The Effect of Dissolved Water on the Tribological Properties of Polyalkylene Glycol and Polyolester Oils

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ACRC TR-70

November 1994

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Prepared as part of ACRC Project 04
Compressor--Lubrication, Friction, and Wear
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THE EFFECT OF DISSOLVED WATER ON THE TRIBOLOGICAL PROPERTIES OF POLYALKYLENE GLYCOL AND POLYOLESTER OILS

Willem Van Glabbeek, Todor Sheiretov, and Cris Cusano

ABSTRACT

The effect of water dissolved in polyalkylene glycol and polyolester oils on the tribological behavior of two material contact pairs in three test environments is evaluated. The material contact pairs are M2 tool steel against 390 aluminum and M2 tool steel against gray cast iron. The three oils are a polyalkylene glycol (PAG) and two polyolester (PE1 and PE2) oils. The test environments are R134a, air and argon. The tests are conducted in a specially designed high pressure tribometer which provides an accurate control of the test variables.

The results indicate that the PAG oil performed better than the esters for both material contact pairs. The wear on the aluminum plates for the tests conducted with the PAG oil in all three environments is greatest at the lowest moisture content levels. From the standpoint of friction and wear, it is beneficial to have a water content level of 5000 ppm or greater in the PAG oil when the plate material is 390 aluminum. The wear on the cast iron plates, when using a PAG oil as the lubricant showed a slight increase with water content in a R134a environment. This trend is opposite when air is the test environment.

Both ester oils lubricated aluminum much better than the cast iron. The difference in the amount of wear can be as high as two orders of magnitude. This is probably due to the ability of the esters to form bidentate bonds with aluminum. Esters do not form such bonds with iron. The plate wear is greater for the PE1 tests than for the PE2 tests for both material contact pairs. This is most likely due to the difference in the viscosity of the oils. In PE2 oil, water does not seem to affect the friction and wear of both aluminum/steel and cast iron/steel contacts when R134a is the test environment. On the contrary, for the aluminum/steel contacts, the water content significantly influences wear when argon or air is the test environment. For the cast iron/steel contacts, the wear is strongly influenced by the water content when the test is conducted in argon, but it is not influenced by the water content when the test is conducted in air.
1. INTRODUCTION

1.1 Overview

For many decades CFC refrigerants have been used extensively in automotive air conditioning compressors and many stationary refrigeration systems. Numerous studies have indicated that the chlorine containing hydrocarbons are one of the major factors that cause the observed depletion of the ozone layer. The decrease in production and use of dichlorofluoromethane (R12), which was required by the Montreal Protocol, has forced the development of replacement refrigerants with thermodynamic properties similar to those of the CFC's. For replacement refrigerants intended to operate in small refrigerators and air conditioners, the miscibility of the refrigerants with lubricants and their tribological characteristics is an important factor. These refrigerant characteristics are essential for an extended operational life of the compressor components.

The primary replacement for R12 is tetrafluoroethane (otherwise designated as R134a). R134a lacks the inherent antiwear properties of the chlorinated refrigerants and is not miscible with the mineral and alkylbenzene oils, which are the lubricants presently used with R12. Within certain temperature and pressure ranges, R134a is miscible with special synthetic lubricants including some polyolester (PE) and polyalkylene glycol (PAG) oils. The tribological properties of R12/oil mixtures are generally not matched by base polyolester and polyalkylene glycol oils. R12 is a good lubricant by itself and enhances the performance of the oil, while R134a does not seem to possess any lubricative properties. This effect is more pronounced for contacts in which the boundary lubrication prevails.

The lubricant in refrigerant systems has an important role in the overall system efficiency. This is due to the direct interaction of the lubricant and refrigerant within the compressor as well as other parts of the system. Performance properties of synthetic lubricants for R134a have been investigated and found to be a necessary alternative to mineral oils [1]. R134a has been shown to act more like an inert gas than R12 [2]. In inert atmospheres, the friction and wear characteristics of materials become more sensitive to small amounts of active impurities [3]. Since automotive air conditioners have seals and rubber tubings, some impurities such as water may enter the system. During their storage, synthetic oils may pick up some water from the atmosphere, thereby increasing its water content level. There is some concern as to how this water, which is dissolved in the oil, will affect the friction and wear properties of the critical tribo-contacts. It is the goal of this study to determine how the friction and wear properties change when a small amount of water, up to the saturation limit, is dissolved in the oil.
1.2 Scope of Research

This research was conducted as a part of a larger project which involves the study of various tribological problems arising from the replacement of the CFC's by ozone-safe refrigerants. This study is a continuation of previous work which treated similar problems [4, 5].

The primary goal of this study is to determine how the friction and wear properties of the material contact pair used in compressors change when a small amount of water up to its saturation limit is dissolved in the oil. The materials used are hardened M2 tool steel for the pin specimen and 390 aluminum and gray cast iron for the plate specimens. The oils under study are polyalkylene glycol and polyolester oils. The refrigerant used is R134a.

