - lauric acid in dodecane - in contact with a simulated bearing surface - thin films of vacuum-deposited iron - was employed in these studies. Fourier Transform

infrared spectroscopy was used to detect the formation of species arising from chemical reactions occurring between the acid molecules and the substrate. Details of the experimental technique and its application to the present program are found below.

#### BACKGROUND

#### CHEMICAL REACTIONS AT LIQUID-SOLID INTERFACES: METAL-CARBOXYLIC ACID SYSTEMS

#### Surface Chemistry and Boundary Films

It has been known for a long time that the addition of a small amount of fatty acid to a pure hydrocarbon solvent or a nonpolar mineral oil can cause considerable reduction in friction and wear in systems lubricated by such fluids. The discovery of this phenomenon stimulated many chemists and engineers to investigate the properties of fatty acids and their solutions in great detail. These early workers performed many studies of the effects on frictional properties of such factors as the molecular weight of the acid, concentration of the acid, composition of the substrate, surface preparation of the substrate, etc., as well as temperature and loading. From these studies it was concluded that the observed decrease in coefficient of friction was due to the formation of a monolayer of a tightly bound soap arising from the chemical reaction of the fatty acid with the substrate.

On the basis of the existence of such layers, Hardy was able to formulate a theory of boundary lubrication which has become generally accepted, although it is somewhat of an oversimplification. The essence of this theory is that friction between unlubricated surfaces is due to surface fields of force. If lubricant is present, polar molecules present in the lubricant are chemisorbed and form a monomolecular film. The polar groups are firmly bound to the metal surface and contact therefore takes place between the non-polar groups, usually methylene chains, at the other

end of the molecule. The efficiency of a given lubricant additive depends on the extent to which these films are able to mask the fields of force of the underlying surfaces.(2)

Bowden and Tabor improved Hardy's theory by considering the fact that lubricated machine elements are not perfectly smooth and because of this, contact between asperities must occur.(3) This modification of Hardy's theory results in better agreement between theory and experimental data on friction behavior. However, there still is difficulty in interpreting other experimental data such as electrical conductivity.

Adamson's pressurized film modification of the Bowden and Tabor theory seems to remove most of these difficulties.(4) It is now widely accepted that boundary lubrication can be completely accounted for by the presence of adsorbed monolayers. However, more recent data obtained in the USSR by Deryagin and later by G. I. Fuks as discussed in Reference(5) cast doubt on the concept that only monolayers are involved in boundary lubrication. These data seem to indicate that the region near a solid in contact with a liquid may have anomalous properties to a depth of many molecular layers. This concept, controversial from its first publication, has been widely attacked on many fronts. However, workers at Battelle Columbus Laboratories concluded after a careful analysis of the data that the results obtained by Fuks could be explained, at least qualitatively, on the basis of an ordered liquid model for thick films.(6) It also was concluded in the initial Battelle studies that much more experimental work on the structure and properties of boundary films is needed in order to test conclusively the concept that more than monolayers are involved in boundary lubrication. Aside from some electron diffraction and x-ray studies of dried soap films in vacuo there is almost no information available in the literature on the structure and properties of boundary films.

In several subsequent programs at Battelle, efforts were made to develop techniques for determining the degree of long-range ordering in boundary films under conditions in which they might be expected to form in

actual lubricated systems, that is, with the bulk fluid from which they are formed still in place. Success was achieved by using polarized attenuated total reflection infrared spectroscopy (ATR) performed by means of a Fourier transform infrared spectrometer.(7) In a later program, an even more powerful tool was developed for the study of chemical reactions at hydro carbon-metal interfaces. This is the use of Fourier transform infrared spectroscopy in combination with a diamond-anvil-high-pressure cell with metallized windows.(8) Both of these techniques, the ATR technique and the diamond cell technique, can provide much information on the interactions of fatty acids and metals that will provide new insights into the mechanisms of the formation and properties of boundary lubricating films.

In the following sections, a brief summary of past spectroscopic work and a detailed description of work performed to date in the metallized diamond cell are presented.

