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Effect of Oxygen, Methyl Mercaptan,  
and Methyl Chloride on Friction  
Behavior of Copper-Iron Contacts

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Donald H. Buckley  
*Lewis Research Center*  
*Cleveland, Ohio*



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## SUMMARY

An investigation was conducted to determine the friction behavior of a copper-iron couple in rider-on-disk friction experiments. A copper rider was made to slide on an iron disk, and an iron rider on a copper disk. The iron and copper disks were sputter cleaned; exposed to oxygen, methyl mercaptan, and methyl chloride to surface saturation at atmospheric pressure; and then run in friction experiments in vacuum. The load was 100 grams and the sliding velocity was 60 millimeters per minute at 25<sup>o</sup> C. Auger emission spectroscopy was used to monitor the surface chemistry in the wear track.

The friction coefficient was lower for a copper rider sliding on an iron disk than for an iron rider sliding on a copper disk with any of the surface films. For both iron and copper disks, methyl mercaptan gave the best surface coverage and was the most effective in reducing friction. For both iron and copper disks, methyl chloride was the least effective in reducing friction. With sliding, copper transferred to iron and iron to copper.

## INTRODUCTION

In many practical lubrication systems, dissimilar metals used as alloys are in solid-state contact. When these surfaces interact with the environment or a lubricant, the qualitative and quantitative nature of the surface films formed will depend on the chemistry of the metals involved.

Iron- and copper-base alloys are two of the most widely used materials in lubrication system components. Since iron and copper are the principal metals interacting in these alloys with the environment and lubricants, their reaction characteristics - both kinetic and thermodynamic - are of interest. Generally, copper-base bearing alloys contact steel shafts, and therefore the metal couple of iron in sliding contact with copper is of direct interest.

Earlier studies have indicated that a monolayer of an adsorbate such as an oxygen- or sulfur-containing species is sufficient to markedly affect friction (refs. 1 to 3). The behavior of surfaces saturated with adsorbed films needs elucidation.

This investigation was conducted to examine copper in sliding contact with iron in a rider-on-disk specimen configuration where a copper rider slid on an iron disk and an iron rider slid on a copper disk. Both configurations were examined in the presence

of three different surface films formed by exposure to oxygen ( $O_2$ ), methyl mercaptan ( $CH_3SH$ ), and methyl chloride ( $CH_3Cl$ ). Sliding friction experiments were conducted in a vacuum system with cylindrical-mirror Auger analysis (CMA) being used to monitor the surface chemistry. A sample scanning positioner allowed for chemical analysis directly in the wear tracks on the iron and copper disks. Friction experiments were conducted at a sliding velocity of 60 millimeters per minute with a load on the rider of 100 grams for a total of 250 repeated passes over the same surface. The disk surfaces were sputter cleaned before the surface-film-forming materials were applied.

## MATERIALS

Only two sets of experimental specimens were used for this investigation: a copper rider and an iron disk, and an iron rider and a copper disk. They were refinished between experiments so that the mechanical properties would be constant from experiment to experiment. The iron specimens were 99.99 percent pure, and the copper specimens were 99.999 percent pure. The oxygen used was 99.995 percent pure (minimum), and both the methyl mercaptan and the methyl chloride were 99.5 percent pure.

## EXPERIMENTAL APPARATUS AND PROCEDURE

The experiments were conducted in a vacuum chamber (fig. 1). The vacuum system was pumped by sorption pumps and an ion pump. Pressure in the vacuum system was read with an ion gage.

### Specimens

The friction-and-wear specimens were a disk specimen 6.5 centimeters in diameter and 1.2 centimeters thick and a hemispherical rider 2.5 centimeters in radius. The specimens are shown in the apparatus schematic in figure 1. The disk specimen was mounted on a drive shaft that was rotated by means of a magnetic drive assembly. The drive assembly provides for rotation at various speeds (in this study, 60 mm/min). For sputter cleaning the rider specimen was mounted in an insulated holder on one end of a stainless-steel shaft. Friction-and-wear experiments were conducted with the rider specimen loaded against the disk surface. As the disk was rotated, the rider scribed a circular wear track on the flat surface of the disk. The load used in this investigation was 100 grams, and the temperature was 25° C.

## Measurements

The friction force between the disk and rider specimens was continuously recorded during the experiment. The beam containing the rider specimen was welded in a bellows assembly that was gimbal mounted to the vacuum system. The gimbal mounting permits deadweight loading of the rider against the disk surface (fig. 1). At right angles to the deadweight loading, the beam containing the rider can move in two directions in the horizontal plane. Movement of the rider (with the disk as it rotates) was restrained by a cable attached to a temperature-compensated strain gage. These gages measured the frictional force between the disk and rider specimens. The frictional force was recorded on a strip chart.

## Specimen Preparation and Cleaning

The disk specimens were finish ground on metallurgical papers to a grit of 600. They were then diamond polished with 3-micrometer, and finally 1-micrometer, aluminum oxide. The disks were rinsed with acetone and then with absolute ethyl alcohol.

The rider specimens were acid cleaned with aqua regia before use to remove metal and other contaminants that might have become embedded in the surface from finishing. They were then scrubbed with levigated alumina, rinsed in water, and finally rinsed in ethyl alcohol.

## Auger Analysis

Elemental analysis of the disk specimen surface could be made before, during, and after the friction-and-wear experiments by using an Auger cylindrical-mirror analyzer with an integral electron gun. The point of rider-to-disk contact passed under the Auger beam just after that point moved out of the contact zone. The Auger analyzer is a commercial unit, the essential elements of which are described in the literature (ref. 4).