Section 2 gives the description of the tests including the contact geometry, material properties, lubricant properties, and operating conditions. Section 3 provides the results, and Section 4, a discussion of the results. Appendix A gives a brief explanation of the apparatus used, the high pressure tribometer (HPT). Appendix B provides an explanation of the procedures involved when conducting the friction and wear tests, Appendix C explains what data measurements were taken, and Appendix D provides information about the structure of various chemical compounds.

2. DESCRIPTION OF THE EXPERIMENTS

2.1 Apparatus

The accurate control of the test environment is of primary importance for the tests conducted in this study. Therefore, all tests were conducted in a specially designed high pressure tribometer (HPT). In the HPT, the test is conducted within the confines of a pressure chamber in which a precise control of the test temperature and pressure is achieved. For the tests conducted, the specimens were completely submerged in the lubricant tested. A more detailed description of this apparatus is given in Appendix A.

2.2 Geometry of Contact

The geometry of contact was chosen in order to be able to consistently and accurately compare data from one test to the next and to obtain measurable wear on the surfaces of the specimens. The contact is between a cylindrical pin and a flat disk. A representation of the contact geometry is given in Fig. 1.
2.3 Materials of the Specimens

The pin is made from hardened M2 tool steel, while the plate is either 390 aluminum or gray cast iron. The 390 aluminum (76.15 Al, 17.0 Si, 1.3 Fe, 4.5 Cu, 0.1 Mn, 0.55 Mg, 0.1 Zn, 0.2 Ti, and 0.1 other elements [6]) is a die cast hypereutectic aluminum-silicon alloy which has an increased hardness over the 380 alloys [7]. It has found many useful applications in recent years, especially for heavy wear uses (including swash plates for automotive air conditioning compressors). The 390 alloy uses a heat treatment process with a T6 temper in which the solution treatment is at a temperature of 495 °C (925 °F), and the aging treatment is at a temperature of 175 °C (350 °F) for 8 hours [8]. The gray cast iron is an alloy of iron, carbon, and silicon in which more carbon is present than can be retained in solid solution in austenite at the eutectic temperature [9]. The carbon that exceeds the solubility in austenite precipitates as flake graphite. Gray irons contain 2.5 to 4% C, 1 to 3% Si, and small amounts of manganese. The gray cast iron used in this study was not heat treated. The relevant geometrical and material data are shown in Table 1.

| Table 1 - Geometry, Material, and Surface Characteristics of the Specimens |
|----------------------------------|---------------------------------|-----------------|
| Geometry                         | Upper Specimen                  | 76.2 mm (3 in.) Ø, Flat Disk |
|                                  | Lower Specimen                  | 6.35 mm (0.25 in.) Ø, Length = 9.5 mm (0.375 in.) |
| Material                         | Upper Specimen                  | 390 Aluminum (Al), Gray Cast Iron (CI) |
|                                  | Lower Specimen                  | M2 Tool Steel |
| Average Hardness                 | Upper Specimen                  | Al: 166 HB (85 RB), CI: 307 HV (31 RC) |
|                                  | Lower Specimen                  | 789 HV (64 RC), |
| Average Surface Finish           | Upper Specimen                  | Al: 0.038 µm Ra, CI: 0.056 µm Ra |
|                                  | Lower Specimen                  | 0.215 µm Ra |
2.4 Surface Characteristics of the Specimens

The surface roughness of the aluminum and gray cast iron plates was measured before each test using a stylus surface profiler as explained in Appendix C.2. The aluminum plates were ground to an average surface roughness of 0.038 μm, while the gray cast iron plates were ground to an average surface roughness of 0.056 μm. The range in the surface roughness readings for the whole set of plates used in the tests was from 0.028 to 0.047 μm for the aluminum plates and 0.026 to 0.117 μm for the gray cast iron plates.

The surface hardness of the aluminum and gray cast iron plates was measured after each test using a Brinell Hardness Tester for the aluminum plates and a Vickers Hardness Tester for the cast iron plates as explained in Appendix C.3. The designations for the Brinell and Vickers Hardness are HB and HV respectively. The aluminum plates had an average surface hardness of 166 HB while the gray cast iron plates had an average surface hardness of 307. HV. The range in surface hardness readings for the whole set of plates used in the tests was from 160 to 170 HB for the aluminum plates and 243 to 373 HV for the gray cast iron plates. Note that in this range of hardness, the Vickers scale and the Brinell scale are identical.

The surface roughness of the M2 tool steel pins was measured before each test using a stylus surface profiler as explained in Appendix C.2. The pins were ground to an average surface roughness of 0.215 μm with a range of 0.167 to 0.283 μm. The average value of the hardness for the pins was 789 HV (64 RC), and the range of the surface hardness was from 664 to 940 HV.

2.5 Test Conditions

The tests using the M2 tool steel pins against 390 aluminum plates were conducted under different conditions than the M2 steel against gray cast iron. These conditions are given in Table 2. Boundary lubrication conditions existed for both the aluminum and the cast iron tests.

