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Effect of Oxygen Concentration in ZDP Containing Oils on Surface Composition and Wear

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EFFECT OF OXYGEN CONCENTRATION IN ZDP CONTAINING OILS ON SURFACE COMPOSITION AND WEAR

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SUMMARY

A pin-on-disk wear study was performed with the lubricants dibutyl sebacate (DBS) and mineral oil (MO) with and without 1 weight percent zinc-dialkyl-dithiophosphatee (ZDP) as an additive. The pin was annealed pure iron and the disk was M-2 tool steel. The selected load and speed guaranteed boundary lubrication. The ambient atmospheric oxygen concentration in an oxygen-nitrogen mixture was varied from 0 percent to 20 percent in order to examine its relationship to ZDP effectiveness. Auger electron spectroscopy combined with argon ion bombardment (depth profiling) was used to determine surface elemental composition on the pin when tested in DBS with and without ZDP. The ambient atmosphere was found to cause large variations in wear rate and surface composition. With MO, ZDP reduced wear under all conditions, but had little advantage over oxides formed at 20 percent oxygen atmosphere. With DBS, ZDP reduced wear at 0 percent oxygen, but gave varied results at other oxygen concentrations. Depth profiling revealed sulfide formation at 0 percent oxygen and probably sulfates at 20 percent oxygen. The results are significant because varied oxygen concentrations can occur under actual lubricating conditions in practical machinery.

INTRODUCTION

Diesters have been used as synthetic lubricants since the 1940's. They have found widespread use primarily in the aircraft industry and more recently in the automotive industry as crankcase lubricants as that industry stressed improved fuel economy and alternative materials (refs. 1 and 2).

Most antiwear additive chemistry was originally developed for mineral oils, and attempts to use the same additives in synthetic fluids have not always been successful. In many cases, the antiwear additives did not provide the same wear protection in the synthetic fluid as in the mineral oil. Generally, little analytical work has been performed to relate surface chemistry to additive performance in diesters. In a study of diesters with additives, Brainard and Ferrante found that the ambient atmosphere greatly affected the wear and surface composition of an iron pin run in dibutyl sebacate (DBS) with and without ZDP as an additive (ref. 3). The specific ZDP additive was zinc-o-l'-di-n-pentylphosphorodithioate. The objective of the present investigation was to evaluate the information obtained from AES (Auger electron spectroscopy) with regard to wear with dibutyl sebacate (DBS) and zinc-dialkyl-dithiophosphate (ZDP), (zinc-o-l'-di-n-pentylphosphorodithioate) as an additive. In addition, wear of an iron pin with mineral oil as a lubricant and ZDP as an additive is included for comparison. A pin-on-disk apparatus was used to perform the wear studies. The ambient atmosphere was varied from dry nitrogen to dry air. AES analysis was performed on samples run with DBS as a lubricant.

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APPARATUS AND PROCEDURE

Wear Measurements

The wear experiments were conducted with a multiple-pin-on-disk device that is commonly used in friction and wear studies (fig. 1). The disks were hardened M-2 tool steel (61 Rockwell C) circumferentially ground to 4 to 8 rms with a diameter of 6.3 centimeters. The pins were hemispherically tipped pure (99.99 percent) annealed iron with a radius of 0.476 centimeter. The disk was mounted on a shaft driven by a slow-speed electric motor. The pin was loaded normal to the surface of the rotating disk; loading was achieved by hanging weights on the rider holder arm. A sliding speed of 2.5 centimeters per second and a load of 4.9 newtons (500 g) were used for all experiments. These conditions provided data that correlated with full-scale automobile engine tests in previously unreported work. The entire apparatus was contained in a clear plastic box that could be continuously purged with dry air or dry nitrogen in order to control the ambient atmosphere. All tests were performed at room temperature.