The primary beam of electrons was directed at the disk surface by an electron gun in the Auger cylindrical-mirror analyzer. The beam was focused on the wear track scribed by the rider in sliding contact with the disk. The beam contact was  $180^\circ$  away from the rider on the disk surface. The beam spot diameter was 0.2 millimeter. The gun contains deflection plates that allow positioning of the beam on the disk surface.

The secondary electrons came off the specimen surface, passed through the outer cylindrical can opening, then passed through slits in an inner cylinder that serves as an energy analyzer, and were collected by the electron multiplier. The elements were

identified by analyzing the detected secondary-electron energies. The Auger electrons that appeared in the secondary-electron distribution chemically identified the surface elements to a depth of approximately four atomic layers.

Auger traces were plotted on an x-y recorder. In this investigation, surfaces were examined before, during, and after sliding.

A sample scanning positioner was incorporated into the Auger spectrometer. With this positioner the wear track could be magnified and visually displayed on a television monitor, and the beam of the electron gun could be positioned directly into the wear contact zone desired. Each data point acquired for Auger peak height ratios was based on three measurements in different regions of the wear track.

A typical Auger spectrum for a copper rider sliding against an iron disk with an adsorbed oxygen film is presented in figure 2. The spectrum was obtained in the wear track after 250 passes of the copper rider over the surface. Auger peaks from the iron disk, the adsorbed oxygen, and the transferred copper are present in the spectrum.

The experimental procedure used in this study may be summarized in the following steps: (1) specimen preparation, (2) installation into the vacuum system and evacuation, (3) CMA characterization of the surface, (4) sputter cleaning of the specimens, (5) identification of surface cleanliness with CMA, (6) gas adsorption, (7) reevacuation to determine presence of adsorbed gas with CMA, (8) sliding for 25 passes in vacuum while continuously measuring friction, and (9) making CMA measurements within the wear track.

## RESULTS AND DISCUSSION

### Oxygen

Iron and copper disks were argon ion sputter cleaned in vacuum, and CMA analysis was used to determine the state of surface cleanliness. When all peaks except those of the metal were absent from the spectrum, the vacuum system was backfilled with oxygen to atmospheric pressure and held there for 20 minutes to saturate the clean disk surface with oxygen. The system was then reevacuated and an Auger trace was taken. The Auger spectra of both iron and copper contained oxygen peaks. A minor carbon contamination peak was also detected for both metals.

Results of sliding friction experiments with the oxygen-covered surfaces are presented in figures 3 and 4. The friction coefficient (fig. 3) was relatively unchanged for each of the disks with repeated passes. However, friction coefficient with the iron disk was markedly different from that with the copper disk: The friction coefficient with the iron disk was one-half that with the copper disk.

The relative Auger peak height ratios for oxygen to copper and oxygen to iron as a function of the number of repeated passes over the surface are presented in figure 4. For equivalent exposures the iron surface contained more oxygen. With repeated passes on both surfaces - to 50 passes for copper and to 100 passes for iron - the surface concentration of oxygen decreased. But no further reduction in the concentration of surface oxygen was observed with additional passes. Even after 250 passes, oxygen was still present in the wear track on both disk surfaces. However, there still was more oxygen on the iron than on the copper. Repeated analyses at three locations on each of the disk surfaces produced the same results.

The friction coefficients of figure 3 do not suggest that friction was sensitive to the reductions in surface oxygen concentrations detected in figure 4. The friction force measured reflects not only the effects of the surface oxygen, but also the forces required to shear in the metal. Copper was detected on the iron disk surface with just a few (6) passes of the copper rider. The spectrum of figure 2 shows that copper transferred to the iron surface. As discussed in this section with reference to oxygen adsorption, the surface concentration of transferred copper was detected after just 6 passes, with no increase in concentration observed to 250 passes.

In simple adhesion experiments with two dissimilar metals in contact, the cohesively weaker metal generally transfers to the cohesively stronger metal (ref. 5). Consistent with that concept, in reference 1 copper was found to transfer to iron. With sliding, however, sufficient interfacial energy can develop, as a result of frictional resistance, to generate interfacial and superficial alloying. Under such conditions, with dissimilar metals with differing cohesive energies in contact, transfer to both surfaces may occur.

The photomicrograph and X-ray map of figure 5 show that, with sliding, iron transferred from an iron disk to a copper rider. Thus, copper transferred to iron and iron to copper in the same experiment. This two-way transfer indicates metal-to-metal contact through the oxygen film. The friction force then is the sum of shearing in the film and shearing in the metal.

### Methyl Mercaptan

Sulfur-containing additives are frequently placed in oils to reduce wear and the propensity for seizure (ref. 6). The simplest hydrocarbon structure containing sulfur is methyl mercaptan. It is desirable to examine such a structure in friction experiments because in practical lubrication systems both carbon and sulfur are present in the lubricant and competitive activity with the surface can occur with these elements.

Sputter-cleaned iron and copper disk surfaces were exposed to methyl mercaptan

at atmospheric pressure for 20 minutes, just as had been done with oxygen. Sliding friction experiments were then conducted with a copper rider sliding on the iron disk and with an iron rider sliding on the copper disk. The friction results obtained are presented in figure 6, and Auger spectroscopy results are presented in figure 7.