<table>
<thead>
<tr>
<th>Operating Conditions</th>
<th>390 Aluminum Tests</th>
<th>Gray Cast Iron Tests</th>
</tr>
</thead>
<tbody>
<tr>
<td>Max. Contact Pressure, MPa (psi)</td>
<td>910 (132,000)</td>
<td>1100 (160,000)</td>
</tr>
<tr>
<td>Type of Motion</td>
<td>Unidirectional</td>
<td>Unidirectional</td>
</tr>
<tr>
<td>Speed, m/s (fpm)</td>
<td>0.30 (58.9)</td>
<td>0.35 (68.7)</td>
</tr>
<tr>
<td>Environmental Pressure, MPa (psig)</td>
<td>0.34 (50)</td>
<td>0.34 (50)</td>
</tr>
<tr>
<td>Environmental Temperature, °C (°F)</td>
<td>21 (69)</td>
<td>21 (69)</td>
</tr>
</tbody>
</table>
Data on the lubricants used are given in Table 3. These lubricants were tested with various amounts of water dissolved in them. By adding to or extracting water from the oil supplied by the manufacturers the water content in the oil could be varied over a wide range. The exact value of the water content was obtained by the Karl Fischer (Aquametry) Method using a "Dead-Stop" Technique [10]. This procedure follows the standard ASTM E293-92a method and is described in more detail in Appendix B.

<table>
<thead>
<tr>
<th>Oil</th>
<th>Oil Type</th>
<th>Family *</th>
<th>Approx. Water Saturation Limit</th>
<th>Viscosity (cS) @ 21°C</th>
<th>Viscosity (cS) @ 40°C</th>
<th>Viscosity (cS) @ 100°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAG</td>
<td>Polyalkylene glycol</td>
<td>Mono</td>
<td>18,000 ppm</td>
<td>213.5</td>
<td>135.0</td>
<td>25.0</td>
</tr>
<tr>
<td>PE1</td>
<td>Polyolester</td>
<td>PEE</td>
<td>4500 ppm</td>
<td>39.8</td>
<td>23.9</td>
<td>4.9</td>
</tr>
<tr>
<td>PE2</td>
<td>Polyolester</td>
<td>PEE</td>
<td>2000 ppm</td>
<td>201.0</td>
<td>91.4</td>
<td>10.2</td>
</tr>
</tbody>
</table>

* PEE - Pentaerythritol ester; Mono - Monoether, Base Oil

The environments for the tests in this study were: (a) R134a refrigerant having a purity 99.9% in the liquid phase and 98.5% in the vapor phase, (b) compressed air, and (c) argon, with a purity of 99.995%. Most of the tests were conducted under a R134a environment which represents the nominal tests conditions. Limited number of tests were conducted under air and argon for comparative purposes. The environmental pressure in all the tests was kept at 50 psig, as indicated in Table 2.

2.6 Test Procedure, Measurements and Analyses

After the specimens were cleaned and installed into the pressure chamber of the HPT, the chamber was closed and purged to a vacuum of at least 200 μm Hg. Then the test environment, R134a, argon, or air was supplied from a pressure vessel. Finally, the lubricant was injected under high pressure into the chamber with a specially constructed apparatus. In cases when R134a was used as the test environment, the refrigerant was allowed to dissolve into the oil for one hour prior to the initiation of the test. A more detailed description of the test procedure is given in Appendix B.

The friction coefficient was monitored and recorded constantly throughout the test by a computer-based data acquisition system. The wear on the plates was determined by measuring the wear scar depth with a stylus surface profiler. A micrometer was used to measure the wear on the plates which have wear scar depths greater than 100 μm. These depths were outside the
measuring range of the profiler. Appendix C provides more information on the measurements used to obtain the data.

In addition to measuring the friction and the wear, other experimental techniques were used to examine the surfaces of the worn specimens and to study oil samples taken after the test. The surface analysis methods used were Scanning Electron Microscopy (SEM) and Auger Electron Spectroscopy (AES). AES was used for semi-quantitative analysis and depth profiling of the major constituent element species on the surface. The oil samples were analyzed by a commercial oil testing company. The methods used were Direct Reading Ferrography, Particle Count, Elemental Analysis (RDE), Infrared Chemical Analysis (FT-IR), and Neutralization Number (TAN/TBN).

3. RESULTS

3.1 Friction and Wear Results for the Tests Conducted in R134a

Tests were conducted with the M2 tool steel pins against the 390 aluminum and the gray cast iron plates. As expected, the wear mainly occurred on the plates rather than on the M2 tool steel pins, since the tool steel is much harder than both the aluminum and the gray cast iron. All wear data presented are obtained from the plate.