For each experiment, newly prepared pin and disk specimens were used. Both the pin and the disk were rinsed with acetone and then scrubbed with a moist paste of 1 micrometer aluminum oxide polishing compound. After the scrubbing, the specimens were rinsed with water and ethyl alcohol and then dried. After the disk was mounted in the apparatus, the disk surface was covered with a thin layer of mineral oil or DBS without any additive. A thin layer of lubricant was used rather than a lubricant reservoir so that equilibrium between the fluid and the atmosphere could be quickly obtained and the fluid would not need degassing.

The plastic box was closed and purged before the experiment. The oxygen concentration in the plastic box was then controlled by flowing dry air and/or dry nitrogen into the box. The oxygen concentration was varied by adjusting flow rates of oxygen and nitrogen. The oxygen content was sensed by an oxygen monitor. The gas mixtures used were 0, 0.2, 2, 5, 10 and 20 percent oxygen.

An electric timer was used to stop the test at predetermined times so that the wear scar diameter could be measured. An impression of the wear scar diameter was made by inserting a piece of aluminum foil between the pin and the disk and then pressing the pin down. The scar diameter was then measured with a vernier-equipped microscope. In this manner, the pin and disk were always returned to the original contact position after the wear measurement.

After several readings over a 40-hour period to ensure that the wear rate was constant (linear by volume), the run was stopped and the DBS or MO was replaced by fresh fluid containing 1 weight percent of ZDP. The run was then continued for 40 more hours to determine the wear rate with the additive present. After the run, the wear volume measurement was fitted by a least-squares method to a linear function of time; a typical wear volume versus time is shown in figure 2. The first 10 hours of each run were ignored to allow for the run-in of new specimens. This was necessary because wear-rate measurements during various phases of the experiment had revealed that the higher wear rate during run-in is not representative of long-term wear behavior.

Auger Analysis

After the wear tests, the pins were rinsed in Freon solvent to remove the residual lubricant. The pins were then mounted in an ultra-high vacuum system that attained a base pressure of $5x10^{-12}$ pascals ($5x10^{-10}$ torr). The 25-micrometer-diameter electron beam for Auger analysis was aimed at the wear scar on a given pin by using a scanning sample positioner.

The electron beam had an energy of 2000 electron volts, a constant beam current of 1.0 microampere, and a beam diameter of approximately 25 micrometers. The low beam current was maintained to minimize beam damage to the surface. After alinement, each sample was depth-profiled (i.e., argon ion beam-sputtered along with AES analysis), in order to obtain its elemental composition as a function of depth (ref. 4). The ion sputtering was performed with a beam energy equal to 3000 electron volts at constant beam current with an argon pressure of $5x10^{-7}$ pascals ($5x10^{-5}$ torr). A focused ion beam was used for depth profiling. The focused ion and electron beam were directed at a 2-millimeter-square aluminum tab. The ion-induced aluminum AES peaks were used to optimize the AES signal and thus aim the ion beam (ref. 5). The pin wear scar was then translated to the aluminum tab position. Since performing depth profiling on the bullets was quite difficult, AES depth profiles were limited to DBS experiments, which were felt to be the more interesting based on previous results (ref. 3).

RESULTS AND DISCUSSION

The results of the wear studies for the iron pin run in mineral oil with and without ZDP as an additive are shown in figures 3 and 4. The same curves for DBS as a base stock are shown in figures 5 and 6. The depth profiles of the pins run in DBS are shown in figures 7 and 8 for oxygen and sulfur, respectively.

Mineral Oil

The wear of iron in MO shown in figure 3 indicates that at low oxygen concentrations without additive, an unexpectedly low wear rate was observed. The results were repeatable with 0 percent oxygen, and a trend developed in the data as the oxygen concentration was varied. In addition, data for the checkpoint which was obtained after data reduction in a completely independent test verified the observations.

