NASA Technical Paper 1545

Surface Chemistry of Iron Sliding in Air and Nitrogen Lubricated With Hexadecane and Hexadecane Containing Dibenzyl-Dilsulfide

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SEPTEMBER 1979

NASA

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Surface Chemistry of Iron Sliding in Air and Nitrogen Lubricated With Hexadecane and Hexadecane Containing Dibenzyl-Dilsulfide

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**Scientific and Technical
Information Branch**

1979

SUMMARY

Pin-on-disk wear experiments were performed on iron specimens slid against steel disks at 3 rpm and at room temperature. Hemispherical specimens were slid under a 4.9-newton (500-g) load for wear measurements, and flat (button) specimens at a 44-newton (4.5-kg) load for X-ray photoelectron spectroscopy (XPS) analysis. The lubricant was hexadecane or hexadecane plus 1 percent by weight dibenzyl-dilulfide (DBDS), and the atmosphere was either air or nitrogen. The flat wear specimens and the wear debris obtrained by filtering the lubricant after an experiment were analyzed by XPS.

The wear and friction showed that the presence of air reduced wear but increased friction and that DBDS reduced friction but had little effect on wear, except that the wear increased somewhat when DBDS was used in air. Wear-scar analysis indicated that oxygen and sulfur competed chemically for the surface with the oxide predominating. Low wear was associated with a thick oxide layer and low friction with a thin, predominantly sulfide layer. Analysis of the wear debris indicated the possible presence of a sulfate in the high wear case (hexadecane plus DBDS in air) and showed the presence of an organic sulfide in the low wear case (DBDS in hexadecane in nitrogen).

INTRODUCTION

The organic disulfides have long been recognized as possible extreme-pressure (ep) additives in mineral oils. Among them, dibenzyl-dilsulfide (DBDS) is one of the most effective (refs. 1 and 2). In attempts to understand the surface chemistry of extreme-pressure additives, several recent investigations have used X-ray photoelectron spectroscopy (XPS) to analyze worn surfaces generated in a variety of tests with sulfur containing additives (refs. 3 to 5). It has been found that sulfide is one prominant constituent of severely worn specimens. There was also evidence that oxide was important in the more mild-wear cases (ref. 5).

This study was to further investigate the importance of oxygen in the mild-wear situation by comparing experiments conducted in air and in nitrogen with and without the additive DBDS. Since XPS analysis of the wear debris might shed additional light on the wear process, it was also the purpose to demonstrate the feasibility of such analysis.

Pin-on-disk wear experiments were conducted at room temperature on iron specimens slid against steel disks at 3 rpm. Hemispherical specimens were slid under a 4.9-newton (500-g) load for wear measurements and flat specimens at 44-newton (4.5-kg) load for XPS analysis. The lubricant was either hexadecane or hexadecane with 1 percent by weight of DBDS, and the atmosphere was either air or nitrogen. The flat wear specimen surface and the wear debris obtained by filtering the lubricant after an experiment were analyzed by XPS.

EXPERIMENT

Friction and Wear Experiments

Two types of wear experiments were performed in a conventional pin-on-disk machine like that shown in figure 1. In the first type of test the rider was a 0.95-centimeter-diameter iron hemisphere with a Rockwell B hardness of 52. In the second type the rider was a 6.3-millimeter-diameter iron button like that shown in the inset to figure 1. The button was pressed against the disk by a conical pin placed in a depression on the back of the button. This allowed the face of the button to rest flat against the disk. The Rockwell B hardness of the button was 60. The disk was 52100 steel and its Rockwell C hardness 59. The apparatus was enclosed in a box that could be purged with nitrogen or opened to laboratory air with 25 to 35 percent relative humidity. All tests were at room temperature.

Before every experiment the disk and buttons were lapped to a 0.5-micrometer finish. The hemispherical rider was polished successively with 240, 320, 400, and 600 grit paper, and then polished with 3-micrometer diamond polish, followed by 1-micrometer alumina in distilled water. The disk and riders were cleaned ultrasonically in trichloroethylene before each experiment.

The commercial hexadecane was used without further purification. It was nominally 99 percent pure and olefin free with a melting point above 18° C. It was used with and without 1 percent by weight of dibenzyl-dilsulfide (DBDS), which was also a commercial material used as received. Before each experiment 20 drops of lubricant were applied to the disk surface.