#### Spectroscopic Studies - Reflection Techniques

In most of the previous spectroscopic work that has been performed on carboxylic acids, attenuated total reflection methods have been used. This work can be roughly divided into two areas: (1) ATR studies of mono- or multi-molecular layered films prepared by a Langmuir-Blodgett technique, (2) studies of acid solutions using a liquid ATR cell. It was found that in the case of one layer Langmuir-Blodgett film (monomeric species with no hydrogen bonding) acid molecules would react with the metal surface (9) to form a metal salt or soap. However, the spectra of the multi-molecular layer acid films indicated carbonyl frequencies ( $1680-1710\text{ cm}^{-1}$ ) indicative of hydrogen bonded dimers and, in these cases, no reaction occurred between the acid and the metal surface.(10) Polarized infrared studies indicated some degree of molecular order in these multi-layered films.(6,9)

In solution studies using a liquid ATR cell, Yang (11) found that only physical adsorption (no chemisorption) of acids occurred at the metal surface and these physically adsorbed films had a random orientation. In general, workers at Battelle Columbus Laboratories agreed with Yang's observations, but in one case, small amounts of chemisorption (reaction to form a metal soap) was observed.(8,12) This reaction occurred only after extended contact between the metal and the acid solution. Some degree of molecular order was detected with the use of polarized infrared radiation. It is important to note that in this work some chemisorption occurred (about half of the available acid reacted to form a metal salt), but the acid carbonyl frequencies indicated only the presence of hydrogen bonded acid dimers (no monomers). Thus the reaction apparently proceeded from dimer to salt without a monomer intermediary. In addition, a chemisorbed multimolecular layer film was detected. Such multi-layered films have been reported by Tompkins (13) and have been observed by us (12) on several occasions. Also, in his work, Tompkins showed spectra of three different acid salts (different carboxylate stretching frequencies) each produced under different conditions. In our laboratory, we have observed several carboxylate frequencies (10, unpublished work) at the same time (i.e., in the same system).

#### Spectroscopic Studies - Diamond Anvil Cell

While there are several spectroscopic techniques for studying solid-air interfaces (which mainly yield information on the solid surfaces), there are few methods available for studies of solid-liquid interfaces. When the solid is a metal film the number of useful techniques becomes even smaller. Infrared spectroscopy combined with attenuated total reflection (ATR) techniques has been used (14) for such studies of liquid-metal interfaces, but availability of the metals has been restricted to those used in ATR crystals. We have demonstrated (7,12) that ATR can be extended to other metals by showing that spectra can be ob-

tained on metal-coated ATR crystals. By coating a thin film of iron onto a germanium ATR crystal, we were able to observe reactions at a liquid-metal interface. However, these ATR experiments are difficult to use for studies of the effects of variables such as temperature and pressure on the interface reactions. In addition, polarized ATR spectra of the adsorbed film yield only limited information on molecular order and film geometry, i.e., the angle the molecule makes with the metal film. Polarized transmission infrared spectroscopy would provide much needed supplemental information on molecular orientation.

By evaporating a thin (500-1000 Å) film of iron onto the diamond windows of a high pressure cell, we found that the surface reactions between a bulk liquid and a metal surface can be studied by transmission infrared spectroscopy. By using such a diamond-window high pressure cell, it also is possible to study the effects of temperature or pressure on these interface reactions. Thus, this technique, which allows direct experimental observation of the chemistry occurring at interfaces while such reactions are taking place, can provide important fundamental data applicable to many areas, i.e., lubrication, corrosion, and adhesion.

The miniaturized, diamond-anvil high pressure cell was obtained commercially (15) and has been described previously. (16,17,18) The working faces of the matched pair of diamonds are about 1 mm in diameter. However, when a gasket (platinum) is used to seal liquids between the diamond windows, the usable cell diameter approaches 0.3 mm. This small sample diameter coupled with the aperture angle and the relatively thick diamond windows means that infrared light throughput is severely curtailed. When 85 percent of this already limited radiation is lost as a result of putting a metal film on the diamond windows, an infrared throughput of 0.1 percent of the original source intensity is obtained. Thus, the instrumental sensitivity and the data-handling capabilities of Fourier Transform infrared systems are required.