Acceptance of these results gives two possible explanations. First, at the low oxygen concentrations, contamination of the oil due to wear debris was taking place, since a flowing system was not used; later in the experiment, oxidation of the surface dominated the wear. Another explanation is that certain oxides, which produce a higher wear rate, may be preferentially formed. This latter explanation can be verified by performing X-ray photoelectron spectroscopy (XPS) studies (ref. 4). If we examine the wear rate with ZDP in MO in figures 3 and 4, we see that the ZDP maintains a relatively low wear rate over the whole oxygen concentration range. It provides no better wear protection than the MO with no additive at 0 percent oxygen or than the oxide coating formed at 20 percent oxygen with the MO and no additive. The results at intermediate exposures suggest that surface reaction films dominate the wear rather than decomposition of the lubricant. Apparently, surface compounds are formed with the ZDP at intermediate oxygen pressures which minimize wear. Brainard and Ferrante (ref. 3) have already shown that a difference in surface composition changes wear rate under similar conditions.

Dibutyl Sebacate

In figures 5 and 6, the results are presented for similar wear tests with dibutyl sebacate as the lubricant. Figures 7 and 8 present depth profiles for the wear surfaces giving oxygen and sulfur concentration as a function of depth on the same surfaces. The horizontal axis corresponds to approximately 10 angstroms per minute. A comparison of wear with and without ZDP again yields some surprising results. In this case, however, the AES depth profiles are available to aid in interpretation. Again there are trends in the data; the relatively small scatter and the fact that all tests were performed independently support the observed results.

At low oxygen concentrations, the presence of the ZDP gives a large reduction in wear (figs. 5 and 6). Examination of figures 7 and 8 reveals that the surface film is composed largely of iron-sulfur compounds. The oxygen sputters away rapidly, indicating that the outer surface was covered with a thin layer of oxygen that was simply the result of adsorption while transporting the specimen to the vacuum system in air. Consequently, the sulfur in the ZDP provides wear protection at low oxygen concentrations. No appreciable amounts of zinc or phosphorus were observed in the wear scars.

At 2 percent oxygen concentration, a large rise in the wear rate occurs both with and without ZDP. Examination of the depth profiles at 2 percent oxygen shows a much thinner surface film containing sulfur and an increased quantity of oxygen. The changes indicate that the presence of oxygen depletes the sulfur when certain compounds are present.

A surprising drop in wear occurs at 5 percent oxygen both with and without ZDP. The depth profiles indicate very thin surface films. No explanation is offered for this result.

At 10 percent oxygen the wear rate rises in both cases but is lower than at 2 percent oxygen. The surface films become thicker, but the quantity of sulfur is much lower than at 0, 2, or 20 percent oxygen, indicating that different compounds may be formed.

Finally, at atmospheric conditions (20 percent oxygen) the wear rate drops to a low level both with and without ZDP, again indicating that the oxide formed at atmospheric conditions is as effective as ZDP in reducing wear. If we examine the depth profiles for atmospheric conditions, we again see a marked change in surface composition. A thick film (possibly a sulfate), composed primarily of iron, sulfur, and oxygen is formed.

This preliminary study indicates that interesting and important results can be obtained by examining the effects of ambient conditions. Conditions can arise in lubricated contacts where oxygen depletion can occur, even though the ambient is apparently normal atmospheric air. As can be seen, both wear and the composition of the surface films formed can vary greatly with ambient atmospheric conditions. These results indicate that these studies should be pursued further.

More information concerning the repeatability of wear rates and surface compositions is desirable. Identification of the specific surface compounds present would be beneficial. Identification can be accomplished with X-ray photoelectron spectroscopy.

Obtaining results such as those reported herein, however, involves considerable difficulties. Both the wear tests and AES depth profiles are very time consuming. Consequently, any attempt to be comprehensive considering the number of possible lubricants, additives, and environments is almost impossible. Some selection of the most important systems must therefore be made.

CONCLUDING REMARKS

Examining the effects of ambient atmosphere on wear and surface composition of iron with a mineral oil lubricant and the additives dibutyl sebacate and zinc-dialkyl-dithiophosphate has produced some interesting results. Large variations in the composition of surface films and wear rates have been observed.

With mineral oil and ZDP as the additives, reduced wear under all oxygen concentrations was observed. However, the additive afforded no advantage over the effects of atmospheric oxygen (20 percent oxygen) present in ordinary air. With dibutyl sebacate, ZDP reduced wear at 0 percent ambient oxygen, but gave differing wear rates and surface compositions with variation in oxygen concentrations.