Experiments with the hemispherical rider were run at a 4.9-newton (500-g) load. The disk rotated at 3 rpm, and the experiments were 30 hours long. Measurements of the wear-scar diameter were made periodically from impressions taken in aluminum foil. Experiments with the buttons were run at a 4.5-kilogram load, which gave approximately the same load per unit area as was achieved in the hemispherical-rider experiments during the 10- to 30-hour period. Tests with the buttons ran 10 hours. The friction force was recorded throughout both types of experiments.

The experiments with the iron buttons provided a surface area large enough (>2 mm diam) for XPS analysis, those with the hemisphere permitted accurate wear measurements. The unit load was made nearly the same in the two types of experiments to make certain that the wear mechanisms were the same. This was confirmed by observing that the friction varied in the same way in both types of experiments.

On completion of a 30-hour experiment with the button rider, the rider was rinsed in Freon and immersed in Freon under nitrogen until it could be analyzed by XPS. The oil and wear debris were washed from the disk with Freon and collected. This wear debris was then filtered while being rinsed repeatedly with Freon. The filter papers were then stored between glass slides under nitrogen until they were analyzed.

X-Ray Photoelectron Spectroscopy Analysis

The worn surfaces of the buttons and the wear debris were analyzed by XPS. The technique, which has been described before (refs. 6 and 7), results in the determination of the binding energies of electrons in atoms near the surface of a sample (<2 nm deep) from the measurement of the kinetic energy of X-ray photoelectrons ejected from the surface. These binding energies are characteristic of the atom emitting the electron and depend on its oxidation state as well. Thus the position of a peak in the spectrum gives both elemental and chemical information.

The apparatus used consisted of a commercial, cylindrical-mirror, electron-energy analyzer with a 25-eV pass energy and a magnesium-target X-ray source operated at 10 kilovolts and 40 milliamperes. The ion gun in the system could be used to ion etch the surface of samples with 5-keV argon ions. The pressure in the vacuum system was below 1.33×10^{-6} pascal except during sputtering when the pressure was 5.3×10^{-3} pascal of argon.

The analyzer was calibrated using the gold ($4f_{7/2}$) binding energy of 84.0 eV. The filter paper, being a nonconductor, charged under the X-ray beam causing spectral shifts up to several volts. Measurements on the iron buttons showed a persistent carbon (1s) peak at 285.0 eV, presumably due to hydrocarbon contamination. The C(1s) peak from the filter paper was also assigned the value 285.0 eV to correct for charging. This gave reasonable values for the other measured binding energies and was correct when measured from the Fermi level at 0 eV in cases where the Fermi level could be accurately determined. The uncertainty in binding energies determined this way was estimated at about 0.5 eV.

The binding energies assigned to various compound and oxidation states were taken from the literature. The iron and oxygen binding energies are from Brundle et al. (ref. 8) and from Carver et al. (ref. 9). Sulfur binding energies are from Kramer and Klein (ref. 10) and Bird and Galvin (ref. 3).

RESULTS

Wear and Friction

The result of a typical wear test is shown in figure 2. The initial high wear rate is followed by a lower, equilibrium wear rate. After equilibrium wear was established, the disk and rider were cleaned and fresh lubricant was used. The wear rate continued at the equilibrium level. Then the rider was removed and refinished. Again, the wear rate was unchanged. Apparently, the initial wear was associated with the formation of a transfer film of iron on the disk. In the remainder of this work only equilibrium wear rates are reported.

Equilibrium wear rates were determined from a least-squares-fit, straight line using all the wear measurements taken after 10 hours of running. All the runs were repeated several times in random sequence. Figure 3(a) shows the average equilibrium wear rates obtained. Standard deviations ranged from 10 to 30 percent of the average values.

The friction force was measured throughout the experiments. An estimate of the average high and low values was made in each case. (See fig. 3(b).)

These results can be summarized by observing that the addition of DBDS to the hexadecane lowered the coefficient of friction, while the presence of air raised it. On the other hand, the presence of air alone reduced the wear rate, while the air and DBDS together raised it. The DBDS in the absence of air had little effect on wear under these conditions.

Wear Scar Analysis

Pin-on-disk tests were run using an iron flat in place of the hemispherical rider used for the wear tests. This provided a surface large enough to be analyzed by XPS. Argon ion etching was used to remove controlled amounts of material and permit analysis at increasing depths below the surface.