(a) M2 Tool Steel Pin Against 390 Aluminum in PE1 Oil

The saturation limit of water in this ester base oil is approximately 4500 ppm at room temperature. The tests with the PE1 oil were conducted in water contents ranging from about 50 to 3500 ppm to insure that no separation of water from the oil would occur. The wear on the plate as a function of the water content in the oil is given in Fig. 2a. The amount of water into the oil does not seem to significantly affect wear. The coefficient of friction as a function of the water content is given in Fig. 3a. The coefficient of friction ranged from 0.069 to 0.099 with an average value of 0.086.

(b) M2 Tool Steel Pin Against Gray Cast Iron in PE1 Oil

These tests were conducted in water contents ranging from about 50 to 1700 ppm. The wear on the plate as a function of the water content in the oil is given in Fig. 2b. The wear on the gray cast iron plates in the PE1 was approximately two orders of magnitude greater than the wear on the aluminum plates using the same oil. The wear on the plates is approximately the same at all water levels. The coefficient of friction as a function of the water content in the oil is given in Fig. 3b. The coefficient of friction was approximately the same for all levels of water, ranging from 0.092 to 0.096 with an average value of 0.095.
Fig. 2 - Wear on the Plate as a Function of the Water Content in R134a Environment
(a) 390 Aluminum in PE1 Oil, (b) Gray Cast Iron in PE1 Oil, (c) 390 Aluminum in PE2 Oil, (d) Gray Cast Iron in PE2 Oil, (e) 390 Aluminum in PAG Oil, (f) Gray Cast Iron in PAG Oil
Fig. 3 - Coefficient of Friction as a Function of the Water Content in R134a Environment
(a) 390 Aluminum in PE1 Oil, (b) Gray Cast Iron in PE1 Oil, (c) 390 Aluminum in PE2 Oil, 
(d) Gray Cast Iron in PE2 Oil, (e) 390 Aluminum in PAG Oil, (f) Gray Cast Iron in PAG Oil
(c) M2 Tool Steel Pin Against 390 Aluminum in PE2 Oil

The saturation limit of water in this higher viscosity ester base oil is approximately 2000 ppm. The tests with the PE2 were conducted in water contents ranging from about 70 to 1600 ppm. The wear on the plate as a function of the water content in the oil is given in Fig. 2c. The wear on the plates was approximately the same for all water content levels. The coefficient of friction as a function of the water content is given in Fig. 3c. The friction coefficient ranges from 0.096 to 0.101, and is fairly steady with an average value of 0.099.

(d) M2 Tool Steel Pin Against Gray Cast Iron in PE2 Oil

These tests were also conducted in water contents ranging from about 70 to 1600 ppm. The wear as a function of the water content in the oil is given in Fig. 2d. The wear on the cast iron plates was almost two orders of magnitude greater than the wear on the aluminum plates tested with the same oil. The wear on the cast iron plates was approximately the same for all water content levels. The coefficient of friction as a function of the water content in the oil is given in Fig. 3d. The friction coefficient ranges from 0.101 to 0.104, and is fairly constant with an average value of 0.103. The higher viscosity PE2 oil performed slightly better than the PE1 as far as the wear is concerned.

(e) M2 Tool Steel Pin Against 390 Aluminum in PAG Oil

The saturation limit of water in the PAG is 18,000 ppm which is much higher than in the esters. The tests with the PAG were conducted in water contents ranging from about 200 ppm to the saturation limit of about 18,000 ppm. The wear on the plate as a function of the water content is given in Fig. 2e. The wear is greatest at the lowest water levels and then decreases as the water level increases up to a value of 5000 ppm. The coefficient of friction as a function of the water content in the oil is given in Fig. 3e. The trend of the coefficient of friction is similar to the wear on the plate. The coefficient of friction is high at the very low water levels and lower at the higher water levels, ranging from 0.068 to 0.097. Some scatter in the data for the coefficient of friction is present, but a trend definitely exists.

(f) M2 Tool Steel Pin Against Gray Cast Iron in PAG Oil

These tests were also conducted in water contents ranging from about 200 ppm to the saturation limit of about 18,000 ppm. The wear on the plate as a function of the water content is given in Fig. 2f. The wear on the plates increased as the water content increased. The wear on the cast iron plates with this oil was two orders of magnitude lower than the wear obtained with both the PE oils. The coefficient of friction as a function of the water content in the oil is given in Fig. 3f. The coefficient of friction increased with increasing water content, ranging from 0.085 to 0.096 with an average value of 0.091.
3.2 Friction and Wear Results for the Tests Conducted in Air and Argon

In addition to the tests conducted in R134a, tests in air and argon were conducted as well. Since these tests were for comparison purposes, only two water content levels were tested with each lubricant and materials contact pair. The values of the water content for the lubricants tested are given in Table 4.