The data of figure 6 show a marked difference in friction behavior with the reversal of metals in the rider-disk couple. The friction coefficients for the copper rider on the iron disk were lower than those for the iron rider on the copper disk, just as was observed with oxygen in figure 3. However, the friction coefficient for the iron rider on the copper disk was less with methyl mercaptan (fig. 6) than with oxygen (fig. 3). At less than 100 repeated passes the friction coefficient for the copper rider on the iron disk was also less with methyl mercaptan than with oxygen, but above 100 passes no difference was detected.

The data of figure 7 indicate a greater concentration of sulfur on the copper disk than on the iron disk. This represents a reversal from figure 4, where the oxygen concentration is greater on the iron disk than on the copper disk. Despite this reversal in adsorbate concentration on the iron and copper disk surfaces, the friction coefficient was consistently higher with the iron rider on the copper disk than with the copper rider on the iron disk. It took relatively few passes to appreciably reduce the sulfur concentration on both disk surfaces (fig. 7). This result is similar to that with oxygen (fig. 4).

Auger emission spectroscopy measurements of the sulfur-to-carbon peak height ratios show that the ratio on both disk surfaces before sliding was comparable - approximately 8.3. After 250 passes the sulfur-to-carbon ratios differed greatly: On the iron disk the ratio was 7.0, but on the copper disk it was 87.0 - indicating marked dissociation of the methyl mercaptan on the copper disk that was not observed on the iron disk.

### Methyl Chloride

Methyl chloride, like methyl mercaptan, has the methyl group; but chloride is substituted for sulfur as the wear- and friction-reducing additive. Methyl chloride was therefore examined in experiments analogous to those with methyl mercaptan so that a direct comparison of these two materials could be made.

Just as with oxygen and methyl mercaptan adsorption, the iron and copper disk surfaces were sputter cleaned and then exposed to methyl chloride at atmospheric pressure for 20 minutes. Friction coefficients and relative Auger peak height ratios of chlorine to the metals iron and copper are presented in figures 8 and 9.

The friction coefficients (fig. 8) were markedly greater for the iron rider sliding



on the copper disk than for the copper rider sliding on the iron disk. This result is analogous to that observed with oxygen and methyl mercaptan.

With methyl chloride, more chlorine was transferred to the iron disk than to the copper disk, as shown in the data of figure 9. The results in figure 9 are comparable to those for oxygen in figure 4. Just as with oxygen and methyl mercaptan, relatively few passes were required to appreciably reduce the chlorine concentration on both disk surfaces.

The chlorine-to-carbon peak height ratios were markedly different on the two disk surfaces: On the iron disk the ratio was 3.0 before sliding and 5.0 after 250 passes. On the copper disk it was 4.8 before sliding and 1.0 after 250 passes. These results suggest that dissociative adsorption of methyl chloride occurs initially with one or the other disk surface or with both. This initial dissociation was not noted with methyl mercaptan, where the initial ratio of sulfur to carbon was the same on both surfaces. In addition, both carbon and chlorine have strong affinities for iron, but carbon does not form any stable compounds with copper and chlorine does. This may account for the enrichment of the iron surface with chlorine after 250 passes. In contrast, on the copper surface the chlorine concentration relative to carbon decreased.

## COMPARISON OF RESULTS

The friction and Auger emission spectroscopy results of this investigation are summarized in figures 10 to 13. In figures 10 and 11 the results with the three species adsorbed on iron are compared, and in figures 12 and 13 the results with those same materials adsorbed on copper are compared. All three species reacted more strongly with iron than with copper (greater face energy of formation). Because the riders were in continuous contact but the disks were in intermittent contact, the films on the riders were displaced or worn away in a relatively short time. Therefore, it is the films formed on the disks that are of concern.

The mechanical properties of the elemental metals differ somewhat, but both metals are relatively soft and therefore deform relatively easily. The differences in behavior for the iron rider on the copper disk and the copper rider on the iron disk therefore cannot be related to differences in mechanical behavior. The most plausible explanation for the differences in friction behavior when the components of the material couple were reversed lies in the tenacity of the films adsorbed on the metal disk surfaces and the resulting stability of the bonds formed. The films are more stable and more resistant to dissociation, displacement, and wear on the iron disk surface than on the copper disk surface.

Figure 10 shows that both adsorbed oxygen and methyl mercaptan afforded better

surface protection on iron than methyl chloride. The Auger spectroscopy data of figure 11 indicate a greater ratio of sulfur to iron throughout the experiment than of chlorine to iron or oxygen to iron.

Figure 12 shows that methyl mercaptan afforded the best surface protection on copper. However, the friction coefficients were all higher than in figure 10, indicating that with the same pair of materials which of the materials is in continuous contact and which is in intermittent contact affects friction behavior. In these studies, friction was lower when the disk was iron and the rider was copper.

The Auger spectroscopy data of figure 13 are in the same relative order as those in figure 11. There appears, however, to be a greater disparity between the ratio of sulfur to copper and the ratios of oxygen and chlorine to copper than was observed with iron in figure 11.

Copper transferred to the iron disk surface in all experiments. Transfer occurred rapidly with essentially no increase in surface copper concentration with repeated passes beyond 25, as indicated in the data of figure 14. Analogous behavior was observed with all three film materials.