Where the oxygen concentration was equivalent to atmospheric oxygen (20 percent), the use of ZDP to reduce wear was of little advantage. Further studies are needed relative to the effects of oxygen concentration on additive effectiveness. Many operating parameters and conditions in real systems can result in increased wear. These parameters and conditions should be studied further.

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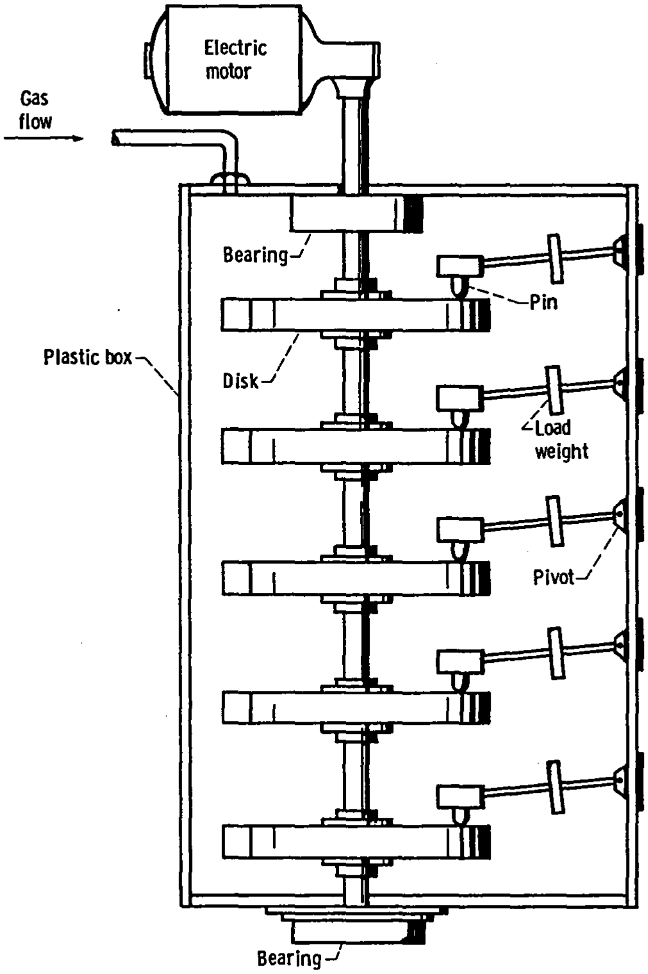

Figure 1. - Multiple-pin-on-disk wear testing apparatus.

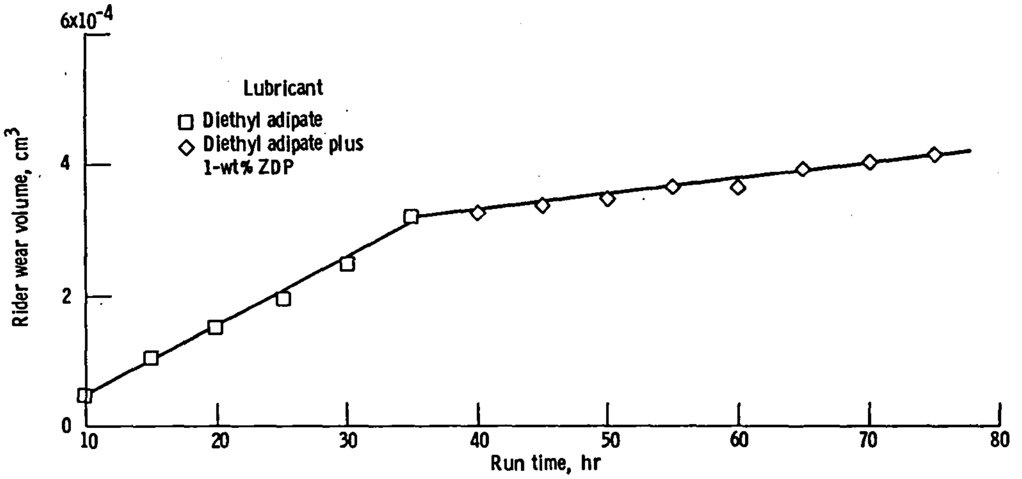

Figure 2. - Wear volume as function of time for pure iron sliding on M-2 tool steel. Sliding velocity, 2.5 cm/sec; load, 4.9 newtons; atmosphere, dry air; lubricant, diethyl adipate (ref. 3).