Table 4 - Water Contents in the Lubricants Tested in Various Environments

<table>
<thead>
<tr>
<th>Lubricant</th>
<th>Low Water Content</th>
<th>High Water Content</th>
</tr>
</thead>
<tbody>
<tr>
<td>PE1</td>
<td>70 ppm</td>
<td>1600 ppm</td>
</tr>
<tr>
<td>PE2</td>
<td>70 ppm</td>
<td>1600 ppm</td>
</tr>
<tr>
<td>PAG</td>
<td>200 ppm</td>
<td>17000 ppm</td>
</tr>
</tbody>
</table>

The choice of the environments for the tests was based on their oxidizing ability. Compressed air is the environment with the highest oxidizing ability. The R134a is considered the least oxidizing environment because of the very high solubility of R134a in the lubricants tested. The refrigerant displaces the less soluble gases from the oils, which probably makes the diffusion of oxygen to the rubbing surfaces negligible. In both the argon and the R134a environments, small amounts of oxygen existed as an impurity.

The friction and wear data for the tests conducted in air and argon are given in Fig. 4 and Fig. 5. In these figures, data for the tests conducted in R134a under similar water content conditions are also shown. From these figures, it is evident that the friction and wear behavior varies with the materials, test environment, type of lubricant used and the amount of water in the oil. It is also clear that the tests conducted in argon produced friction and wear results which are intermediate between tests conducted in R134a and air.

For all environments, the wear on the aluminum plates decreased with the water content when the PAG oil was used as the lubricant. For the cast iron plates, the water seems to have a slight adverse effect in PAG oil + R134a, and a beneficial effect in PAG + air. The PE2 oil, on the other hand, seems not to be sensitive to the amount of water for both the cast iron and aluminum plates when R134a is the test environment, but to be very sensitive when oxygen is present.

The variations in the friction coefficient are less pronounced but in most cases they follow the same trends as the wear on the plate. The coefficients of friction reported in Fig. 5 are time averages for the whole test. In most of the tests the coefficient of friction was almost constant throughout the test with a slight decreasing tendency. In some tests, however, it decreased rapidly in the first few minutes and then attained a steady value. Some typical records of the coefficient of friction are shown in Fig. 6.
Fig. 4 Wear Results for the Tests Conducted In Various Environments
(a) Wear on the 390 Aluminum Plate, and (b) Wear on the Gray Cast Iron Plate
Fig. 5 Coefficient of Friction for the Tests Conducted In Various Environments
(a) M2 Steel/390 Aluminum, and (b) M2 Steel/Gray Cast Iron
Fig. 6 - Typical Records of the Coefficient of Friction
(a) M2 Steel/390 Aluminum Tested in Air and PE2 Oil with 70 ppm Water,
(b) M2 Steel/390 Aluminum Tested in R134a and PE2 Oil with 56 ppm Water,
(c) M2 Steel/Gray Cast Iron Tested in Air and PAG Oil with 20,000 ppm Water.
The record given in Fig. 6a is representative of the cases when the coefficient of friction remained high up to the end of the test. This behavior was associated with high wear and high roughness of the wear scar. The record shown in Fig. 6b was typical for the aluminum plates tested in R134a. The coefficient of friction showed a rapid decrease in the beginning of the test which probably corresponds to the wearing off of the preexisting oxide layer. The record shown in Fig. 6c was typical for the majority of the tests conducted on cast iron plates.

3.3 Surface Morphology of the Specimens

For aluminum plates lubricated with the PAG oil, a large difference in the amount of wear was obtained between the low and high water levels. Large difference in the wear results was also obtained with specimens tested in PE oils when the environment was changed from R134a to air and argon. In order to better understand the friction and wear behavior of the aluminum specimens, both the virgin and worn surfaces of several aluminum plates were examined using a Scanning Electron Microscope (SEM) and an Auger Electron Spectroscopy (AES). Data for the specimens tested is given in Table 5. The specimens examined with the SEM were #31 and #35. The objective was to find out if there are any differences in the surface morphology of the aluminum plates after having been tested in different amounts of water.

<table>
<thead>
<tr>
<th>Specimen</th>
<th>Wear, ( \mu m )</th>
<th>Wear Scar Roughness, ( \mu m \text{ Ra} )</th>
<th>Lubricant</th>
<th>Water Content, ppm</th>
<th>Environment</th>
</tr>
</thead>
<tbody>
<tr>
<td>#31</td>
<td>0.76</td>
<td>0.12</td>
<td>PAG</td>
<td>14600</td>
<td>R134a</td>
</tr>
<tr>
<td>#35</td>
<td>9.65</td>
<td>0.45</td>
<td>PAG</td>
<td>600</td>
<td>R134a</td>
</tr>
<tr>
<td>#114</td>
<td>2.73</td>
<td>0.27</td>
<td>PE2</td>
<td>56</td>
<td>R134a</td>
</tr>
<tr>
<td>#116</td>
<td>25.0</td>
<td>0.84</td>
<td>PE2</td>
<td>56</td>
<td>Air</td>
</tr>
<tr>
<td>#125</td>
<td>3.34</td>
<td>0.23</td>
<td>PE2</td>
<td>2000</td>
<td>Air</td>
</tr>
</tbody>
</table>

Figure 7 shows the virgin and worn surface of aluminum plate #31 at 400 X magnification. Some dark areas exist on the virgin surface, one of which is marked number 1 in Fig. 7a. The survey spectrum showed that these dark areas consist primarily of silicon. The white surfaces marked 2 in Fig. 7a are found to contain large amounts of copper. Some small pits exist on the virgin surface shown in Fig. 7a. These pits generally lie on the edges of the dark silicon regions. Larger and more pits are seen on the worn surface than on the virgin surface indicating that during the wear process the dark silicon grains are extracted from the surface of the aluminum plate. Figure 8a,b shows the pits on the worn surface of plate #31 at
150 X and 1000 X magnifications. The survey spectrum for the smooth area on the worn surface showed that it is composed primarily of aluminum with silicon and copper present as well. The survey spectrum for the pit, on the other hand, showed that it is composed primarily of silicon.

