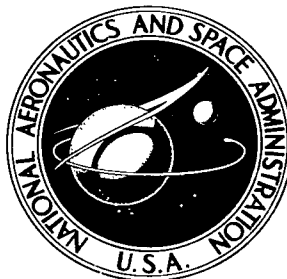
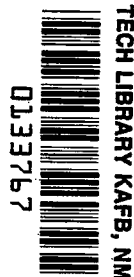


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**FRICTION OF IRON LUBRICATED WITH
ALIPHATIC AND AROMATIC HYDROCARBONS
AND HALOGENATED ANALOGS**

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16. Abstract An investigation was conducted to determine the influence of oxygen and various organic molecules on the reduction of the friction of an iron (011) single crystal surface. A comparison was made between aliphatic and aromatic structures, all of which contained six carbon atoms, and among various halogen atoms. Results of the investigation indicate that hexane and benzene give similar friction coefficients over a range of loads except at very light loads. At light loads, the friction decreased with an increase in the load where the halogens fluorine and chlorine are incorporated into the benzene molecular structure; however, over the same load range when bromine and iodine were present, the friction was relatively unchanged. The aliphatic compound chlorohexane exhibited lower friction coefficients than the aromatic structure chlorobenzene at very light loads. With the brominated benzene structures, however, friction was essentially the same. Oxygen was more effective in reducing friction than were the simple hydrocarbons.			
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FRICITION OF IRON LUBRICATED WITH ALIPHATIC AND AROMATIC HYDROCARBONS AND HALOGENATED ANALOGS

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SUMMARY

An investigation was conducted to determine the influence of oxygen and various organic molecules on the reduction of the friction of an iron (011) single crystal surface. A comparison was made between aliphatic and aromatic structures, all of which contained six carbon atoms, and among various halogen atoms. An Auger emission spectroscopy analysis was used to monitor the surface species present on the iron after adsorption. Friction experiments were conducted with a gold single crystal (111) pin sliding on the iron at loads of 1 to 30 grams and at a sliding velocity of 0.7 millimeter per minute.

Except for very light loads, the test results indicate that hexane and benzene give essentially the same friction results when lubricating iron. With the addition of halogens to the benzene structure, the friction decreases with an increase in the load for fluorobenzene and chlorobenzene. Chlorohexane exhibited lower friction coefficients at light loads than did chlorobenzene. With the brominated structures, however, friction was essentially the same. Oxygen was more effective in reducing friction than was either hexane or benzene, and oxygen from the air will displace hexane or benzene from an iron surface.

INTRODUCTION

Hydrocarbons are the most widely used materials in lubrication systems. Generally the lubricating oils are principally aliphatic in nature but contain some aromatic structures (refs. 1 to 3). Very little experimental work has been done to establish the relative differences in the lubricating characteristics of aliphatic and aromatic hydrocarbons fundamentally. Aromatic structures, such as the polyphenyl ethers, have be-

come increasingly important in recent years for lubricating advanced aircraft engine components because of their superior thermal stability to aliphatic structures.

The objective of this investigation was to compare the ability of analogous aliphatic and aromatic structures (same number of carbon atoms) in the reduction of the friction of iron metal. The lubricants were bled into a vacuum system and allowed to interact with a sputter cleaned iron (011) single crystal surface. Auger emission spectroscopy was used to monitor the presence of surface films. Sliding friction experiments were conducted with a gold hemispherical pin (single crystal) contacting the iron under loads of 1 to 30 grams. Gold was selected as a sliding material because of its relative chemical inactivity to the adsorbates examined, thus eliminating an experimental variable. A single crystal of iron was used to simplify surface characterization. The sliding velocity was 0.7 millimeter per minute, and all experiments were conducted in a vacuum of 1.33×10^{-8} newton per square meter (10^{-10} torr) at 23° C.

APPARATUS

The vacuum system used in this investigation contained the necessary components for measuring adhesion, load, and friction and was capable of Auger and LEED surface analyses. The mechanism for measuring adhesion, loading, and friction is shown schematically in figure 1.

A gimbal mounted rod projects into the vacuum system. The beam contains two flats machined normal to each other with strain gages mounted thereon. The end of the rod contains the gold single crystal pin specimen. The load applied by moving the rod toward the disk was measured by the appropriate strain gage. The adhesion force (i. e., the force necessary to separate the pin and disk after being loaded together) can be measured in the direction opposite to that of the load application by the same strain gages.

Tangential motion of the pin along the disk surface is accomplished through the gimbal assembly. Under an applied load the friction force is sensed by the strain gage normal to that used to measure load.

Multiple wear tracks could be generated on the disk specimen surface by the translational motion of the disk or pin. Pin sliding was in the vertical direction of figure 1.

The vacuum apparatus of figure 1 contained an Auger spectrometer. The electron beam for analysis could be focused on any disk site desired. This was accomplished with a disk manipulation device.

The vacuum system was a conventional vacsorb and ion pumped system capable of readily achieving pressures of 1.33×10^{-8} newton per square meter (10^{-10} torr) as measured by a nude ionization gage within the specimen chamber. Sublimation pumping

was also used for more rapid achievement of the ultimate pressure desired.