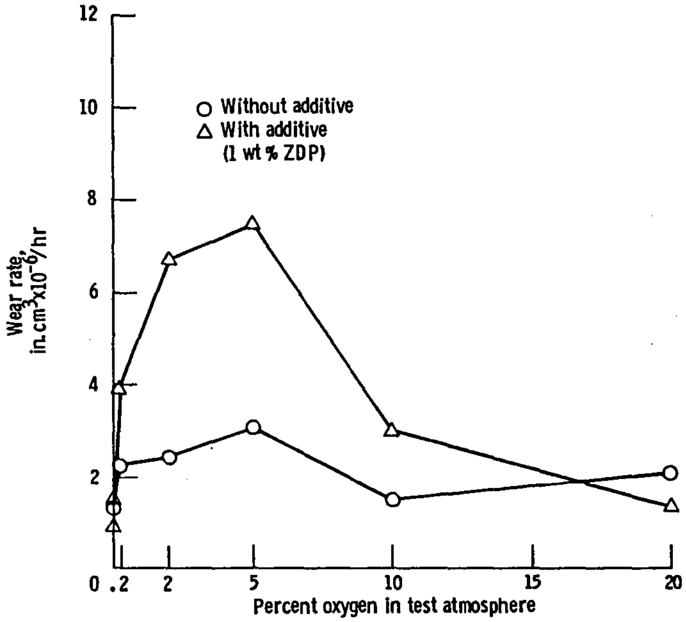

Figure 3. - Wear rate as a function of atmospheric oxygen concentration for pin in mineral oil with & without additive at a load of 5 Newtons and sliding speed of 2.5 cm/sec.

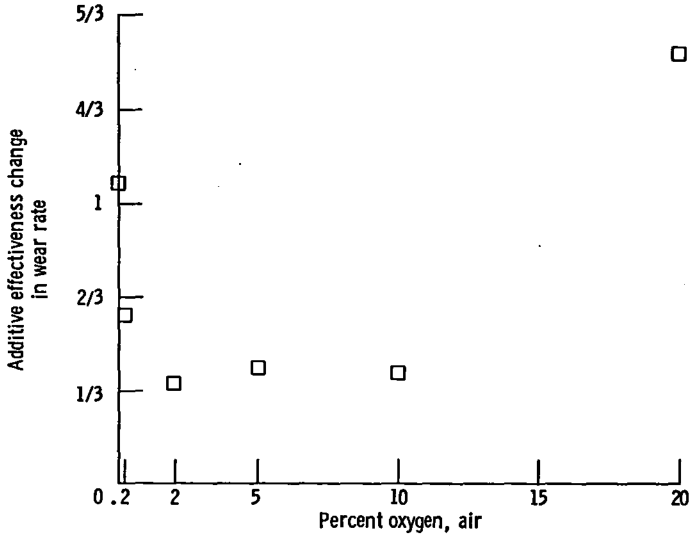

Figure 4. - Wear rate change for ZDP added to mineral oil lubricating pure iron at a load of 5 newtons, 2.5 cm/sec.