Both dark and white regions exist on the virgin surface of plate #35, similar to that of plate #31. Figure 8c,d shows the worn surface of aluminum plate #35 at 150 X and 1000 X magnifications. Pits again are seen on the worn surface of the aluminum plate and can be attributed to the removal of the silicon from the surface. The pits are larger and greater in number.

The same two specimens on which an SEM analysis was performed were used in the AES analysis. With the AES a depth profile of the major elements in the metal can be obtained up to a depth of approximately 2.5 μm. An AES analysis was performed on the virgin surface before sputtering, on the worn surface before sputtering, and on the worn surface after sputtering. For both specimens, approximately the same amounts of aluminum, silicon, sodium, carbon, and oxygen are present on the virgin surface and on the worn surface before sputtering. The worn surface after sputtering contains less oxygen than before sputtering, and also contains some copper which was not present before sputtering.
Fig. 8 - SEM Micrographs of the Worn Surface of 390 Aluminum Plates Tested in a Mixture of R134a and PAG Base Oil
(a) Plate #31, 150 X Mag. (b) Plate #31, 1000 X Mag.
(c) Plate #35, 150 X Mag. (d) Plate #35, 1000 X Mag.
From the AES depth profile for plate #31 given in Fig. 9a, it is seen that the amount of carbon decreases and the amount of aluminum increases with the depth. The amount of oxygen is quite large up to a depth of about 0.25 µm where it drops off to a level which is considered in the noise range of the AES. This suggests that there may be an aluminum oxide formed on the surface of the plate which has a thickness of approximately 0.25 µm.

From the AES depth profile for plate #35 given in Fig. 9b, it is seen that the amount of carbon decreases rapidly up to a depth of 0.2 µm, after which it remains at a concentration level which is considered to be in the noise range. The concentration of aluminum steadily increases with the depth. The amount of oxygen steadily decreases with the depth, but is still present at a depth of 2.5 µm which is the limit of the AES. This suggests that there may be an aluminum oxide formed on the surface of the plate which has a thickness up to 2.5 µm.

The percent concentration of the various elements found on the virgin and worn surfaces of the aluminum plates tested in 600 and 14600 ppm of water is given in Table 6. The virgin surfaces of both aluminum plates had approximately the same concentrations of carbon, oxygen, aluminum, and silicon. Aluminum Plate #35 had small concentrations of calcium and chlorine which aluminum plate #31 did not have. On the other hand plate #31 contained small concentrations of sodium and nitrogen which plate #35 did not contain. Because only a small area of the surface of the plates are analyzed, the small concentrations of Ca, Cl, Na, and N may have existed elsewhere on the surfaces of the plates. The worn surfaces which were analyzed before sputtering of both plates also showed approximately the same concentrations of carbon, oxygen, aluminum, silicon, calcium sodium and potassium. The worn surface before sputtering on plate #35 showed some traces of magnesium which was not found on plate #31. The largest differences between plates #31 and #35 are on the worn surfaces after sputtering. Plate #35 contained twice as much carbon, half as much silicon, and 10% less aluminum than plate #31. Both plates contained approximately the same amount of copper, but the largest difference in atomic concentration was oxygen. Plate #35, which was tested in the lower water content, contained 21.41% oxygen on the sputtered surface, while plate #31, which was tested in the higher water content, only contained 6.21% oxygen on the sputtered surface. It is possible that the different surface roughness of the plates after the tests may have attributed to the different amount of oxygen observed, but it is unlikely that this is the sole reason for such a large difference.

From Fig. 9 it is also evident that both plates #31 and #35 had considerable amount of oxygen at depths exceeding 0.1 µm. The latter value is considered to be the highest oxide thickness that can be generated through a passivation process by simply exposing metal surfaces to air [11, 12]. Hence, it may be concluded that the additional thickness of the oxide layer was somehow formed during the rubbing process. The role of water in this oxide formation, however, is still unclear.