EXPERIMENTAL PROCEDURE

The iron single crystal surfaces were mechanically polished on metallurgical papers down to 600 grit. The crystals were then electropolished in one part of perchloric acid in two parts glycerol. The surfaces were rinsed with water and 200 proof ethyl alcohol.

The iron and gold specimens were placed in the vacuum chamber and the system was evacuated. It was baked out overnight after which the pressure was in the 10^{-8} newton per square meter range.

Argon gas was bled into the vacuum system to a pressure of 10 micrometers. After a 1000-volt dc potential was applied to the specimen, it was sputter bombarded for 30 minutes. After sputtering, the surface was examined with Auger emission spectroscopy (AES) to establish the surface cleanliness. Where the surface was not clean the sputtering process was repeated. The gold pin was heated to 250° C to remove adsorbates, previous experiments having shown this to be sufficient (ref. 4). All friction experiments were conducted with the system reevacuated to a pressure of 10^{-8} newton per square meter.

The gold pin was loaded against the iron flat by mechanically deflecting the rod through a gimbal assembly with the gold pin in contact with the iron. When the proper load had been applied, sliding was initiated by moving the rod in a vertical direction parallel to the disk surface. The friction force was continuously recorded during sliding.

In those experiments where lubricants were employed, they were bled into the vacuum system after sputter cleaning. AES was used to monitor the elements present on the surface after the surface was exposed to the lubricating species. Table I presents the molecular structure of the species adsorbed.

RESULTS AND DISCUSSION

Clean Surfaces

The gold single crystal hemispherical pin was brought into contact with the iron surface under a 1-gram load. The coefficient of friction measured when sliding began was extremely high; complete seizure ultimately occurred. Examination of the

sliding wear track on the iron surface revealed the presence of transferred gold. The gold was detected with AES.

Hydrocarbons

A sputter cleaned iron surface was exposed to hexane. The hexane was admitted into the vacuum system when the pressure was at 10^{-8} newton per square meter. The pressure was allowed to rise to 10^{-1} newton per square meter with hexane, and the system was held at that pressure for 30 minutes. This was sufficient exposure to allow the least active of the adsorbates to saturate the surface with a chemisorbed layer. The system was then reevacuated to 10^{-8} newton per square meter.

An Auger spectrum for the iron surface obtained after evacuation of the hexane is presented in figure 2(a). Both carbon and iron peaks are detected in the Auger spectra. The presence of iron in the spectrum indicates less effective coverage of the iron surface by hexane than was observed with titanium in reference 4. Elements can be detected by AES to a depth of about four to five atomic layers.

The iron is not shielded in figure 2(a) by the carbon. Since multilayer adsorption of hexane is unlikely, the hexane chain can be bonded at one end to the iron surface and extend above it (as proposed by Godfrey) for the bonding of even larger molecules to metal surfaces (ref. 5). This was observed with titanium in reference 4. Alternately, the chains are laying flat on the surface since Auger peaks for iron would be anticipated in such a case.

Friction experiments were conducted on the surface represented in figure 2(a). This surface was sputter cleaned and then exposed to benzene under the same conditions used for hexane. The results obtained are presented in the Auger spectrum of figure 2(b). In figure 2(b) a large Auger peak for carbon is detected, and intense peaks for iron are observed. It would appear from the Auger spectrum that both hexane and benzene do not completely mask a iron surface. With titanium, however, complete masking of the metal by hexane was observed in reference 4.

Friction experiments conducted with the two different hydrocarbons yielded the results presented in figure 3. In figure 3 the friction coefficient is plotted as a function of load for the iron surface saturated with hexane and benzene. While some scatter exists in the data, the friction coefficient decreases with increasing load for both hydrocarbons to a load of about 10 grams; beyond 10 grams no change is noted. Despite the differences at light loads between hexane and benzene, the friction coefficients over the range of loads examined are comparable beyond 10 grams.

It might be concluded from the data of figure 2(b) that the benzene ring lies on the surface with a number of carbon atoms bonding directly to the iron. With the hexane

data of figure 2(a), however, it is uncertain whether the hexane chain stands above the surface with anchoring occurring by a single carbon atom as was observed with titanium (ref. 4) or if it is lying flat on the surface.

When a six carbon atom chain is compared with six carbon atoms in a ring or aromatic structure, the friction coefficient beyond a 10-gram load is independent of the structural configuration of the carbon atoms and the manner in which they bond to the surface. This is the same type of result observed with titanium (ref. 4).

Attempts were made to displace the hydrocarbons hexane and benzene from the iron surface. The surfaces were exposed to air for 30 minutes. The films were both displaced from the iron surface by oxygen as indicated in figure 4 for hexane. With titanium neither hexane nor benzene was displaced by oxygen (ref. 4).

