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**FRICTION DIFFERENCES BETWEEN
ALIPHATIC AND AROMATIC STRUCTURES
IN LUBRICATION OF TITANIUM**

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16. Abstract <p>Sliding friction experiments were conducted with a titanium (0001) single crystal surface with various adsorbed aliphatic and aromatic compounds containing the same number of carbon atoms. An Auger emission spectroscopy analysis was used to monitor the presence of the organic lubricating compounds. Results of the investigation indicate that hexane and benzene give the same friction coefficients over a range of loads. At light loads the friction decreased with an increase in the halogen atom size where the halogens chlorine, bromine, and iodine are incorporated into the benzene molecular structure. The aliphatic compounds chlorohexane and bromohexane exhibited lower friction coefficients than the aromatic structures chlorobenzene and bromobenzene.</p>		
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FRICTION DIFFERENCES BETWEEN ALIPHATIC AND AROMATIC STRUCTURES IN LUBRICATION OF TITANIUM

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SUMMARY

An investigation was conducted to determine the influence of various organic molecules in the reduction of the friction of a titanium (0001) single crystal surface. All of the organic structures contained six carbon atoms; a comparison was made between aliphatic and aromatic structures and among the various halogen atoms. An Auger emission spectroscopy analysis was used to monitor the surface species present on the titanium after adsorption. Friction experiments were conducted with a gold pin sliding on the titanium at loads of 1 to 30 grams and at a sliding velocity of 0.7 millimeter per minute.

The results of the study indicate that hexane and benzene give essentially the same friction results in lubricating titanium. With the addition of halogens to the benzene structure the friction decreases with an increase in the size (with the exception of fluorine) of the halogen atom, chlorine > bromine > iodine. Bromohexane and chlorohexane exhibited lower friction coefficients at light loads than did bromobenzene or chlorobenzene.

INTRODUCTION

Hydrocarbons are the most widely used materials in lubrication systems. Lubricating oils are principally aliphatic in nature but they do contain some aromatic structures (refs. 1 and 2). Very little fundamental experimental work has been done to establish the relative differences in the lubricating characteristics of aliphatic and aromatic hydrocarbons. Aromatic structures such as the polyphenyl ethers have become increasingly important in recent years for lubricating advanced aircraft engine components because of their superior thermal stability compared to aliphatic structures. Titanium, generally considered to be very difficult to lubricate (ref. 3), is widely used

in alloys for aircraft and aerospace mechanisms.

The objective of this investigation was to compare the ability of the analogous aliphatic and aromatic structures (same number of carbon atoms) in reducing the friction of titanium metal. The lubricants were bled into a vacuum system and allowed to interact with a sputter cleaned and annealed titanium (0001) 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 titanium under 1- to 30-gram loads. The sliding velocity was 0.7 millimeter per minute, and all sliding experiments were conducted in a vacuum (1.33×10^{-8} N/m²(10^{-10} torr)) at 23° C.

APPARATUS

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

A gimbal mounted beam 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 titanium crystal flat was a disk 12 millimeters in diameter. The gold pin, selected because of its inactivity with the hydrocarbons, had a 2.0-millimeter radius on the end that contacted the titanium flat. The load applied by moving the beam toward the disk was measured by the strain gage. The adhesion force (i. e., the force necessary to separate the pin and disk after being loaded together) is measured in the direction opposite to that of bond application by the same strain gage.

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.

Almost any load measuring sensitivity can be achieved by properly thinning the flats in the beam. Full scale deflection on a conventional strip chart recorded with forces of from 0.1 to 11.0 newtons resulting from load, adhesion, or friction force could be achieved.

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 in which the components of figure 1 were contained also had a LEED diffraction system (used only initially to characterize the titanium surface) and an Auger spectrometer. The electron beam of both could be focused on any disk site desired by moving the titanium disk.

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 titanium 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 ethyl alcohol. The surfaces were rinsed with water and 200 proof ethyl alcohol.

The titanium 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 1.33×10^{-8} newton per square meter (10^{-10} torr) range.