### SUMMARY OF EXPERIMENTAL RESULTS

During the year's effort on this task, the experimental program yielded the following results:

- 1) Rates of reaction of lauric acid-dodecane solutions with iron surfaces increase dramatically at 100 C.
- 2) When an iron surface is cleaned by solvent wash after reacting with lauric acid, and then subjected to reaction with a fresh aliquot of lauric acid solution, the rates of reaction are much slower and the products are very different than in the first reaction.
- 3) Preliminary ESCA work indicates that the iron film on the diamond windows of the high pressure cell has a 50 Å layer comprised of ~60% FeO and ~40% Fe<sub>2</sub>O<sub>3</sub>.
- 4) No measurable reaction occurs if the pressure is sufficiently high to maintain the solid phase.

In addition, the experimental equipment has been upgraded to include:

- 5) Installation of a laser Raman spectrometer and modification of this system with microscope foreoptics to permit precise pressure measurements with the ruby fluorescence technique.
- 6) Construction of a combined beam condenser-microscope which allows continuous visual observation of samples in the diamond high pressure cell with a simple mirror flip to obtain infrared spectra of the samples.

### Details of Experimental Program

The experiments were conducted with samples contained in a diamond anvil high pressure cell with platinum gaskets to prevent lateral extrusion of the sample. Pressure bearing surfaces of the diamond windows were sputter coated with a film of iron prior to use. Replicate samples were used and data were obtained on 10% solutions of lauric acid in dodecane and on the two pure components. Temperature was controlled by the internal Nichrome heater of the diamond cell and monitored by a thermocouple in one of the stainless steel pistons of the cell. Infrared spectra were obtained with a Digilab FTS-14 Fourier Transform spectrometer system equipped with a Harrick 6X beam condenser and an MCT (mercury-cadmium-telluride) detector. Pressures were measured by the ruby fluorescence technique using a J-Y Ramanor 2000 M Raman system interfaced with a microscope for diamond cell work. The ruby fluorescence was excited by a Lexel 95 argon ion laser operating at ~200 mw at 5145 Å.

After loading the sample and microscopic chip of ruby, an infrared spectrum was taken at ambient temperature. Then the pressure was increased to the desired level (measured by the fluorescence method) and an infrared spectrum obtained at ambient temperature. Heating was begun, and spectra were obtained at frequent intervals.

After several series of experiments, it was obvious that no measurable reaction occurred at temperatures below 60 C or when the pressure was sufficient to maintain a solid phase of the sample. Between 60 C and 99 C and in the liquid phase, some reaction occurred as evidenced by decreasing acid carboxyl absorption (at  $1710\text{ cm}^{-1}$ ) and increasing carboxylate ion absorption ( $\sim 1550\text{ cm}^{-1}$ ), but it required many hours for a major part of the acid to react. Shortly after the temperature reached 100 C, however, reaction was complete in three or four minutes.

The spectra in Figure 1 are illustrative of the changes seen. A slight decrease in the acid carboxyl at  $1710\text{ cm}^{-1}$  is accompanied by a weak new band at  $1530\text{ cm}^{-1}$ . Further decrease in the  $1710\text{ cm}^{-1}$  band, however, is accompanied by a second new band at  $1555\text{ cm}^{-1}$ , with the first  $1530\text{ cm}^{-1}$  band remaining approximately constant. Intensity changes with time of these three bands are shown in Figure 2.

No special precautions were taken to have a "clean" iron surface on the diamond windows. Normally, the diamonds would stand for several days following depositing of the iron film so that the usual atmospheric oxidation would have occurred on the film surface. ESCA data on the film on a glass substrate (adjacent to the diamond anvil during the deposition) showed the top 50 Å of the film to be a mixture of FeO and  $\text{Fe}_2\text{O}_3$  in the ratio 4:3. It was decided to see if a second reaction would duplicate the first. Correspondingly, after completion of a reaction at 100 C (as judged by complete absence of acid carboxyl absorption at  $1710\text{ cm}^{-1}$ ) the cell was disassembled and the diamond windows washed with hexane and with water until no spectral absorption was seen. Then a second sample of the lauric acid-dodecane solution was loaded and reacted at 100 C. Reaction did occur (Fig. 3) but at a much slower rate, no 1530 component was seen and the major absorption was at 1550.