Halogen Containing Hydrocarbons

Halogen atoms present in organic molecular structures are generally very effective in lubricating solids. Sliding friction experiments were conducted with halobenzene adsorbed on an iron surface in the same manner already described for hexane and benzene. The Auger spectrum presented in figure 5 indicates a nearly complete masking of the iron by fluorobenzene. The friction results obtained are presented in figure 6. The friction at a 1-gram load was lower than was observed with benzene in figure 3. Friction was lower with fluorobenzene at all loads indicating that the presence of fluorine in the benzene structure improves friction behavior.

Chlorobenzene was adsorbed on a clean iron surface, and sliding friction experiments were conducted on this surface. An AES trace of the surface containing the chlorobenzene is presented in figure 7(a). It is of interest to note in figure 7(a) the presence of the chlorine peak, which is the largest peak in the spectrum. It appears from the iron peaks as if chlorobenzene more effectively covers iron than was observed with benzene.

Friction coefficients obtained with chlorobenzene are presented in figure 6. At loads less than 10 grams the friction coefficient decreased with an increase in load. Above 10 grams, load friction coefficients were not greatly different.

Similar experiments to those conducted with the chlorine substituted benzene were conducted with brominated benzene. Bromine was present on the surface as well as carbon. Friction data for bromobenzene are presented in figure 6. Friction was, in general, lower than was observed with the fluorinated and chlorinated structures at loads of 10 grams or less. Above 10 grams, the friction coefficients were comparable for all three halogenated structures.

The iron surface was next exposed to the last of the halogens. Iodobenzene was

bled into the vacuum system with the exposure of the iron being the same as for the benzene, chlorobenzene, and bromobenzene.

The Auger emission spectrum for the iron surface with iodobenzene is presented in figure 7(b). The only Auger peak detected is a very large carbon peak. Neither iodine nor iron peaks are present. The iron is completely masked. The absence of iodine does not of necessity indicate dissociative adsorption. The iodine is much more weakly bonded than is the chlorine or bromine and thus may be subject to electron beam induced desorption in the process of the AES analysis (ref. 6). These results are very analogous to those observed with the adsorption of iodobenzene on titanium.

The friction coefficients obtained with the iodobenzene are presented in figure 6 with the friction coefficients of the other halogenated benzene structures. At the light loads, the friction was less than was observed with fluorobenzene and chlorobenzene and comparable to that obtained with bromobenzene.

The effect of the halogen atom in benzene on friction for iron can readily be seen in the data of figure 6. At the light load of 1 gram, the friction coefficient decreases with an increase in load for the fluorobenzene and chlorobenzene. When the load is increased to 10 grams, the friction is relatively comparable for all four halogenated structures and the nature of halogen is seen to have little effect.

With the adsorption of the structures chlorobenzene and bromobenzene to the iron surface, both of the halogens chlorine and bromine were observed in the AES analysis of the surfaces. Neither fluorine nor iodine was observed with the adsorption of fluorobenzene and iodobenzene.

It is of interest to note that a much larger concentration of carbon is present on the iron surface with the adsorption of iodobenzene than is observed with the adsorption of benzene. The difference is readily discernable when comparing the AES spectra of figures 2(b) and 7(b); these spectra were obtained under the same conditions. This condition may result because with dissociation of the iodobenzene on the iron surface the resultant molecular fragments are chemically more reactive than the fully saturated benzene structure.

The aliphatic structures chlorohexane and bromohexane were adsorbed to saturation on a clean iron surface. The AES spectrum for chlorohexane is presented in figure 8(a) and for bromobenzene in figure 8(b). In figure 8(a) only a carbon peak is detected. There is a complete absence of any iron or chlorine. Chlorine could be exposed with either heating or mild ion bombardment of the surface with argon. Since AES analyzes to a depth of about four to five atomic layers, there is an absence of iron in the spectrum and chlorine can be identified in the film by removing carbon. It is postulated that the aliphatic chain is anchored to the iron by means of the chlorine with the chain length standing above the surface.

Surface coverage of the iron by chlorohexane is much more effective than was

observed for chlorobenzene in figure 7(a). With chlorobenzene iron peaks were observed.

The AES spectrum for bromohexane on iron (fig. 8(b)) indicates the presence of iron peaks, a bromine peak, and a smaller carbon peak; this finding suggests that the bonding is different from that observed for chlorohexane. Friction data obtained with the surface films of figures 8(a) and (b) are presented in figure 9. The friction coefficients are essentially the same, indicating that despite differences in surface films very little effect of these differences is seen in friction behavior.

In figure 9 the friction coefficients obtained with the two halogenated hydrocarbons (chlorohexane and bromobenzene) are essentially the same for the entire range of loads investigated. The friction coefficients are approximately 1.0, which is nearly the same as the values obtained in figure 6 for the halogenated benzene compounds at loads about 10 grams. With chlorobenzene (fig. 7(a)) the friction was considerably higher at light loads than it was for chlorohexane (fig. 6). This difference may be explained by the difference in ability of these two halogenated hydrocarbons to shield the iron (figs. 8(a) and (b)). The effect is seen only at light loads, because at higher loads such thin surface films are readily penetrated by surface asperities. Metal to metal contact and adhesion contributes more heavily to the measured friction force. The large forces required to shear the metal interfacial bonds mask the film effects.