Argon gas was bled into the vacuum system to a pressure of 10 micrometers. A 1000-volt dc potential was applied to the specimen which was sputter bombarded for 30 minutes before the oxygen was removed by heating at 200° C for 30 minutes. After sputtering the surface was examined with Auger emission spectroscopy to establish the surface cleanliness. Where the surface was not clean the sputtering process was repeated. All friction experiments were conducted with the system re-evacuated to a pressure of 1.33×10^{-8} newton per square meter (10^{-10} torr).

The gold pin was loaded against the titanium flat by mechanically deflecting the beam through a gimbal assembly with the gold pin in contact with the titanium. When the proper load, as indicated on a strip chart recorder, had been applied, sliding was initiated by moving the beam 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. Auger emission spectroscopy was used to monitor the elements present on the titanium surface after exposure of the surface to the lubricating species.

The gold pin was not sputter cleaned, but was simply heated to 500° C for 30 minutes. Gold does not chemisorb the hydrocarbons of this study and was selected for that reason.

RESULTS AND DISCUSSION

Surface Cleaning

An Auger emission spectrum for the titanium single crystal surface prior to cleaning is presented in figure 2. In addition to titanium peaks, both carbon and oxygen are present on the surface.

After sputter bombarding the titanium surface of figure 2 with argon ions ($10\text{ }\mu\text{m}$ pressure at a 1000-V potential for 30 min), the Auger emission spectrum of figure 3 was obtained. The carbon has been completely removed from the surface and only a small oxygen peak persists. Titanium is a very good "getter" of active gases such as oxygen. It was felt that the oxygen was scavenged from the environment after sputtering even though the vacuum system pressure was 1.33×10^{-8} newton per square meter (10^{-10} torr). The surface was therefore resputtered numerous times with the result that, even if the time for taking the Auger trace after sputtering was varied, the oxygen remained. It was concluded that the titanium contained dissolved oxygen.

The gold single crystal hemispherical pin was brought into contact with the titanium surface under a 1-gram load. Complete seizure of the surfaces in contact occurred. An examination of the sliding wear track on the titanium surface revealed the presence of transferred gold. The gold was detected with Auger emission spectroscopy and the spectrum obtained is presented in figure 4. Auger peaks for both gold and titanium were detected.

Hydrocarbons

A sputter cleaned titanium surface was exposed to hexane. The hexane was admitted into the vacuum system when the pressure was at 1.33×10^{-8} newton per square meter (10^{-10} torr). The pressure was allowed to rise to 1.33 newtons per square meter (10^{-2} torr) with hexane and the system was held at that pressure for 30 minutes. The system was then re-evacuated to 1.33×10^{-8} newton per square meter (10^{-10} torr).

An Auger spectrum for the titanium surface obtained after evacuation of the hexane is presented in figure 5. Only two peaks are detected, one large carbon peak and a small titanium peak. The near absence of titanium (in the absence of oxygen) in the spectrum indicates an effective coverage of the surface by hexane. Auger emission spectroscopy can detect elements to a depth of about four to five atomic layers.

Since the titanium is nearly completely shielded (fig. 5) by the carbon and multi-layer adsorption of hexane is unlikely, the hexane chain must be bonded at one end to the titanium surface and extend above it as proposed by Godfrey for the bonding of even

larger molecules to metal surfaces (ref. 4). If the chains were lying flat on the surface Auger peaks for titanium would be anticipated (possibly oxygen).

Friction experiments were conducted on the surface for which an Auger spectrum is presented in figure 5. The 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 6. In figure 6 a small Auger peak for carbon is detected. Intense peaks for titanium are observed and the oxygen contamination which was not seen in figure 5 is seen in figure 6. It would appear from the Auger spectrum that hexane does a more effective job than does benzene in masking a titanium surface for equivalent exposures to the two hydrocarbons.

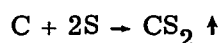
Friction experiments conducted with the two different hydrocarbons yielded the results presented in figure 7. In figure 7 the friction coefficient is plotted as a function of load for the titanium surface containing hexane and benzene. While some scatter exists in the data, the friction coefficient decreases with increasing load for both hydrocarbons. Despite the marked differences in the surface coverage with carbon between hexane and benzene (figs. 5 and 6) the friction coefficients over the range of loads examined are comparable.