#### Discussion

The above experimental observations are significant and exciting. We cannot offer an explanation at this time for the dramatic increase in reaction rate at exactly 100 C in this system. This experimental fact, however, probably holds the key to the mechanism of the reaction and the structures involved. We have found no experimental evidence that the acid monomer is involved in the reaction but neither can we prove with the present data that the active species is the free end group of a polymeric chain of hydrogen bonded acids. Narrowing the search to the 100 C

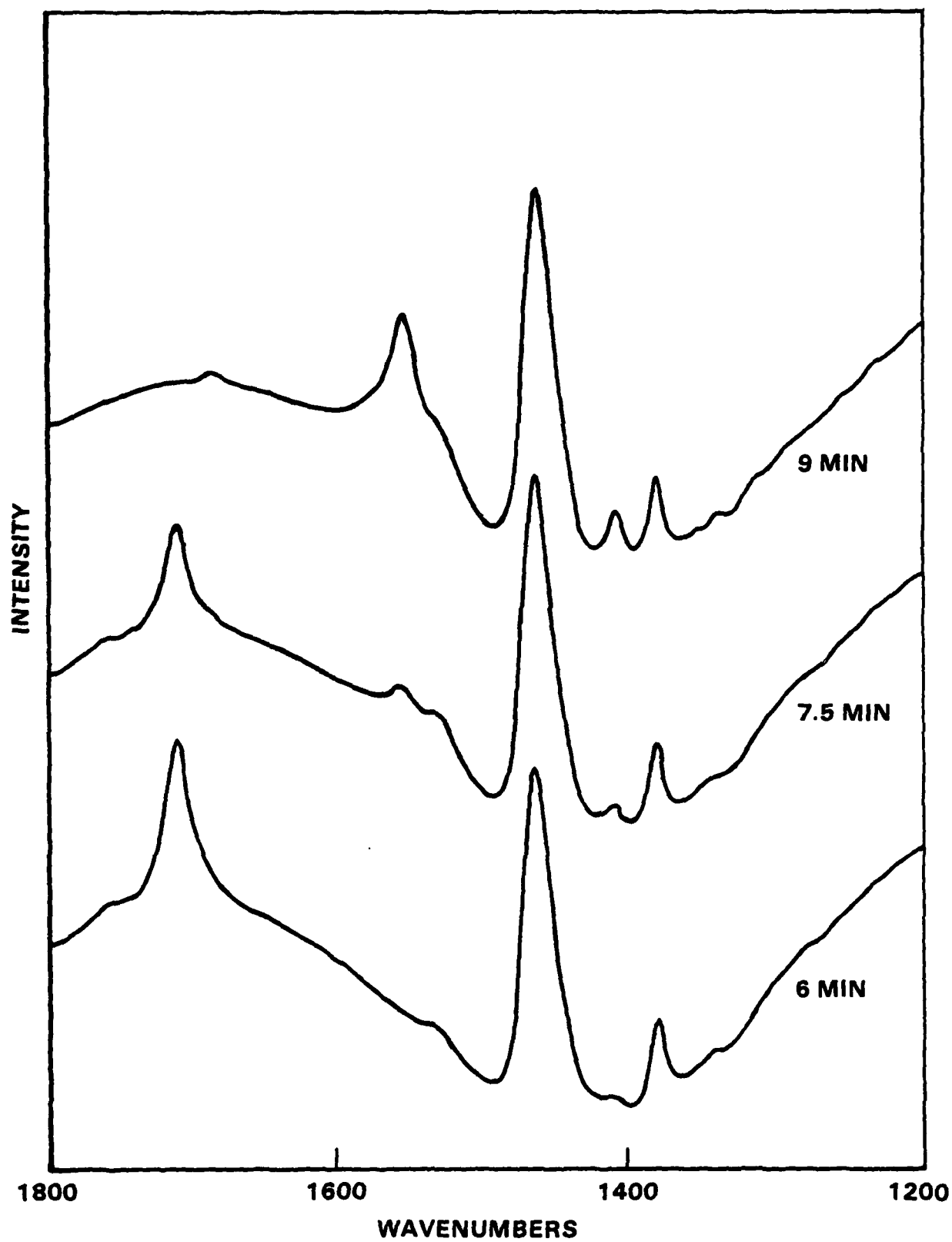


FIGURE 1. INITIAL KINETICS OF THE LAURIC ACID-IRON REACTION AT 100°C

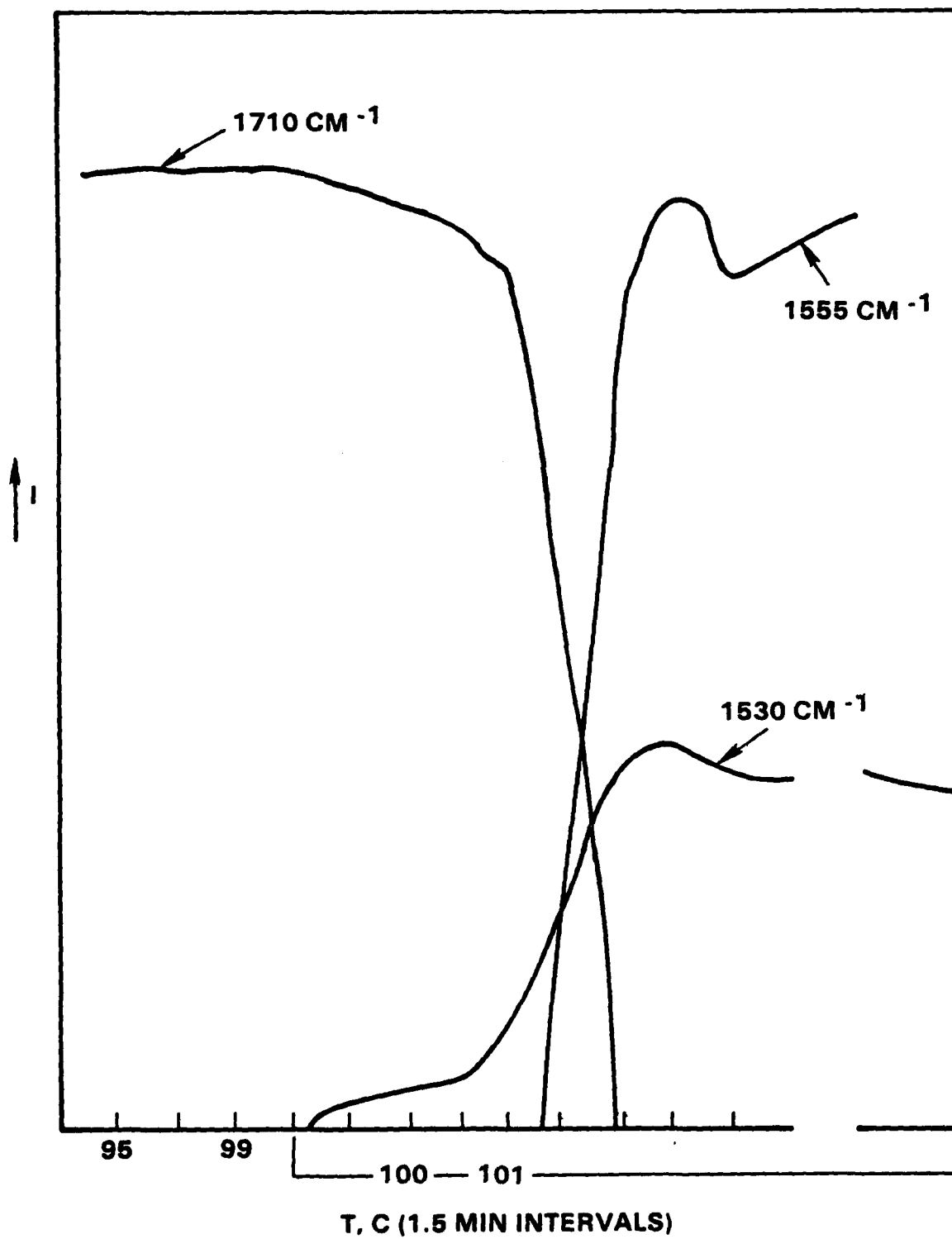


FIGURE 2. TEMPERATURE DEPENDENCE OF THE IRON-LAURIC ACID REACTION

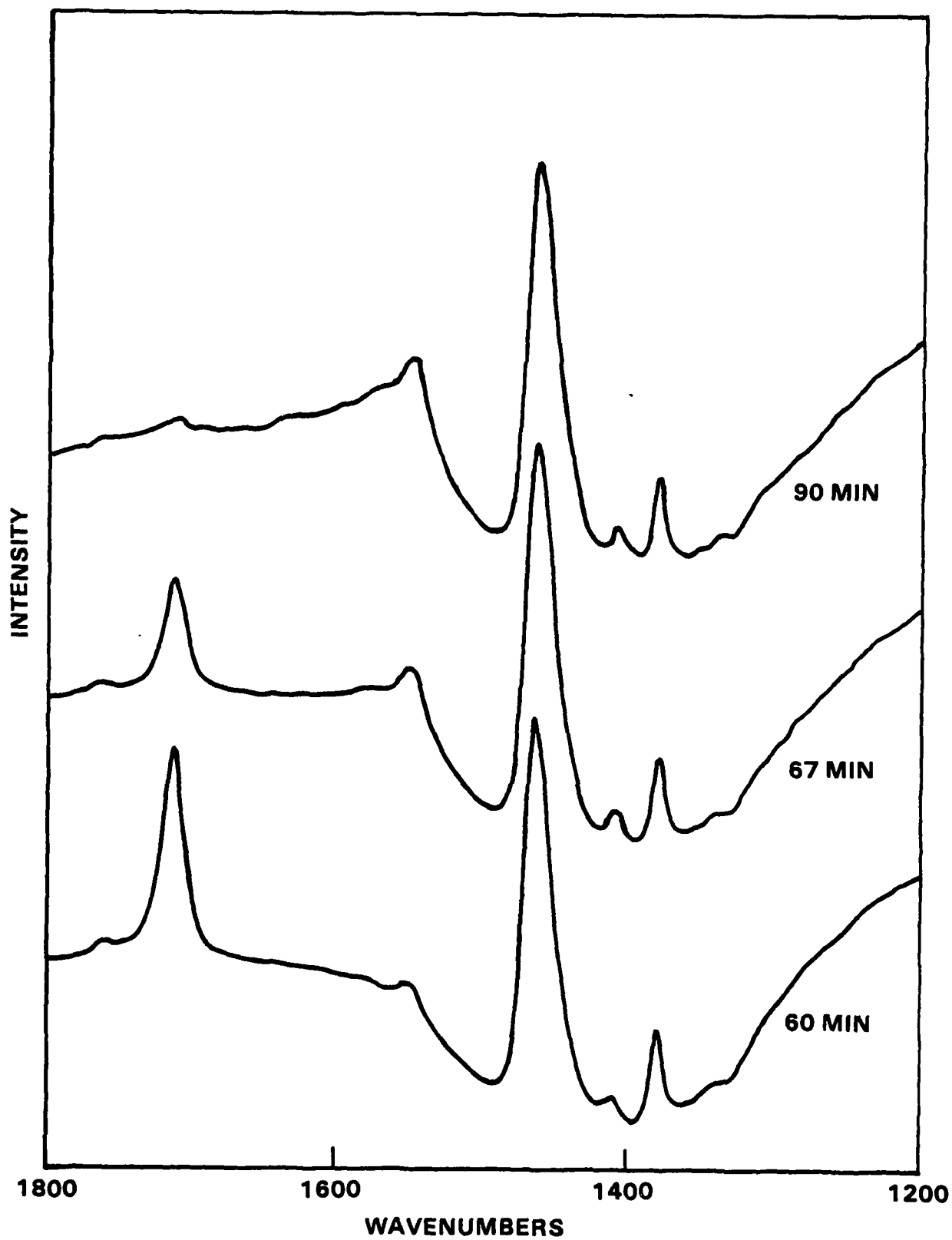


FIGURE 3. KINETICS OF THE LAURIC ACID-IRON REACTION AT 100°C AT LATER TIMES

temperature region greatly enhances the possibility of answering that question.

It is not surprising that an oxide surface would react differently than a pure metal surface. Our experimental observation of differences in the simple experiments described, however, suggest a series of experiments which may allow us to elucidate the very confusing literature reports on different carboxylate frequencies on metal surfaces.

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