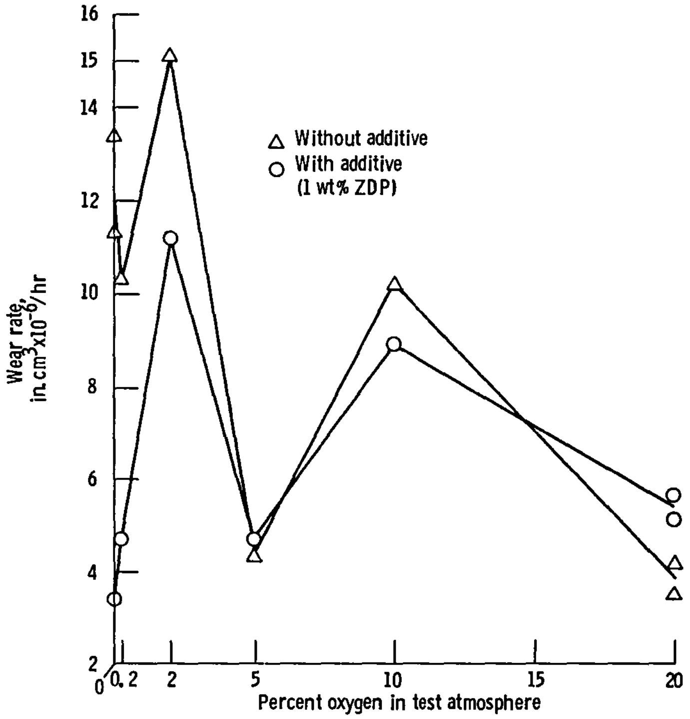

Figure 5. - Wear rate as a function atmospheric oxygen concentration for pin in dibutyl sebacate with and without additive for a load of 5 newtons and sliding speed of 2.5 cm/sec.

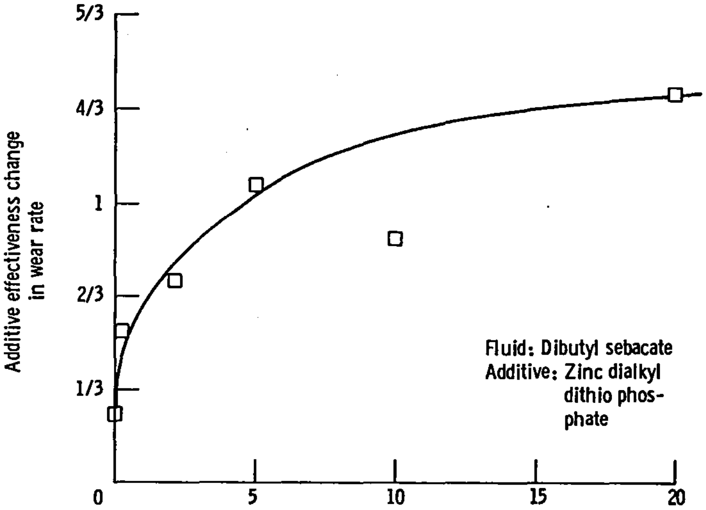

Figure 6. - Wear rate change for ZDP added to dibutyl sebacate lubricating pure iron at a load of 5 newtons, 2.5 cm/sec.