It might be concluded from the data of figure 6 that the benzene ring lies on the surface with a number of carbon atoms bonding directly to the titanium. With reference to the data of figure 5, the hexane chain stands above the surface with anchoring occurring by a single carbon atom.

Normally, for straight chain aliphatic hydrocarbons, for an increase in carbon chain length there is a decrease in the friction coefficient (ref. 5). Here, however, when a six carbon atom chain is compared with six carbon atoms in a ring or aromatic structure the friction coefficient is independent of the structural configuration of the carbon atoms and the manner in which they bond to the surface.

Attempts were made to displace the hydrocarbons hexane and benzene from the titanium surface. The surfaces were exposed to oxygen at 10 micrometers for 30 minutes. The film remained intact and were not displaced from the titanium surface by oxygen.

The titanium surfaces containing the hexane and benzene were heated for 30 minutes at 500⁰ C. An Auger spectrum for the hexane is presented in figure 8. Heating caused a diminishing of the carbon peak intensity and the development of a very large sulfur peak. The diminution of the carbon peak intensity can exist from interaction with the sulfur and from desorption. The sulfur has diffused from the titanium bulk to the surface upon heating. The sulfur combines with the carbon in all probability according to the equation



Since carbon disulfide is volatile, it would leave the surface and thus cause the carbon to decrease in intensity. Similar results were obtained with benzene.

Alcohols

When active groups are added to basic hydrocarbon molecules the affinity of the structure for a metal increases and generally friction decreases (ref. 5). Thus, the lubricating properties are generally improved with the addition of hydroxyl, carboxyl groups, and halogens. Phenol and n-hexyl-alcohol have the same number of carbon atoms and each contains a hydroxyl group except the former in a ringed structure and the latter is a straight chain. Both were adsorbed to titanium. An Auger spectroscopy analysis confirmed the presence of both.

Friction experiments were conducted with both adsorbates present. The results obtained are presented in figure 9. For a 1-gram load the friction coefficient with n-hexyl alcohol was less than that obtained with phenol. The friction coefficient with n-hexyl alcohol remained less than that observed with phenol to about a 15-gram load. Beyond 15 grams the friction coefficient was essentially the same for the two adsorbates.

Halogens Containing Hydrocarbons

Halogen atoms present in organic molecular structures are generally extremely effective in the lubrication of solids. Sliding friction experiments were conducted with fluorobenzene adsorbed on a titanium surface in the same manner already described for hexane and benzene. Friction results obtained are presented in figure 10. The friction for a 1-gram load was lower than that observed with benzene in figure 7.

Chlorohexane and chlorobenzene were adsorbed on titanium surfaces, and sliding friction experiments were conducted on these surfaces. An Auger emission spectroscopy trace of the surface containing the chlorobenzene is presented in figure 11. It is of interest to note in figure 11 that the carbon peak is larger than was observed with benzene. It is the largest peak in the spectrum. Chlorobenzene appears to cover titanium more effectively than was observed with benzene. Similar traces were obtained with chlorohexane.

Friction coefficients obtained with chlorobenzene and chlorohexane are presented in figure 12. At loads of less than 10 grams the friction coefficient was lower with the aliphatic structure than it was with the aromatic structure. Above that load friction coefficients were not greatly different.

Similar experiments to those conducted with chlorine substituted compounds were

conducted with brominated materials. An Auger emission spectrum for bromobenzene on the titanium surface is presented in figure 13. Bromine is present on the surface and carbon is the largest peak as was observed with chlorobenzene; however, there was an absence of oxygen with bromobenzene. It appears as if the bromobenzene more effectively covered the titanium since the titanium peaks have nearly disappeared.

Friction data for both bromobenzene and bromohexane are presented in figure 14. Friction is lower below 15 grams than was observed with the chlorinated structures in figure 13.

At loads up to 15 grams the bromobenzene exhibited higher friction than the bromohexane. These results are consistent with the observations of figure 13 for the chlorinated analogs - namely, that the aromatic structures exhibit at the light loads higher friction coefficients than the aliphatic structures.