Figure 4 shows the Fe$(2p_{3/2})$ peaks from the samples run in straight hexadecane. The large width of the peaks is characteristic of oxidized iron, and their position indicates primarily Fe^{2+} in both cases. These spectra were taken after 30 seconds of sputter etching, which is sufficient to remove much of the surface contamination. It is known that ion bombardment will reduce iron oxides, and this might be the reason the Fe^{2+} appears more prevalent than Fe^{3+}. However, the Fe^{2+} state was dominant in one spectrum even before sputtering.

The Fe$(2p_{3/2})$ peaks from the specimen run in hexadecane with 1 weight percent DBDS are shown in figure 5. In the sample run in air the Fe^{2+} state again predominated, possibly due to the sulfide as previously indicated. In the sample run in nitrogen, however, metallic iron was the dominant species (fig. 5(b)). This indicates an unusually thin passive layer on the surface of this sample.

The thickness of the surface layer is of interest in all cases, but, because the worn surfaces were rough, depth profiling by ion-beam etching would be unreliable. Furthermore, reduction of the iron oxides could occur in the ion beam. Figure 5(c) illustrates that after a few minutes of bombardment a substantial metallic-iron peak appeared. Experiments on oxide powders indicated, however, that this degree of ion etching did not cause appreciable reduction of the iron oxide. It was due, therefore, to the appearance of the underlying metal. The ion etching time required to produce a detectable metallic-iron peak is, thus, a measure of the thickness of the oxide overlayer. That time was 3 minutes for the samples run in straight hexadecane in nitrogen and in hexadecane plus DBDS in air. In the case of the sample run in hexadecane plus DBDS in nitrogen the metallic-iron peak always dominated. It is concluded that the thickness of the reacted layer on the surfaces can be ordered as follows:

$$\begin{aligned} &\text{hexadecane in air} > \text{hexadecane in } N_2 \\ &\qquad \cong \text{hexadecane + DBDS in air} \gg \text{hexadecane + DBDS in } N_2 \end{aligned}$$

The relative amounts of oxide and sulfide in the reacted layer were estimated from the 530.0-eV O(1s) peak (metallic oxide) and the 161.0-eV S(2p) peak (sulfide). The relative peak heights are shown in figure 6. The peak heights were measured after sufficient sputtering for each to reach its maximum value. The arbitrary scales in figure 6 have been chosen so that they are roughly proportional to actual concentrations of oxygen and sulfur. The variation in oxide peak heights is due to the different oxide overlayer thicknesses as noted above. Even the small amount of sputtering used here was enough to bring some of the underlying metal into the analyzed volume on the hexadecane in nitrogen and hexadecane plus DBDS in air specimens.

It is important to notice that the ordinate scale of figure 6(b) is such that only on the sample run in hexadecane plus DBDS under nitrogen was the reactive film primarily sulfide. Furthermore, running in air with that lubricant did not so much reduce the amount of sulfide as dilute it in a much thicker oxide layer.

To summarize these results, it can be said that the addition of DBDS to the hexadecane lead to a thinner reacted layer on the wear scar, while the presence of air lead to a much thicker layer. The reacted layer was primarily oxide (Fe^{2+}) if air was present.

Wear Debris Analysis

The filter paper on which the wear debris was collected was analyzed with XPS. Since the paper itself contains oxygen, that peak was disregarded in the spectra. Attention was thus focused on the iron and sulfur peaks.

The $Fe(2p_{3/2})$ peaks were essentially no different from those of figure 4 except that the peaks occurred at 710.5 to 711.6 eV, which indicates primarily Fe^{3+}. The implication is that the wear debris is more heavily oxidized than the wear scars.

In figure 7 the S(2p) peaks from the wear debris of the experiments in hexadecane plus DBDS are shown along with a peak from one of the wear scars for comparison. The sample run in air resulted in only a small amount of sulfur, and that in the form of the sulfate, presumably iron sulphate ($FeSO_4$). The sample run in nitrogen had far more sulfur in the wear debris, as might be expected from the predominance of sulfur in the wear scar. The binding energy, however, was neither sulfide nor sulfate. The binding energy of the sulfur in many organic sulfur compounds is near this value. Benzyl mercaptide is shown in figure 7 because it has been proposed as one of the products of DBDS reaction with iron (ref. 2). Because of uncertainties in binding-energy measurements and because of the large number of organic sulfides that could produce binding energies near this value, the presence of a peak does not imply the presence of a particular compound.