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Table 6 - Atomic Concentration of 390 Aluminum Plates Tested in a R134a Environment and PAG Oil with Water Content of 600 and 14600 ppm

<table>
<thead>
<tr>
<th>Element</th>
<th>Aluminum Plate #31 (14600 ppm of Water)</th>
<th>Aluminum Plate #35 (600 ppm of Water)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Virgin</td>
<td>Worn, bs*</td>
</tr>
<tr>
<td>Carbon</td>
<td>41.43</td>
<td>31.44</td>
</tr>
<tr>
<td>Oxygen</td>
<td>18.72</td>
<td>21.92</td>
</tr>
<tr>
<td>Aluminum</td>
<td>23.86</td>
<td>28.40</td>
</tr>
<tr>
<td>Silicon</td>
<td>12.35</td>
<td>13.88</td>
</tr>
<tr>
<td>Calcium</td>
<td>-</td>
<td>1.24</td>
</tr>
<tr>
<td>Sodium</td>
<td>2.03</td>
<td>1.92</td>
</tr>
<tr>
<td>Potassium</td>
<td>-</td>
<td>1.21</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Chlorine</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Magnesium</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>1.62</td>
<td>-</td>
</tr>
</tbody>
</table>

*bs - before sputtering, as - after 40 min. of sputtering (approximately 2.6 µm depth)

Table 7 - Atomic Concentration of 390 Aluminum Plates Tested in PE2 Oil

<table>
<thead>
<tr>
<th>Element</th>
<th>Concentration (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Plate #114 (R134a Environment)</td>
</tr>
<tr>
<td></td>
<td>Plate #114 (56 ppm of Water)</td>
</tr>
<tr>
<td></td>
<td>Worn, bs*</td>
</tr>
<tr>
<td>Carbon</td>
<td>18.35</td>
</tr>
<tr>
<td>Oxygen</td>
<td>25.64</td>
</tr>
<tr>
<td>Aluminum</td>
<td>44.36</td>
</tr>
<tr>
<td>Silicon</td>
<td>8.62</td>
</tr>
<tr>
<td>Copper</td>
<td>-</td>
</tr>
</tbody>
</table>

*bs - before sputtering, as* - after 10 min. of sputtering (approximately 0.1 µm depth)
Fig. 9 - AES Depth Profiles of 390 Aluminum Plates Tested in PAG Oil and Under R134a Environment
(a) Plate #31, Water Content of 14600 ppm
(b) Plate #35, Water Content of 600 ppm
AES analysis was also performed on three other specimens, designated as #114, #116, and #125 in Table 5. These were also 390 aluminum specimens from test conducted with the PE2 oil. These specimens were chosen because of the large variations in the wear results (more than an order of magnitude) and test conditions. It was hypothesized that some differences in the condition of the surfaces may have caused this large variations in wear. The atomic concentrations of selected elements on the worn surface before and after sputtering are given in Table 7 and the depth profiles are shown in Fig. 10. These three depth profiles look almost identical and are not very illuminating as to the reason for the differences in the wear behavior. Note that, for all specimens which were tested in PE2 oil, the oxide layer thickness did not exceed 0.1 μm. These oxide layer thicknesses, as stated above, are close to the values that can be expected as a result of a passivation process.

SEM surface analyses were also performed on the cast iron plates. The steel pins were examined only under optical microscope. The results from these analyses also did not indicate the reason for the observed differences in the friction and wear behavior.

3.4 Analyses of Used Lubricants

Used lubricants samples were collected for low and high water content conditions given in Table 4. The samples were sent to a commercial lubricant-testing company for analysis. Among the analyses performed on the samples were particle count, total acid number (TAN), ferrography and microscopic examination of the wear particles. Some of the results from these analyses are shown in Fig. 11. Wear data for the tests from which oil samples were taken for analysis are presented in Fig. 11a. Comparing Figures 11a and 11b, it is seen that, for the PAG oil and aluminum plates, higher percentage of corrosive wear corresponds to higher wear. For the PE2, for both the aluminum and cast iron plates, the trend is opposite, i.e. higher percent of corrosive wear corresponds to lower overall wear. The variations in the acid number of the oils is given in Fig. 11c.

This suggests that whenever the corrosive wear was the predominant wear mechanism, the overall wear in the PE was low. This also suggests better protection of the surface by the lubricant and the continuous formation of new protective layer which is eventually worn off. When the lubricant fails to form protective layer, other mechanisms such as adhesive and/or abrasive wear are favored. These mechanisms are probably responsible for the higher wear observed in these cases. This behavior is similar to the action of some additives which also attack the metal surface to form a protective film.
Fig. 10 - AES Depth Profiles of 390 Aluminum Plates Tested in PE2 Oil
(a) Plate #114, Water Content of 56 ppm, R134a Environment, (b) Plate # 116, Water Content of 56 ppm, Air Environment, (c) Plate # 125, Water Content of 2000 ppm, Air Environment
Fig. 11 Wear on the Plates and Results from the Oil Sample Analysis
(a) Wear on the Plate, (b) Percent Corrosive Wear, and (c) Total Acid Number of the Sample
4. BACKGROUND, OVERVIEW AND DISCUSSION OF THE RESULTS

4.1 Previous Studies on the Tribological Effect of Water Content in Oils

The results presented in Section 3 indicate that the presence of water into the lubricant can significantly affect the friction and wear of the contact. In most of the cases, the presence of water reduced the friction and wear of the boundary lubricated contacts considered in this study.