The titanium surface was next exposed to the last of the halogens. Iodobenzene was bled into the vacuum system with the exposure of the titanium being the same as for the benzene, chlorobenzene, and bromobenzene.

The Auger emission spectrum for the titanium surface with iodobenzene is presented in figure 15. The only Auger peak detected is that of carbon. Neither iodine nor titanium peaks are present. The titanium 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 an Auger spectroscopy analysis (ref. 6).

Friction coefficients obtained with the iodobenzene are presented in figure 16. A comparative curve is presented for bromobenzene from figure 15. The friction at the light loads was less than was observed with bromobenzene.

The effect of the halogen atom in benzene on friction for titanium can be seen in the data of table I. At the light load of 1 gram, the friction coefficient decreases with an increase of atom size of the halogen with the exception of fluorine. When the load is increased at 30 grams the friction is relatively comparable and the nature of the halogen has little effect.

In table II the effect of aromatic against aliphatic structure is seen at a 1-gram load. The aliphatic exhibits lower friction coefficients at the light load of 1 gram. At the higher loads, 30 grams, differences are not significant.

SUMMARY REMARKS

As a result of sliding friction experiments with titanium containing adsorbed surface films of aliphatic and aromatic organic structures the following observations are made:

1. No detectable difference in friction was observed between benzene and hexane

in the lubrication of titanium.

2. The addition of halogens in the benzene structure improved the friction reducing ability of the benzene on titanium. At light loads (e.g., 1 g), with the exception of fluorine the friction decreased with increasing size of the halogen atom - chlorine > bromine > iodine.

3. The aliphatic molecule containing the halogen chlorine or bromine gave lower friction coefficients at light loads (e.g., 1 g) than analogous aromatic structures.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, September 26, 1975,
506-16.

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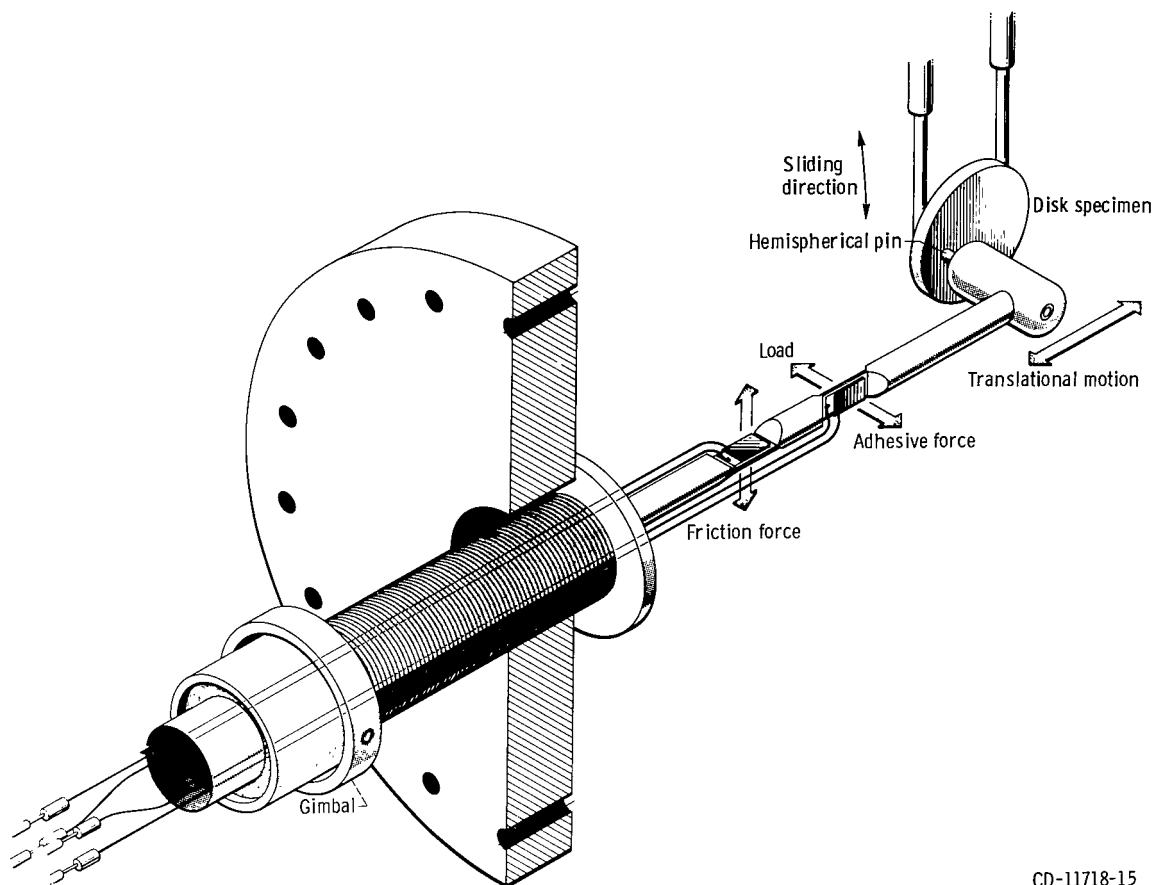
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TABLE I. - FRICTION
COEFFICIENT WITH HALO-
GENATED BENZENE