Analysis of the wear debris shows that generally it was similar to the reacted layer in the wear scar but further oxidized. The exception was hexadecane plus DBDS in nitrogen, in which case the sulfur compound was primarily an organic sulfide.

DISCUSSION

In comparison with the other organic disulfides, DBDS is usually considered a good extreme-pressure additive, but a poor antiwear additive. The wear results presented bear out the latter observation. In these experiments the extreme-pressure behavior of an additive might best be revealed by the friction data, especially the friction maxima, since these reflect the strength of asperity contacts (the initial stages of seizure). The addition of DBDS to the hexadecane decreased the friction maxima by 1/3 and 1/2 in air and nitrogen, respectively. These results demonstrate appreciable extreme-pressure activity.

In these experiments the atmosphere was rapidly incorporated in the oil. This was demonstrated by changing the atmosphere during an experiment from nitrogen to air and back to nitrogen. The wear rate and friction changed accordingly and usually within minutes. Thus, air can be considered an oil additive. Clearly, it was a good antiwear additive in these experiments; however, it caused the maximum friction to increase by factors of 3 to 4. It appears to be not only poor, but antogonistic as an extreme-pressure additive.

The friction and wear results indicate that DBDS and air had competing effects; that is, they were competing chemically at the wear-scar surface. Oxygen (which we take to be the active component of the air) dominated in the wear scars when it was present, or when DBDS was absent. This could be a concentration effect or an effect of the greater chemical activity of oxygen (ref. 11). The only sulfur compound found in the wear scars was sulfide. This agrees with previous analyses (refs. 3 to 5).

The thick layer of oxide formed in air without DBDS was evidently more protective than the thin layers formed in the other three cases. This may be because the thin, brittle oxides break up under the rubbing stress, while a thicker oxide has enough structural integrity to remain intact. A thin, easily removed layer would act as a low-shear-strength, interfacial layer in the rubbing contact and would tend to reduce friction (ref. 12). The cases where the layer is thin did indeed exhibit lower friction than the thick oxide case, and the lowest friction was observed for the sample which had the thinnest reacted layer. Besides being the thinnest layer, the reacted surface of the sample run in DBDS without air was primarily sulfide. Iron sulfide is softer than any iron oxide and its presence would further reduce friction.

The wear debris gave evidence of another possible friction-reducing mechanism that could be active in this case. Organic molecules bound to the metal surfaces have long been recornized as effective in reducing friction (ref. 13). Also, the initial formation of a mercaptan at the metal surface has been proposed as one step in the interaction of dilsulfide additives with iron (ref. 2). The presence of an organic sulfide in the wear debris, for this case, indicates that there is an organic strongly bound to the iron and that it is being worn from the surface. The fact that it was not detected in the wear scar could simply mean that it wears as rapidly as it forms.

The wear debris in the other three cases was simply an oxidized form of the wear-scar layer material. This very likely occurred after the wear process when the wear particles with large surface areas and high temperatures were exposed to the residual gas in the oil. It is possible, however, than the presence of sulfate in the wear debris from experiments with the hexadecane plus DBDS in air is evidence of the corrosivity of the DBDS.

CONCLUSIONS

Wear experiments for iron sliding on 52100 steel were conducted in hexadecane and in hexadecane plus 1 weight percent dibenzyl-disulfide (DBDS) both in air and in nitrogen. The friction and wear results were compared with X-ray photoelectron spectroscopy

(XPS) analysis of the worn surfaces and the wear debris, and the following conclusions are drawn:

(1) Oxygen and DBDS compete chemically for the surface, with oxygen predominating unless it is excluded deliberately.

(2) A very thick oxide layer, which is formed in air with straight hexadecane, results in the lowest wear and the highest friction.

(3) Differences between the XPS analysis of the wear scars and the wear debris are especially significant.

(4) The lowest friction occurs with hexadecane plus DBDS in the absence of air. In this case the surface film is primarily sulfide and extremely thin. Further, the wear debris shows evidence of an organic sulfide compound. All of these features are consistent with low friction.

(5) The highest wear occurs when both DBDS and air are present. The presence of sulfate in the wear debris could indicate that a corrosive compound is formed, in this case, leading to abnormally high corrosive wear.