Oxygen Effects

The friction data presented thus far for the simple hydrocarbons and the halogenated hydrocarbons were obtained with saturated films of these materials on clean iron surfaces. Since oxygen is usually present on metals in the form of oxides, the question arises as to the effectiveness of these materials in reducing friction relative to oxygen. Oxygen was therefore adsorbed to a clean iron surface in the same manner employed in the adsorption of the other materials. The AES spectrum for this surface is presented in figure 10.

Sliding friction experiments were conducted on the oxygen film of figure 10, and the results obtained are presented in figure 11. The friction coefficient, which was approximately 1.0 at all loads, was comparable to that obtained with the halogenated hexane structures in figure 9 and the halogenated benzene structures at loads beyond 10 grams in figure 6. It was less than that obtained, however, with hexane and benzene as indicated by the reference curve for these two materials (fig. 11). Thus, for clean iron surfaces, oxygen is a more effective "lubricant" than is either hexane or benzene.

As discussed earlier, oxygen will displace both hexane and benzene from an iron surface completely. AES spectra for the iron surface containing these hydrocarbons are completely devoid of carbon after room temperature and pressure exposure of these surfaces to oxygen of the air as shown in figure 4. Only the oxygen and iron peaks are present.

The halogenated hydrocarbons will adsorb chemically to an oxide covered iron surface as indicated in the Auger spectrum for chlorohexane on such a surface in figure 12. The spectrum of figure 12 indicates the presence of chlorine in addition to carbon, oxygen, and iron. This differs from that seen in figure 8(a) for the adsorption of chlorohexane to a clean iron surface.

The friction characteristics for the oxidized iron surface containing the chlorohexane were very similar to those observed for oxygen and chlorohexane on clean iron.

CONCLUSIONS

The following conclusions were obtained as a result of sliding friction experiments with iron containing adsorbed surface films of oxygen, aliphatic, and aromatic organic structures:

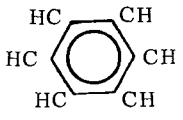
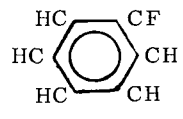
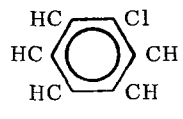
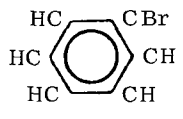
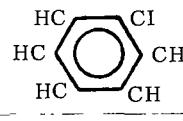
1. At loads in excess of 10 grams very little difference is observed in the friction behavior of aliphatic hexane and aromatic benzene in the lubrication of iron.
2. At light loads (less than 15 g) chlorohexane exhibits lower friction than does chlorobenzene. This can be explained from Auger spectra which indicate that chlorohexane more effectively covers the iron surface than does chlorobenzene.
3. Similar friction behavior occurs at all loads for brominated benzene and brominated hexane.
4. Oxygen is more effective in reducing the friction of clean iron than either of the hydrocarbons hexane (aliphatic) or benzene (aromatic).
5. Oxygen will displace, at room temperature, either hexane or benzene from a clean iron surface.

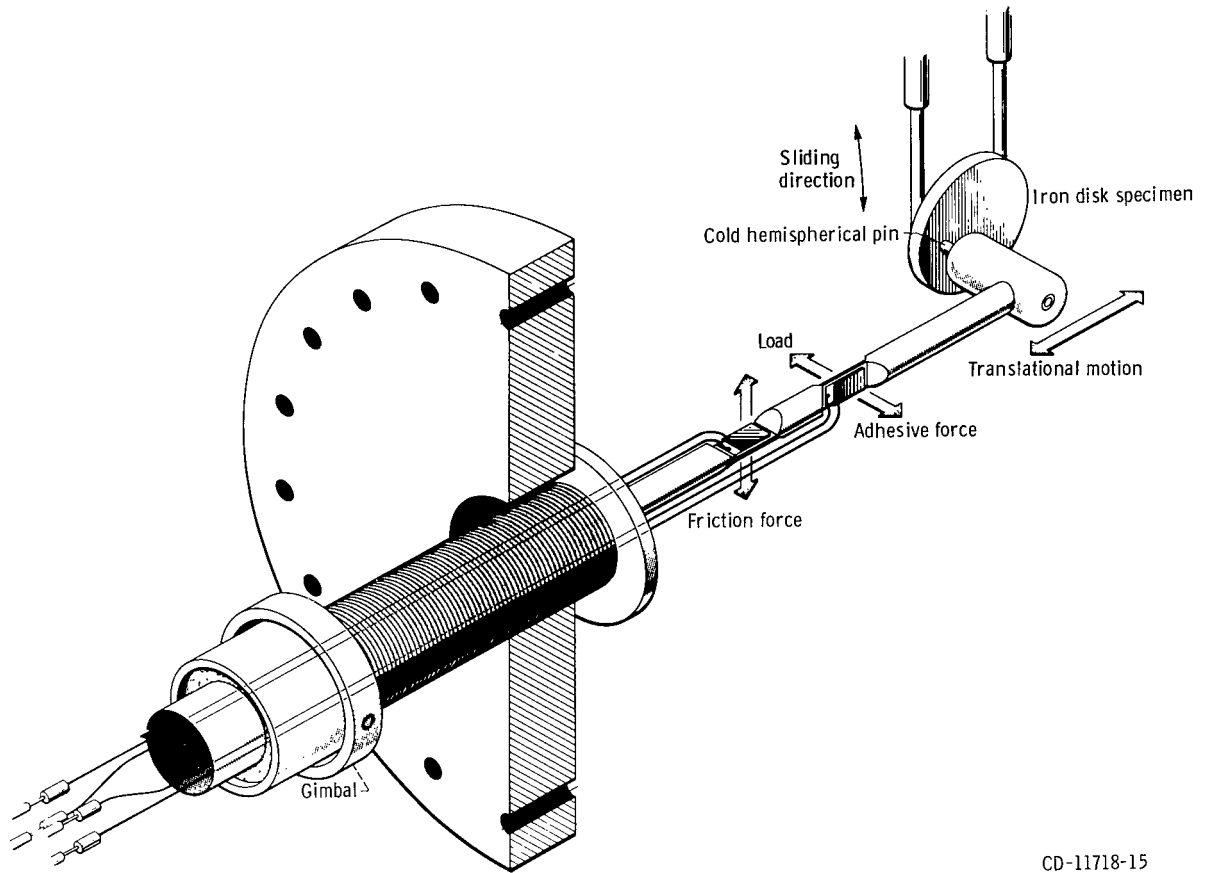
Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, February 4, 1976,
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TABLE I. - MOLECULAR STRUCTURES OF
ADSORBING SPECIES