Compound	Load, g	
	1	30
Fluorobenzene	3.0	1.8
Chlorobenzene	6.0	1.8
Bromobenzene	4.0	2.0
Iodobenzene	3.0	2.0

TABLE II. - FRICTION CO-
EFFICIENT AS FUNCTION
OF STRUCTURE FOR
1-GRAM LOAD

Halogen	Parent structure	
	Hexane	Benzene
Fluorine	3.0	---
Chlorine	4.0	6.0
Bromine	3.0	4.0
Iodine	---	3.0



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

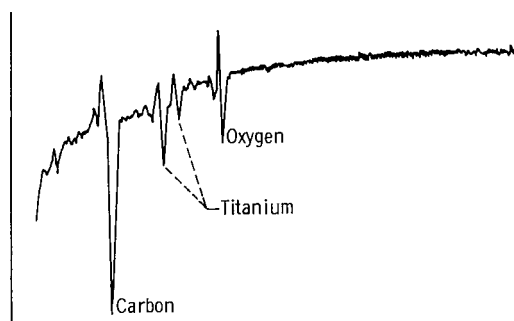


Figure 2. - Auger spectrum for titanium (0001) surface after insertion into vacuum system.

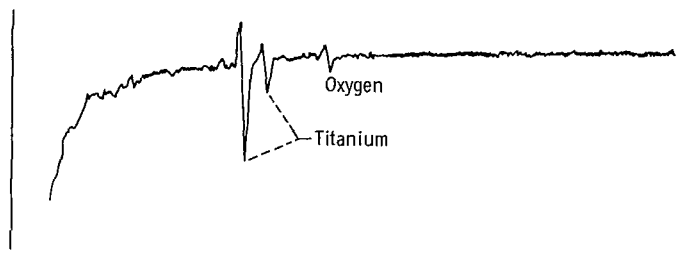


Figure 3. - Auger spectrum for titanium (0001) surface after sputter cleaning with argon.

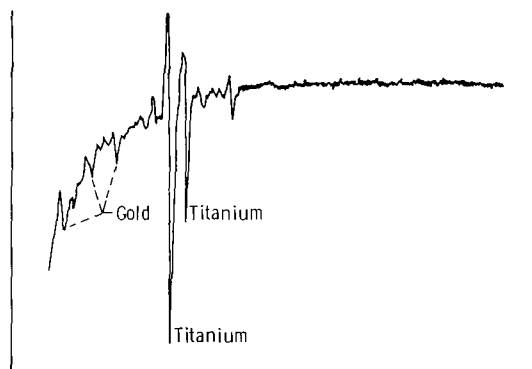


Figure 4. - Auger spectrum for titanium (0001) surface after gold (111) rider slid across surface.

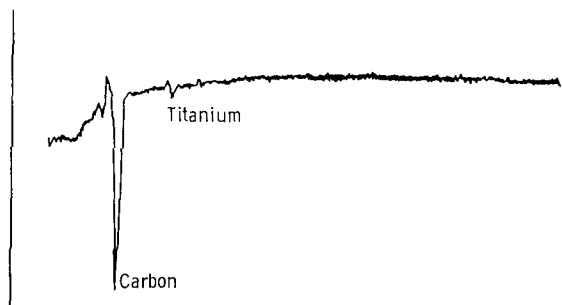


Figure 5. - Auger spectrum for titanium (0001) surface saturated with hexane (10 μm for 30 min).