## CONCLUSIONS

Based on the friction and Auger emission spectroscopy experiments conducted in this investigation with copper in sliding contact with iron saturated with oxygen, methyl mercaptan, or methyl chloride the following conclusions were drawn:

1. Friction was lower for a copper rider sliding on an iron disk than it was for an iron rider sliding on a copper disk.
2. On a copper disk, methyl mercaptan was the most effective in reducing friction and methyl chloride was the least effective. On an iron disk, methyl mercaptan and oxygen were nearly equally effective in reducing friction and again methyl chloride was the least effective.
3. On both iron and copper disks, methyl mercaptan gave the best surface coverage and oxygen the worst.
4. At the low speeds and light loads used, copper transferred to iron and iron to copper.
5. Because methyl mercaptan and methyl chloride adsorbed on both iron and copper, Auger spectroscopy detected carbon and either sulfur or chlorine on the surfaces.

Lewis Research Center,

National Aeronautics and Space Administration,

Cleveland, Ohio, June 16, 1978,

506-16.

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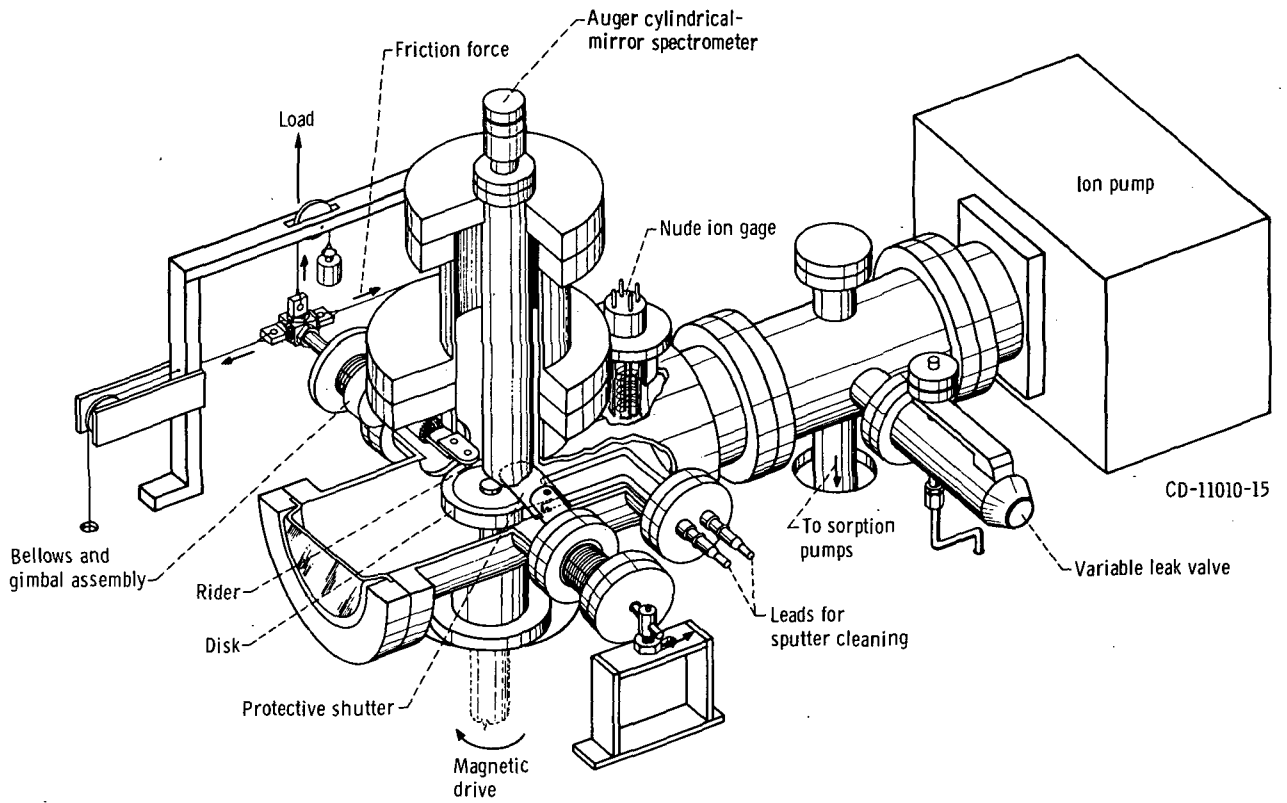


Figure 1. - Friction apparatus with Auger spectrometer.

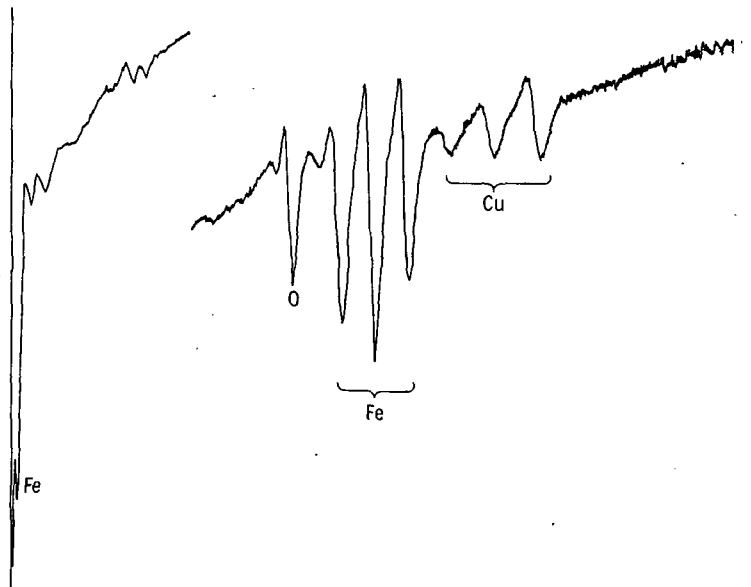


Figure 2. - Auger spectrum for iron disk surface in presence of adsorbed oxygen after 250 passes of a copper rider.