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, June 14, 1979,
506-16.

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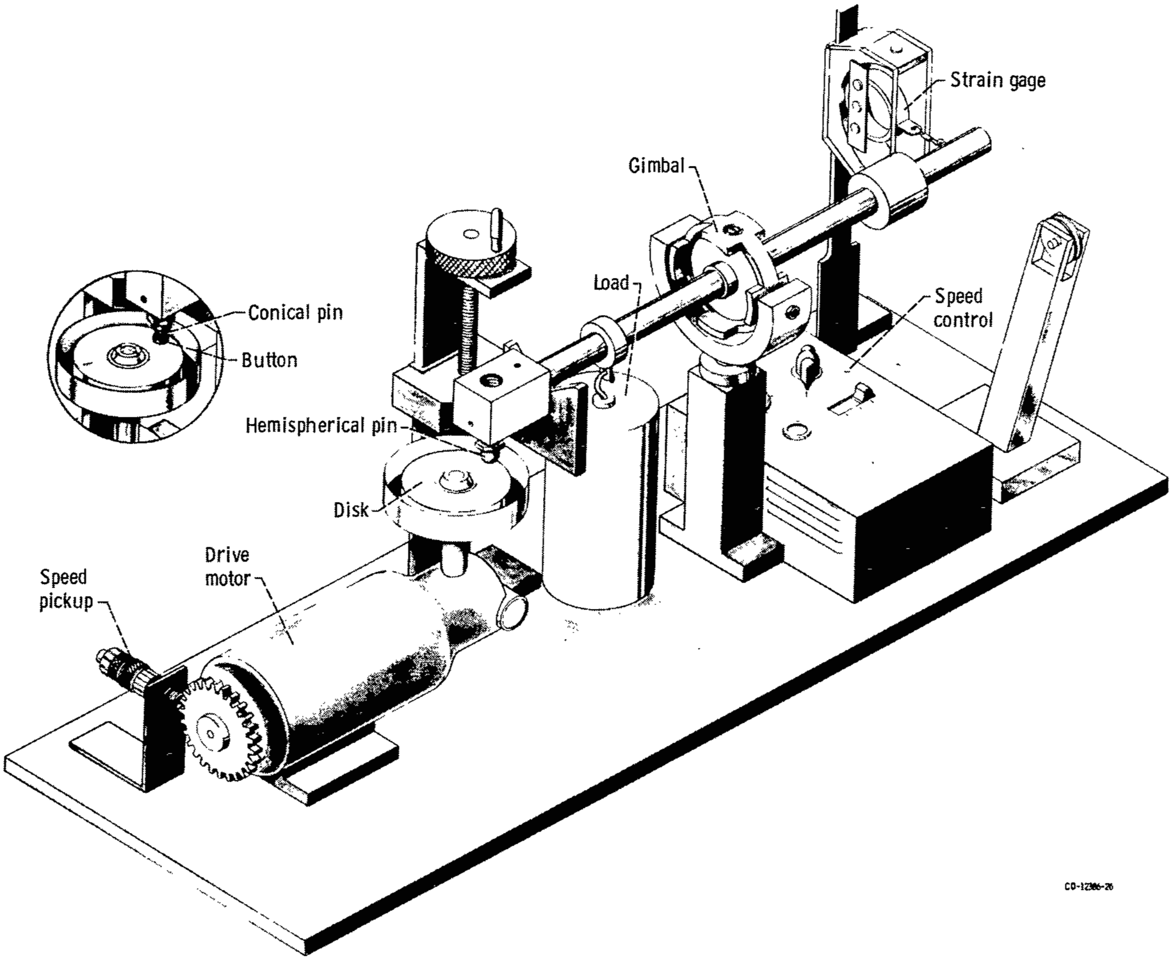


Figure 1. - Pin-on-disk friction and wear tester showing alternative rider configuration (inset).