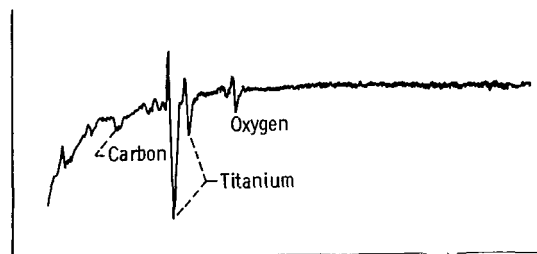


Figure 6. - Auger spectrum for titanium (0001) surface after exposure to benzene (10 μm for 30 min).

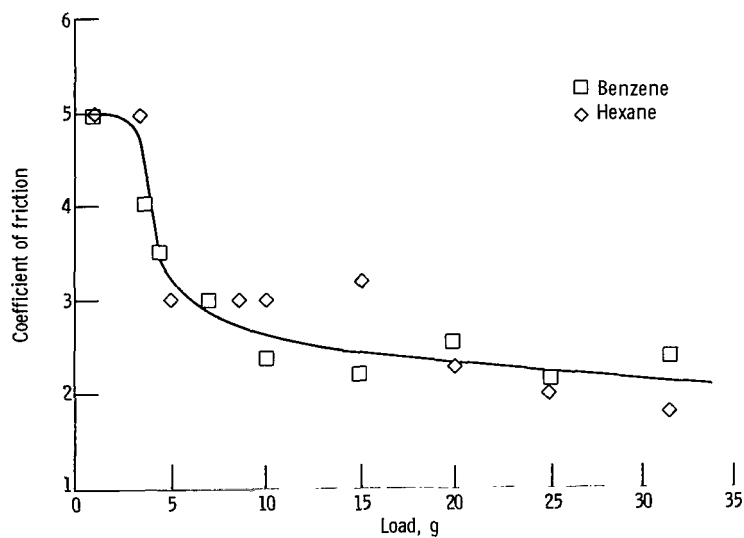


Figure 7. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23 $^{\circ}$ C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of hexane and benzene (1.33 N/m^2 , 30 min exposure).

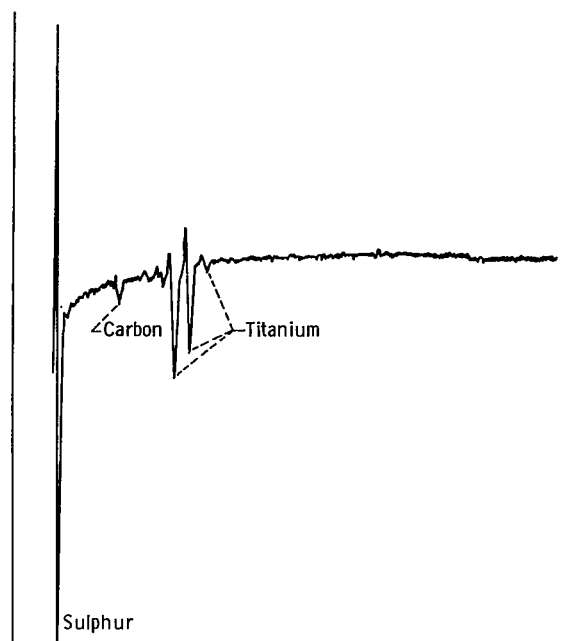


Figure 8. - Auger spectrum for titanium (0001) surface after exposure to hexane and subsequent heating to 500° C for 30 minutes.