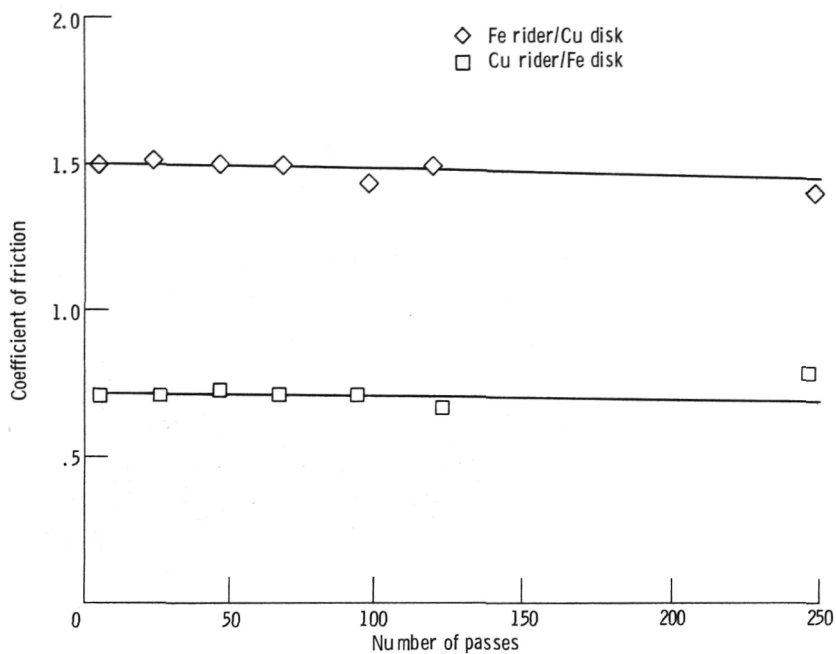


Figure 3. - Coefficient of friction as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed oxygen. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

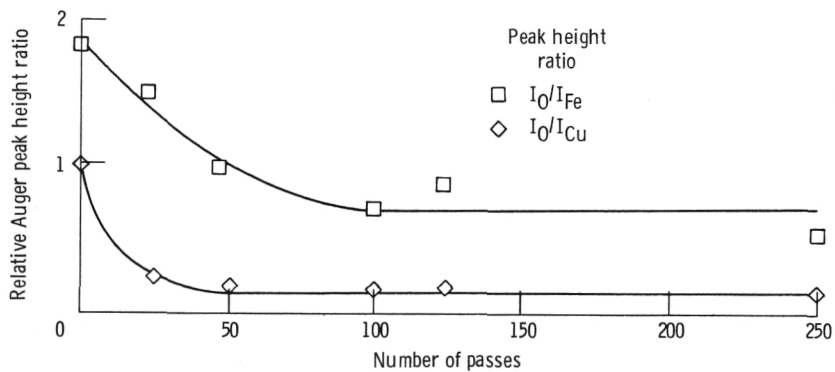
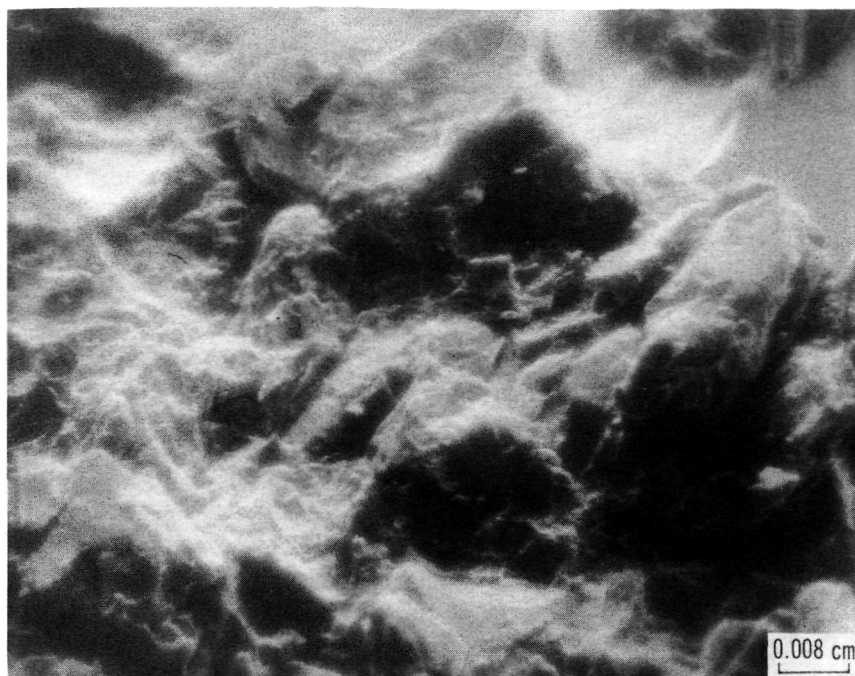
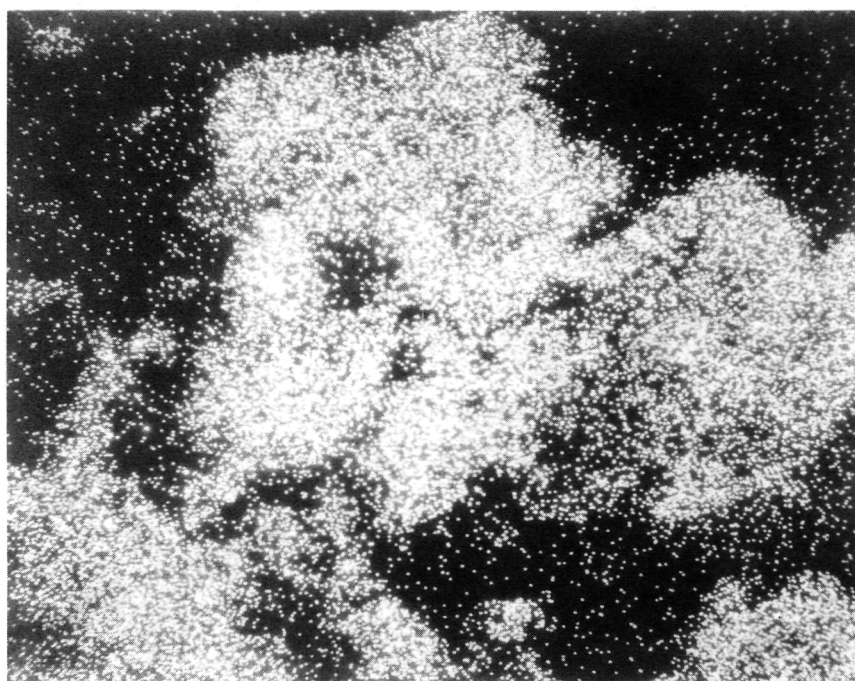