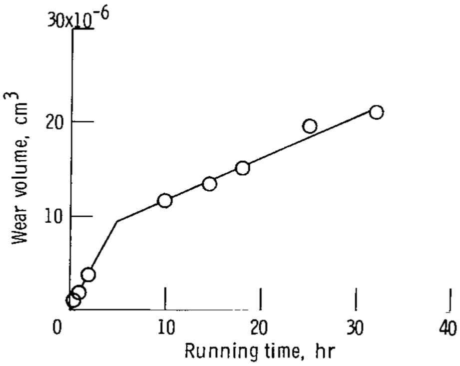
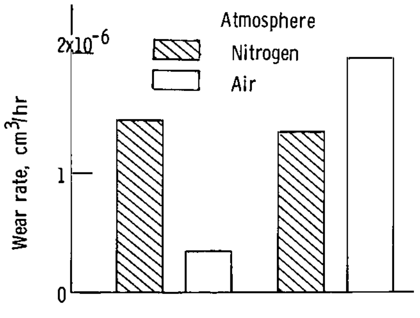
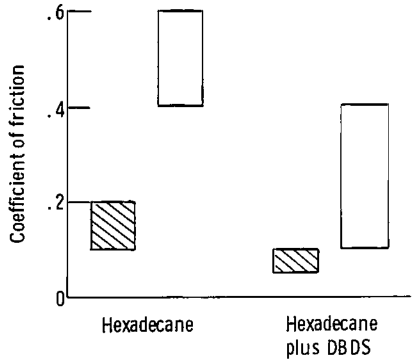


Figure 2. - Typical wear versus time curve. Iron rider on 52100 steel disk; lubricant, hexadecane; atmosphere; nitrogen; sliding speed, 3 rpm; load, 4.9 N (500 g).



(a) Wear rate.



(b) Coefficient of friction.

Figure 3. - Equilibrium wear and friction of iron rider on 52100 steel disk. Sliding speed, 3 rpm; load, 4.9 N (500 g); room

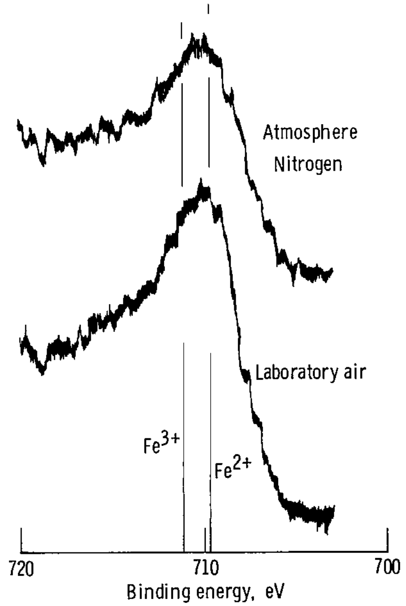


Figure 4. - Fe $2p_{2/3}$ peaks from wear scars. Lubricant, hexadecane; sputter etch duration, 30 seconds.

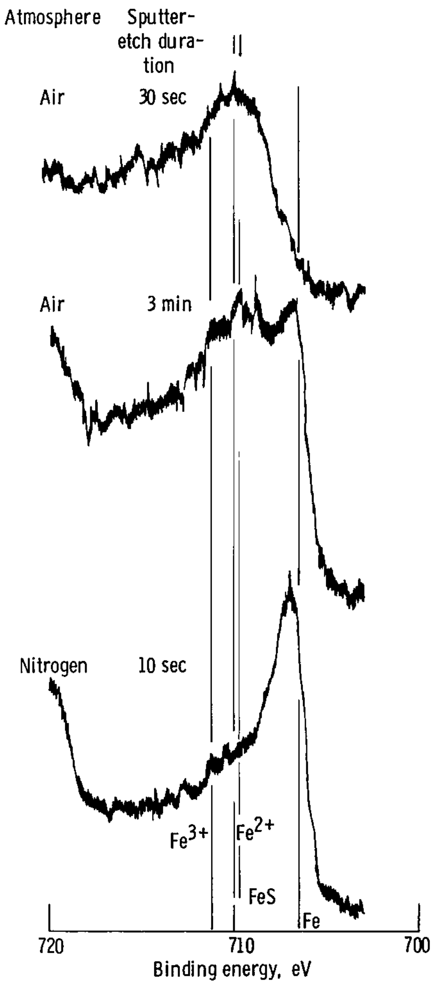
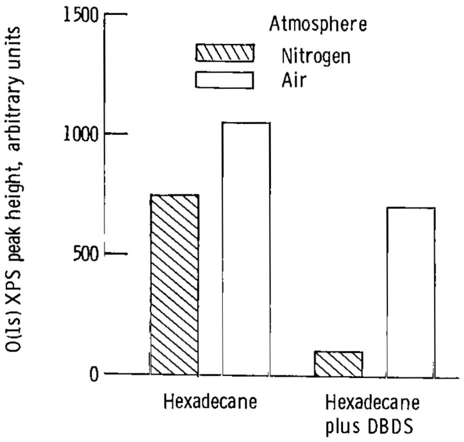
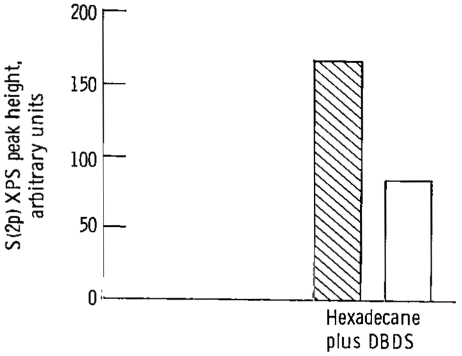