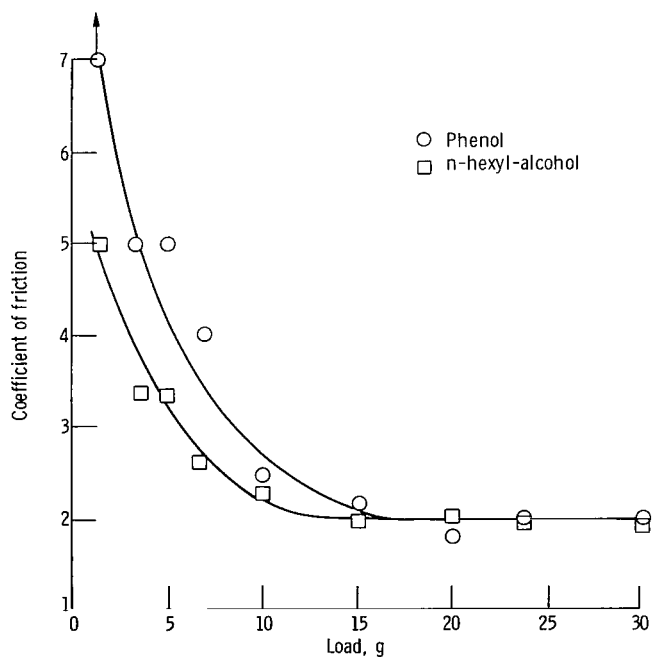


Figure 9. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of phenol and n-hexyl-alcohol (1.33 N/m^2 , 30 min exposure).

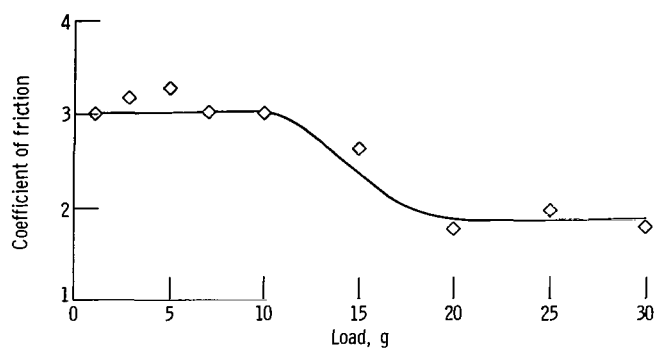


Figure 10. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of fluorobenzene (1.33 N/m^2 , 30 min exposure).

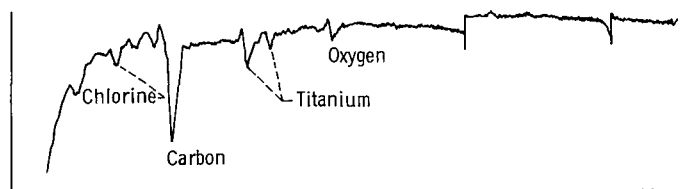


Figure 11. - Auger spectrum for titanium (0001) surface after exposure to chlorobenzene ($10 \mu\text{m}$ for 30 min).

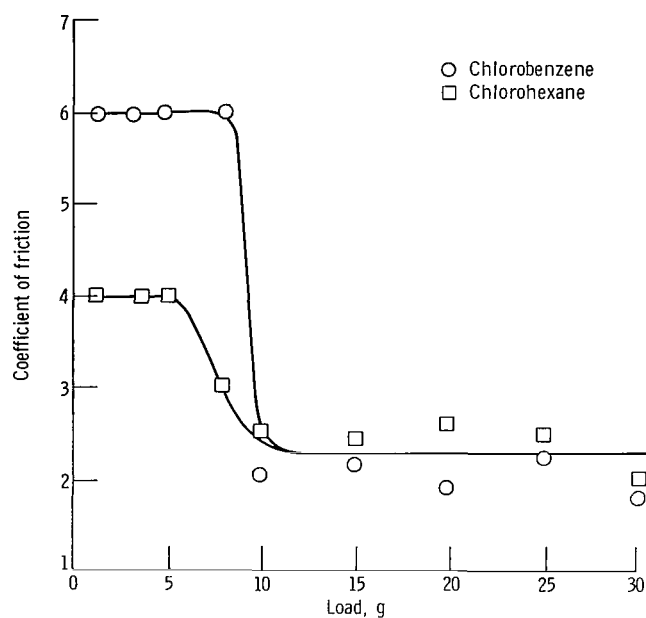


Figure 12. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of chlorobenzene and chlorohexane (1.33 N/m^2 , 30 min exposure).