Hexane	$\text{H}_3\text{-C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
Benzene	
Chlorohexane	$\text{ClH}_2\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
Bromohexane	$\text{BrH}_2\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
Iodohexane	$\text{IH}_2\text{C-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_2\text{-CH}_3$
Fluorobenzene	
Chlorobenzene	
Bromobenzene	
Iodobenzene	



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Figure 1. - High-vacuum friction and wear apparatus.

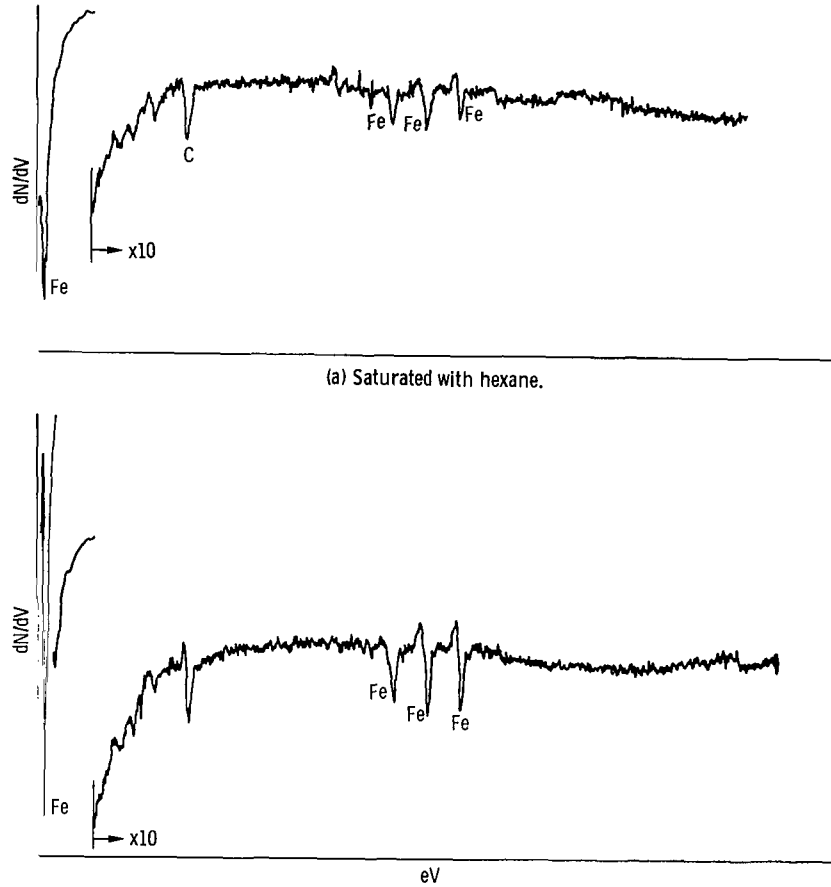


Figure 2. - Auger spectrum for iron (011) surface.