Figure 4. - Relative Auger peak height ratios of oxygen as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed oxygen. Sliding velocity, 60 min/min; load, 100 g; temperature, 25° C.



(a) Photomicrograph.



(b) Iron  $K_{\alpha}$  X-ray map (40 000 counts).

Figure 5. - Scanning electron micrograph and X-ray map of iron transfer from iron disk to copper rider in presence of absorbed oxygen.

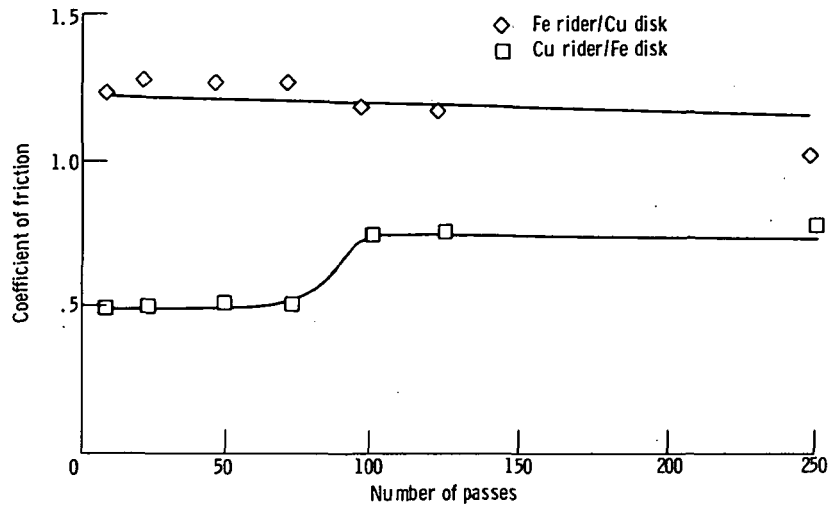


Figure 6. - Coefficient of friction as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed methyl mercaptan. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25<sup>o</sup> C.

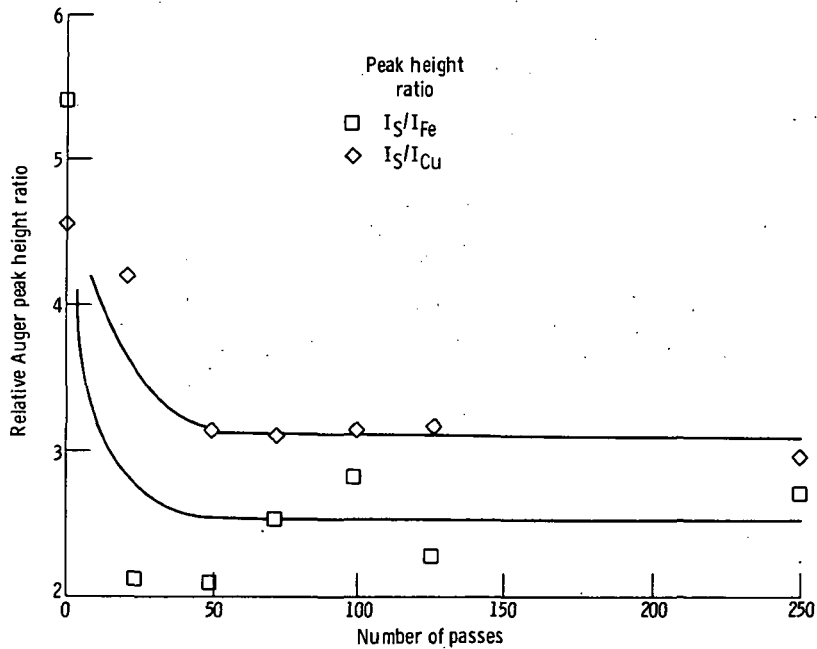


Figure 7. - Relative Auger peak height ratios of sulfur as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed methyl mercaptan. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25<sup>o</sup> C.