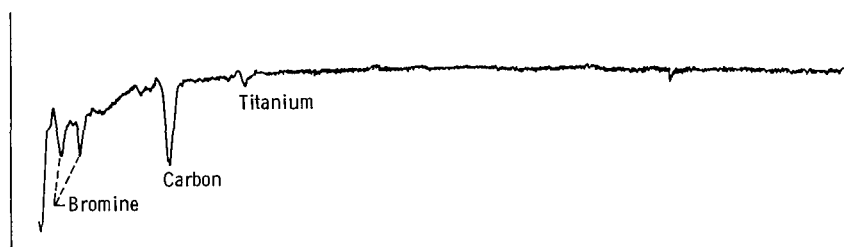


Figure 13. - Auger spectrum for titanium (0001) surface after exposure to bromobenzene ($10 \mu\text{m}$ for 30 min).

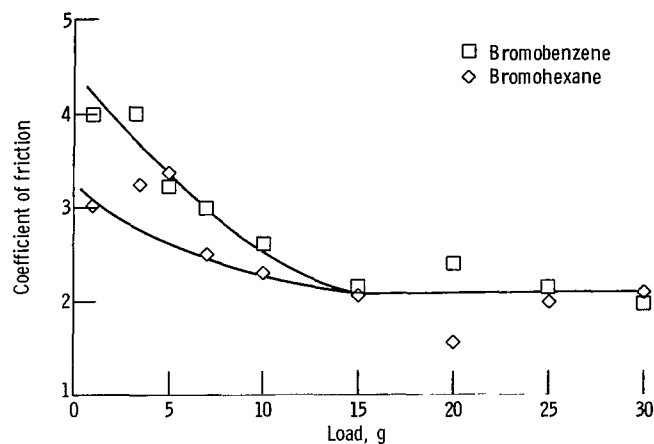


Figure 14. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23° C; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of bromobenzene and bromohexane (1.33 N/m^2 , 30 min exposure).

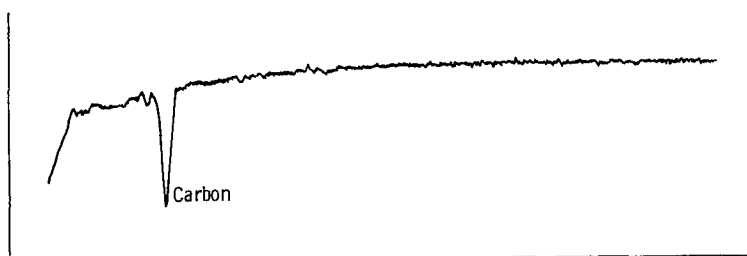


Figure 15. - Auger spectrum for titanium (0001) surface exposed to iodobenzene ($10 \mu\text{m}$ for 30 min).

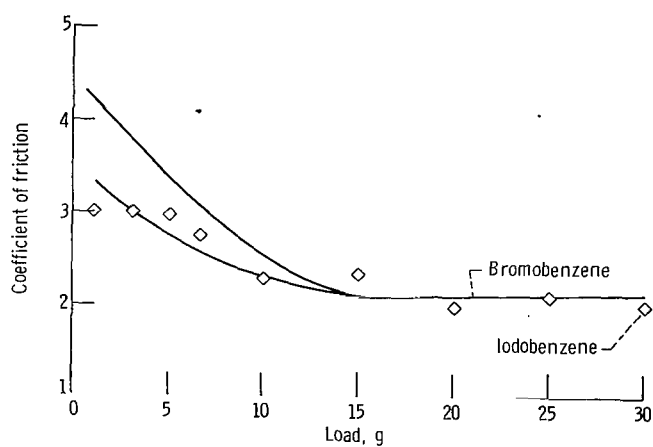


Figure 16. - Coefficient of friction for single crystal gold (111) sliding on single crystal titanium (0001). Sliding velocity, 0.7 millimeter per minute; temperature, 23°C ; and pressure, 1.33×10^{-8} newton per square meter (10^{-10} torr). Titanium surface saturated with adsorbed film of iodobenzene and bromobenzene (1.33 N/m^2 , 30 min exposure).

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