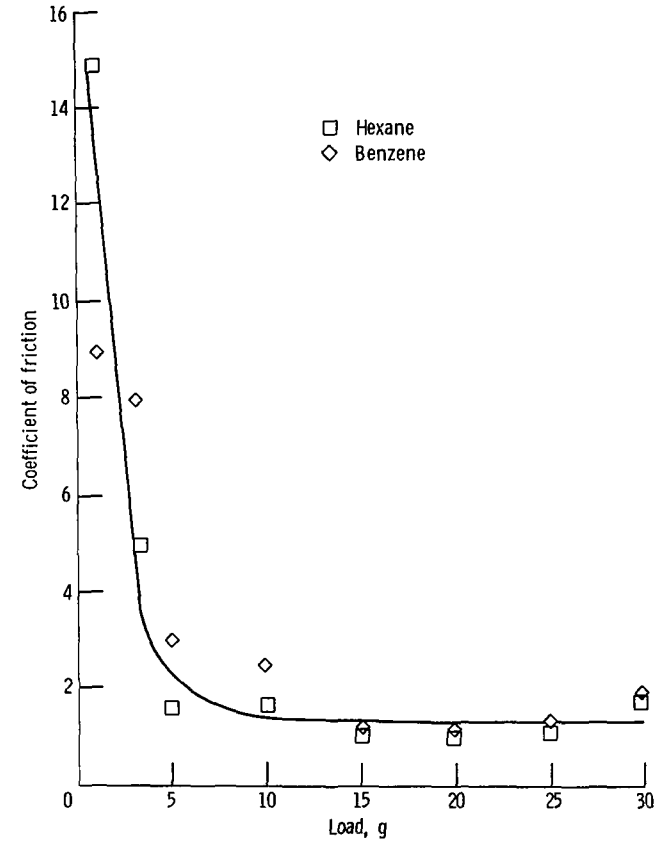


Figure 3. - Friction coefficient for gold (111) single crystal sliding on iron (011) single crystal with iron surface saturated with hexane and benzene.

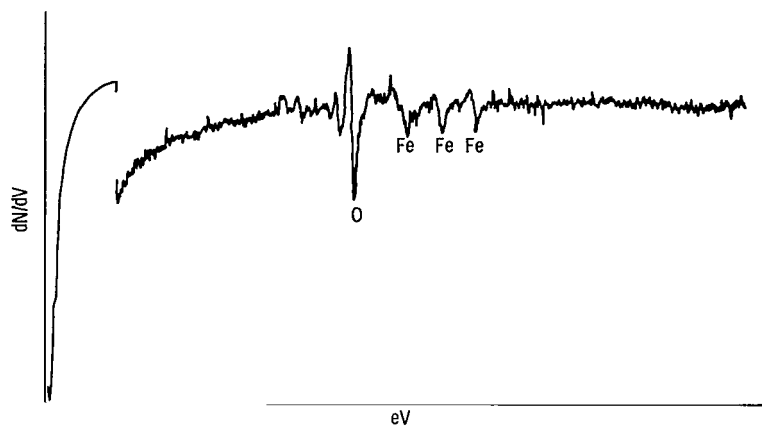


Figure 4. - Auger spectrum for iron (011) surface saturated with film of hexane exposed to air for 30 minutes.

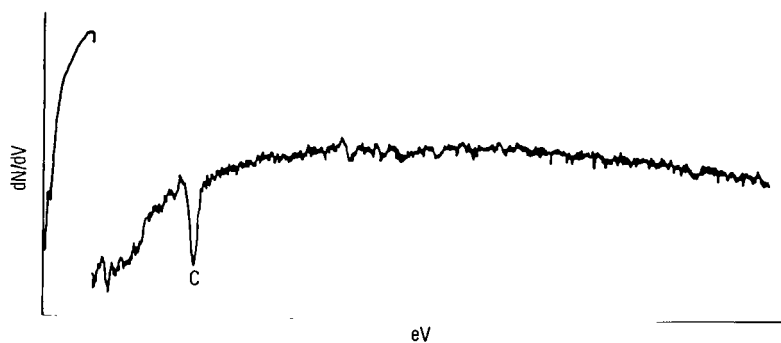


Figure 5. - Auger spectrum for iron (011) surface saturated with fluorobenzene.

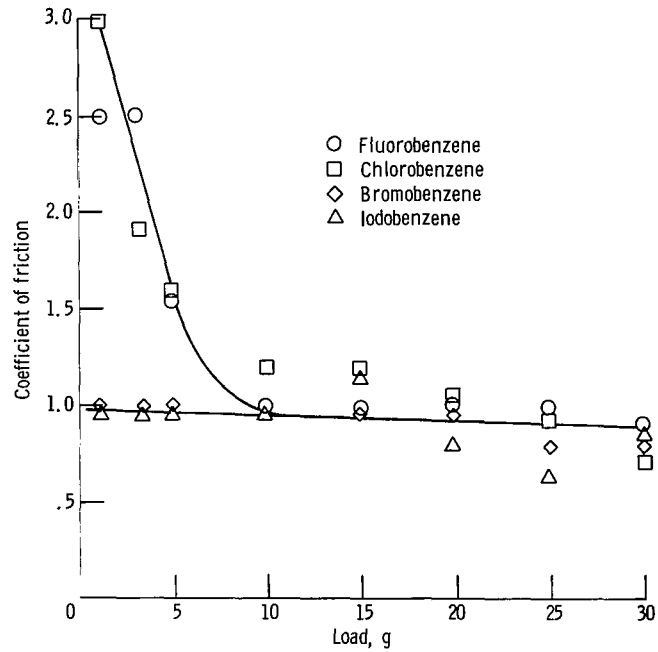


Figure 6. - Coefficient of friction for gold (111) single crystal sliding on iron (011) single crystal with iron surface saturated with halogenated benzene compounds.