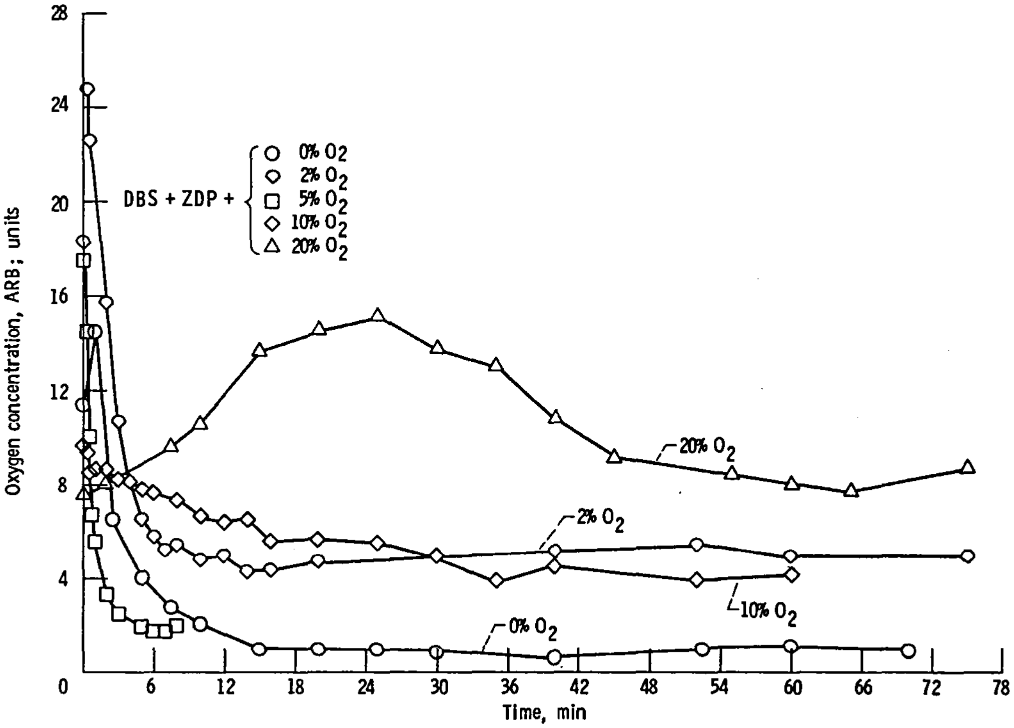

Figure 7. - Oxygen AES depth profiles of an iron pin run in dibutyl sebacate with 1 w/o zinc-dialkyl-dithio phosphate as an additive for various oxygen concentrations in an oxygen-nitrogen mixture. (1 min approximately equivalent to 10 A^{0}).

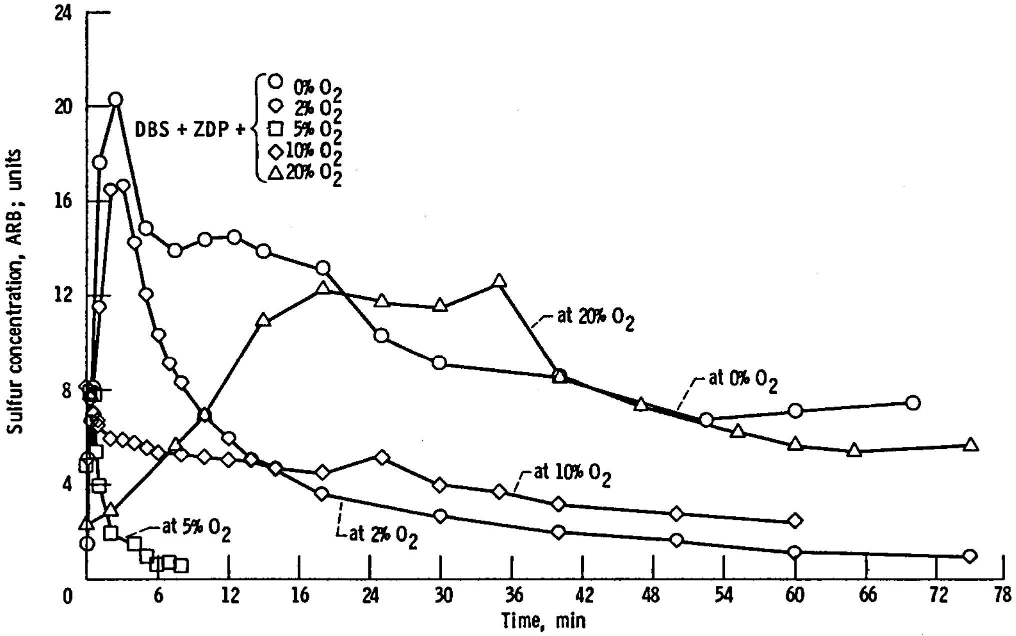

Figure 8. - Sulfur AES depth profiles of an iron pin run in bibutyl sebacate with 1 w/o zinc dialkyl–dithio phosphate as an additive for various oxygen concentrations in an oxygen nitrogen mixture. (3 min approximately = $10A^0$).

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16. Abstract

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