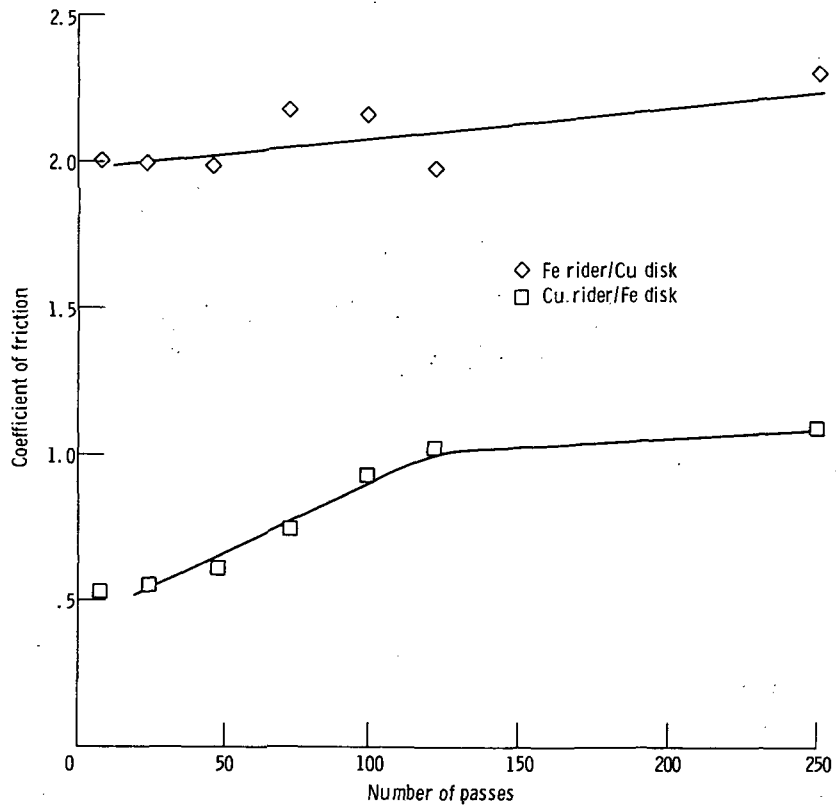


Figure 8. - Coefficient of friction as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed methyl chloride. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.



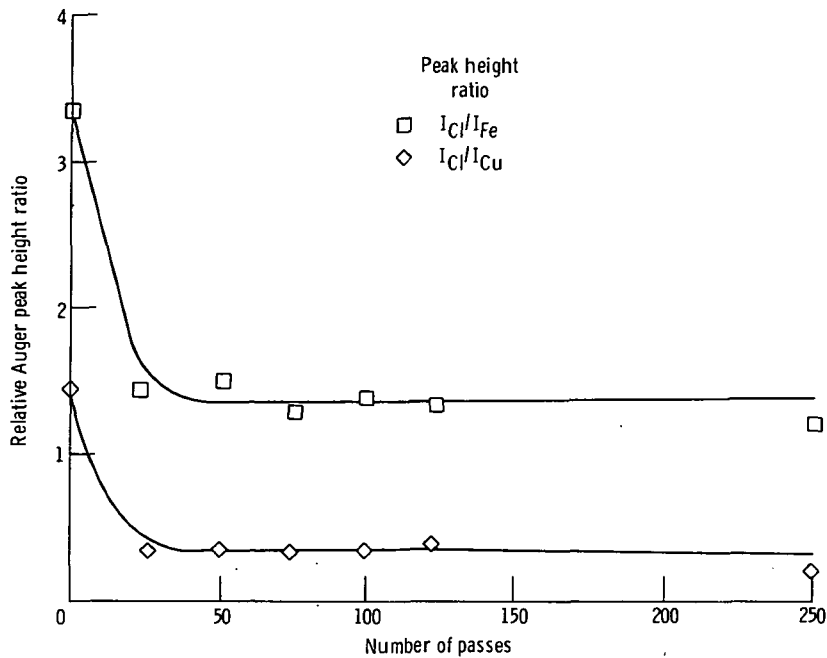


Figure 9. - Relative Auger peak height ratios of chlorine as function of number of repeated passes for iron-copper rider-disk couples with disk surfaces sputter cleaned and saturated with adsorbed methyl chloride. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

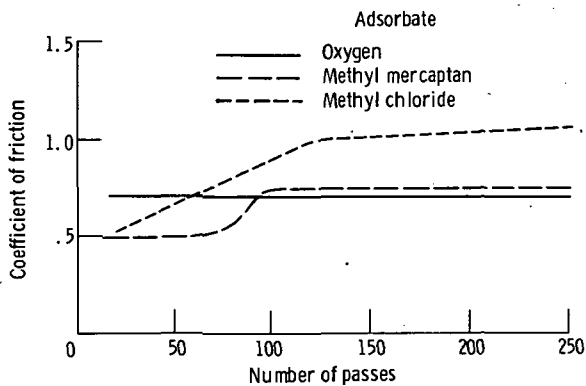


Figure 10. - Coefficients of friction as function of number of repeated passes of copper rider with three adsorbates on sputter-cleaned iron disk surface. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