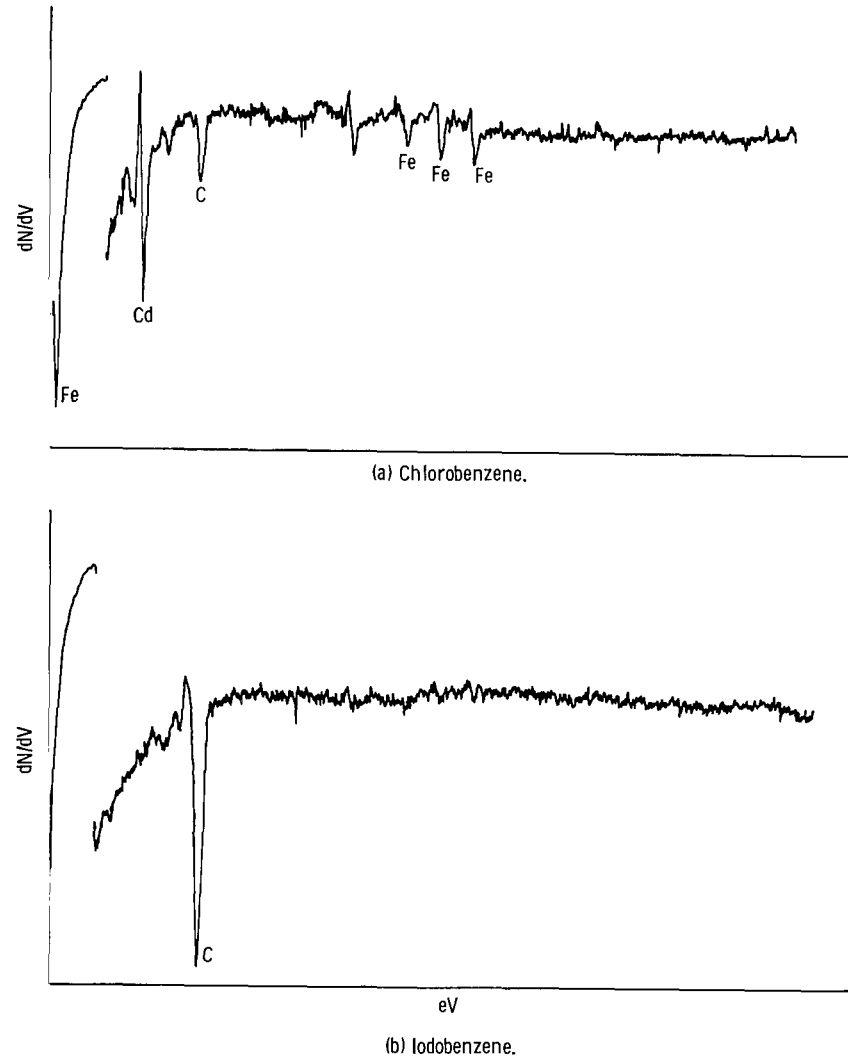


Figure 7. - Auger spectrum for iron (011) surface saturated with chlorobenzene and iodobenzene.

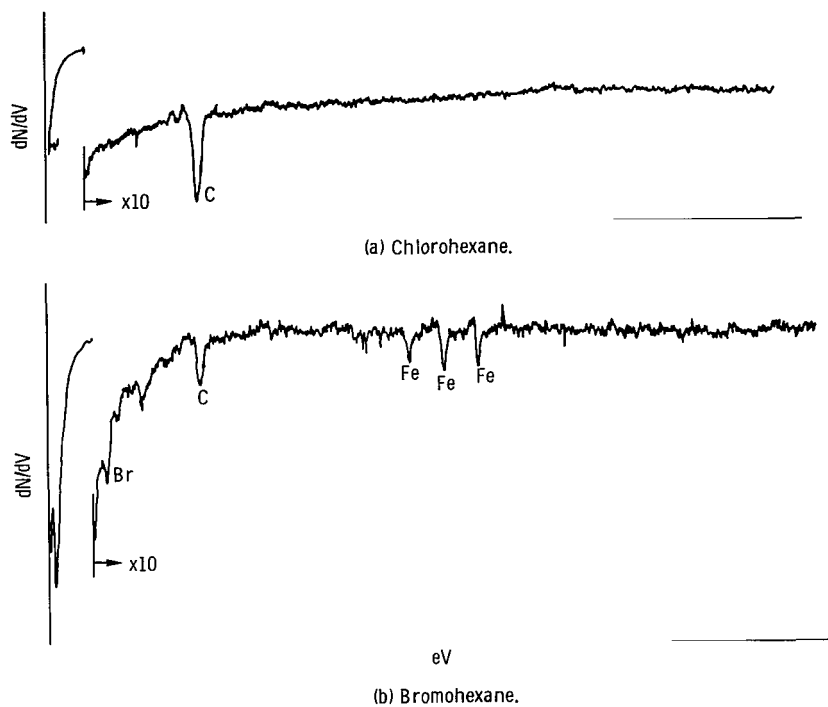


Figure 8. - Auger spectrum for iron (011) surface saturated with chlorohexane and bromohexane.