Figure 5. - Fe $2p_{3/2}$ peaks. Lubricant, hexadecane plus DBDS.



(a) O(1s) Peak heights, 530.0 eV.



(b) S(2p) Peak heights, 161.0 eV.

Figure 6. - Wear-scar composition (sufficient sputter etching to reach maximum in each constituent).

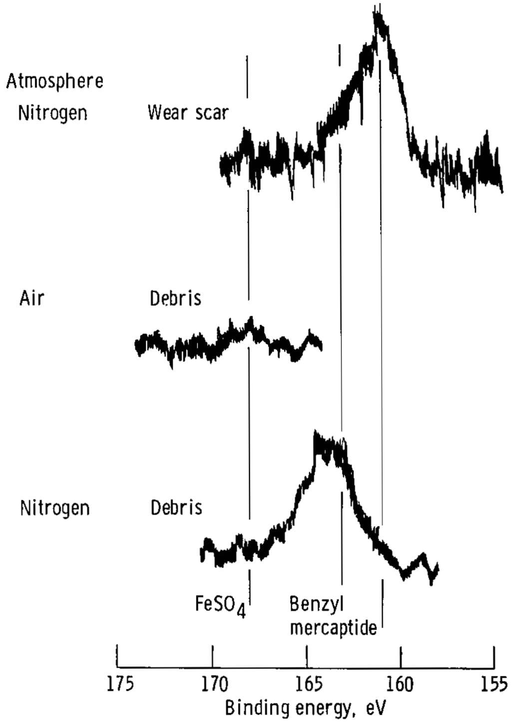


Figure 7. - S(2p) Peaks from wear debris and wear scar.

1. Report No. NASA TP-1545	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle SURFACE CHEMISTRY OF IRON SLIDING IN AIR AND NITROGEN LUBRICATED WITH HEXADECANE AND HEXADECANE CONTAINING DIBENZYL-DILSULFIDE		5. Report Date September 1979 6. Performing Organization Code
7. Author(s) Donald R. Wheeler		8. Performing Organization Report No. E-9956
9. Performing Organization Name and Address National Aeronautics and Space Administration Lewis Research Center Cleveland, Ohio 44135		10. Work Unit No. 506-16 11. Contract or Grant No.
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		13. Type of Report and Period Covered Technical Paper 14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

Wear experiments were conducted on iron sliding in hexadecane and hexadecane plus 1 weight percent dibenzyl-dilsulfide (DBDS) in atmospheres of air and nitrogen at room temperature. The wear scars and the wear debris were analyzed by X-ray photoelectron spectroscopy. The presence of air reduced wear but increased friction, while DBDS reduced friction but had little effect on wear except that the wear increased somewhat when DBDS was used in air. Wear-scar analysis indicated that oxygen and sulfur competed chemically for the surface, with the oxide predominating. Low wear was associated with a thick oxide layer and low friction with a thin predominantly sulfide layer. Analysis of the wear debris indicated the presence of a sulfate in the high wear case (hexadecane plus DBDS in air), and showed the presence of an organic sulfide in the low wear case (hexadecane plus DBDS in nitrogen).

17. Key Words (Suggested by Author(s)) Friction; Wear; Lubrication; Extreme-pressure additives; DBDS; X-ray photoelectron spectroscopy; ESCA	18. Distribution Statement Unclassified - unlimited STAR Category 23

19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 14	22. Price* A02

* For sale by the National Technical Information Service, Springfield, Virginia 22161

NASA-Langley, 1979

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