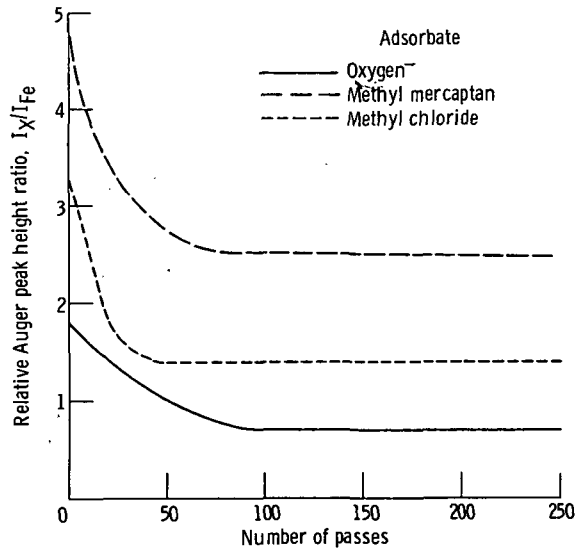


Figure 11. - Relative Auger peak height ratios of sulfur, chlorine, and oxygen to iron from an iron disk as function of number of repeated passes. (Sulfur peak arises from adsorption of methyl mercaptan, chlorine from adsorption of methyl chloride, and oxygen from itself.) Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

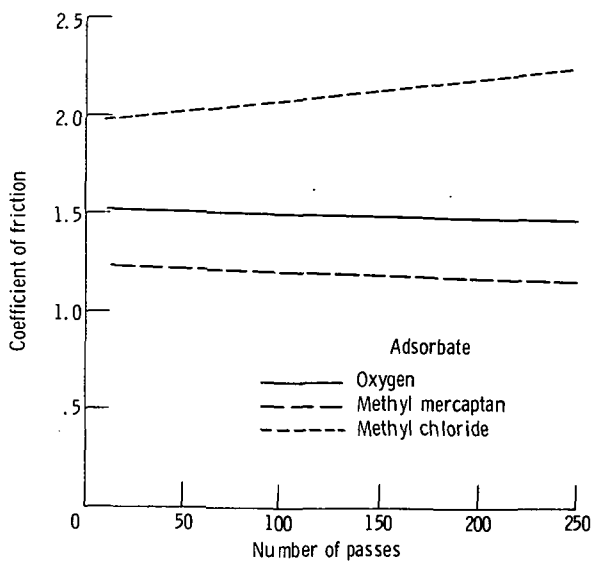


Figure 12. - Coefficient of friction as function of number of repeated passes of iron rider with three adsorbates on sputter-cleaned copper disk surface. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

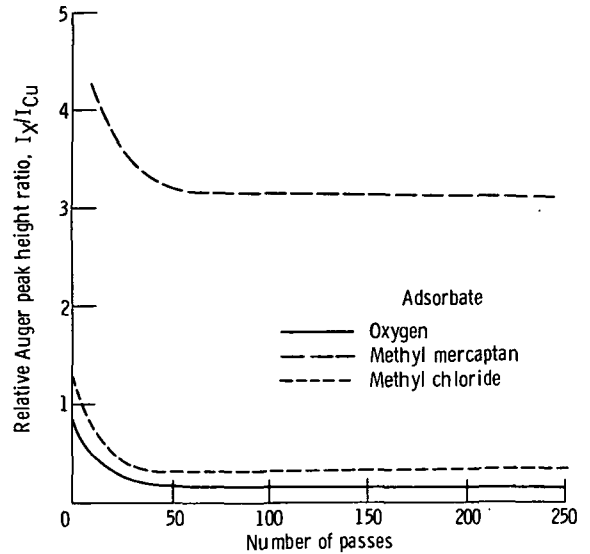


Figure 13. - Relative peak height ratios of sulfur, chlorine, and oxygen to copper from a copper disk as function of number of repeated passes. (Sulfur peak arises from adsorption of methyl mercaptan, chlorine from adsorption of methyl chloride, and oxygen from itself.) Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

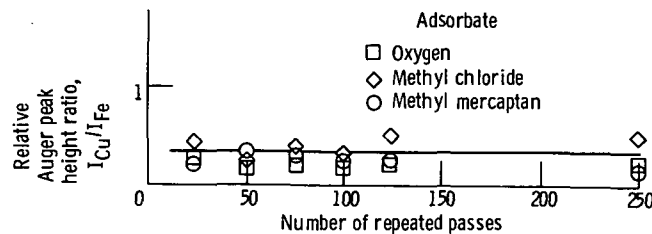


Figure 14. - Relative Auger peak height ratios of copper to iron as function of number of repeated passes of copper rider with three adsorbates on sputter-cleaned iron disk. Sliding velocity, 60 mm/min; load, 100 g; temperature, 25° C.

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16. Abstract Sliding friction experiments were conducted with an iron rider on a copper disk and a copper rider on an iron disk. The sputter-cleaned iron and copper disk surfaces were saturated with oxygen, methyl mercaptan, and methyl chloride at atmospheric pressure. Auger emission spectroscopy was used to monitor the surfaces. Lower friction was obtained in all experiments with the copper rider sliding on the iron disk than when the couple was reversed. For both iron and copper disks, methyl mercaptan gave the best surface coverage and was most effective in reducing friction. For both iron and copper disks, methyl chloride was the least effective in reducing friction. With sliding, copper transferred to iron and iron to copper.			
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