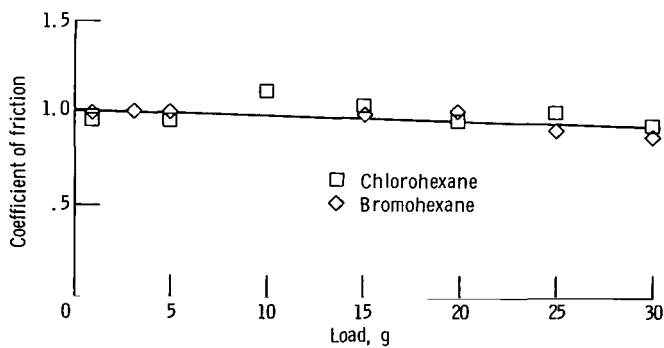


Figure 9. - Coefficient of friction for gold (111) single crystal sliding on iron (011) single crystal with iron surface saturated with halogenated hexane compounds.

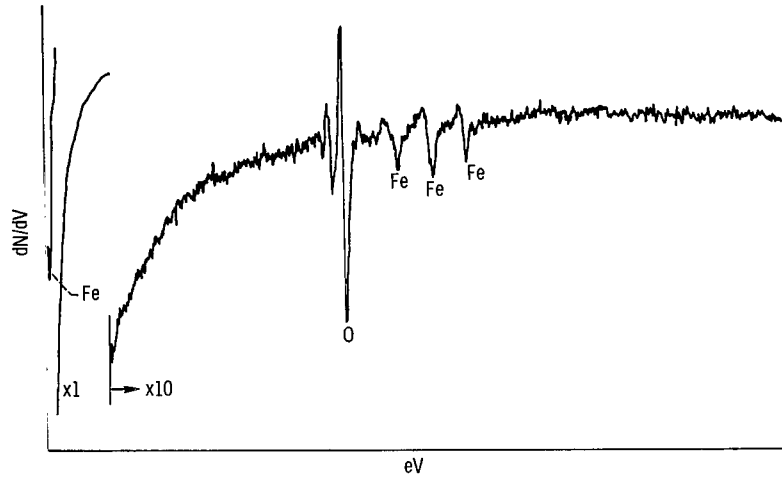


Figure 10. - Auger spectrum for iron (011) surface after exposure to air for 30 minutes.

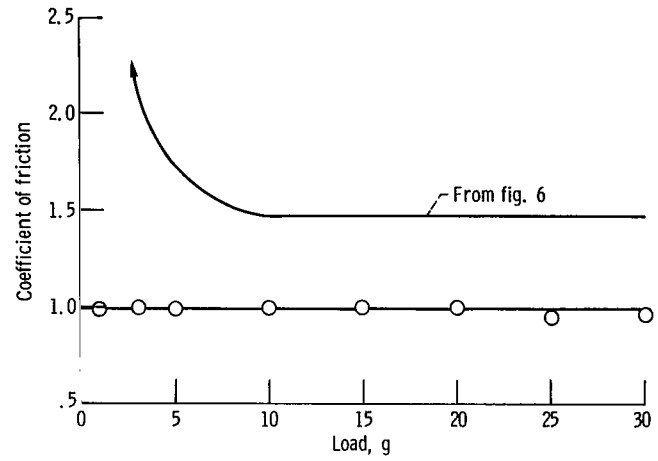


Figure 11. - Comparison of friction coefficient for iron single crystals in presence of oxygen and hydrocarbons.

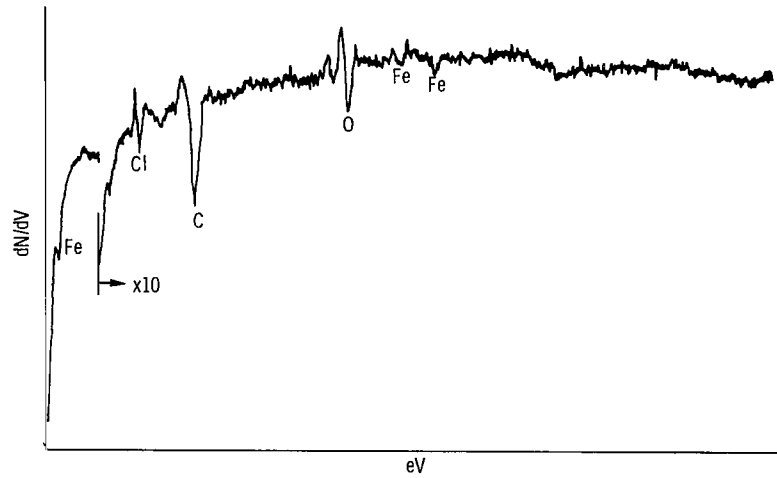


Figure 12. - Auger spectrum for iron (011) surface containing an oxide film and saturated with chlorohexane.

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