The effects of water dissolved into the lubricant have not been studied in much detail. Most of the research available in the open literature is devoted to the effect of water dissolved in mineral oil on surface fatigue of rolling element bearings [13, 14]. These studies have proven that water contents as low as 100 ppm can be very detrimental. Schatzberg and Felsen [13] suggested that sub micron-size surface cracks are generated early in a rolling contact fatigue experiment. These cracks act as fine capillaries in which water concentrates. The water promotes crack growth by aqueous corrosion and hydrogen embrittlement. These results show a trend opposite to the results obtained in this study. On the other hand, surface fatigue and sliding wear are generally considered different modes of failure and no direct comparison of the results can be made.

There is very little in the literature about the effect of water in lubricants under boundary lubrication conditions. Most of the data available pertain to dry sliding like the work done by Nield and Griffin [15] where steel and wrought iron were tested in air with various humidity. A study which addresses the effects of atmospheric air and moisture on the wear under lubricated conditions is done by Appledoorn, Goldman, and Tao [16]. They tested several lubricants containing hydrocarbons with various affinity towards metal surfaces. The results showed that, with non-polar lubricants, the presence of air and water was detrimental. The polar lubricants, however, showed a different behavior. The wear in tributyl phosphate was the same in dry argon and in wet air, and the wear in a silicate ester was lower in wet air than in dry argon.

There are some other indications that water may have beneficial effect on the friction and wear of boundary lubricated contacts. Hotten [17] has found that certain additives perform better in water emulsions that in oils. One of his explanations for this behavior is that water promotes surface chemical reactions. Similar conclusions have been drawn by Overfelt and Wart [18]. Tingle [19] suggests that the presence of water may promote chemisorption of surface active groups from the lubricant on metal surfaces. Similar conclusions were made by Hirst and Lancaster [20].
4.2 Overview on the Effects of the Test Environment on Friction and Wear

As shown earlier, the test environment can have a significant effect on friction and wear. This is probably due to the dissolution of gases from the environment into the oil. The gas molecules diffuse to the contact surfaces and may attack them. Such a chemical reaction may be promoted by the high local temperature and by the catalytic properties of some of the metals. Virtually all gases are to some extend soluble in oils [21]. On the other hand, even very small solubility may supply sufficient quantities of gas molecules to the contact surfaces for a chemical reaction which competes with the wear process [16, 22].

The gases used as test environments in this study posses different chemical activities. Argon is inert. Oxygen, as it may be expected, is very active and is able to oxidize the metal surfaces even if it is found only as an impurity in the test atmosphere. Mizuhara, Akei, and Matsuzaki [2] found that only 0.15% of oxygen may significantly affect friction and wear. R134a is inert in a certain range of conditions, but it may also react with the metal surfaces to produce metal fluorides if the local temperature gets high enough. Thermal decomposition can not occur spontaneously because R134a does not decompose up to 1170 °K [23]. The estimated flash temperature at the contacts under study is 580°C. This value was obtained by applying Jaeger's general analysis for two semi-infinite bodies in relative motion [24]. Even though the estimated temperature at the interface can be considered only as a rough approximation, it may be concluded that R134a probably did not decompose under the conditions studied. The above arguments suggest that oxygen was the major active component in the gas environments tested.

The role of oxide layers on the friction and wear properties of metal surfaces under sliding conditions has been studied by numerous investigators. There is, however, significant controversy in the conclusions drawn by various researchers. Most of the research done is on the role of oxides under dry lubrications conditions and at elevated temperatures. There is considerably less information on the effects of oxides in lubricated contacts. There is also a controversy about the effect of the oxide layer thickness and the wear mechanisms involved. Rabinowicz [25] has determined that oxides are able to lubricate when the oxide layer is much harder than the substrate and the oxide layer has a thickness of 0.01 μm or greater. Blouet and Courtel [26] slid pure aluminum on tool steels submerged in various lubricants and discovered that the coefficient of friction and wear rate decreased significantly when the thickness of the aluminum oxide reached a critical value of 0.07 μm. Overfelt, Wert, and Hunt [18] have experimentally observed in lubricated tests that when aluminum alloys are slid against steels, the aluminum oxide produced improved the friction and wear properties independent of oxide thickness and subsurface alloy. Similar conclusion were made by Sargent [22]. Komvopoulos, Saka, and Suh [28] demonstrated that oxide films of any thickness may be effective depending on the normal and tangential surface tractions. Whitehead [26], on the other hand, indicated
that thin films of aluminum oxides can be penetrated even at low loads thus allowing high friction and wear to exist. As indicated above, there is significant controversy in these studies which is probably due to the different wear mechanisms involved. Which one of these mechanisms will dominate the wear process is determined by a complex interaction of many factors. This is why the results from these studies may not be directly comparable, unless they were performed under exactly the same conditions.

Another issue related to the formation of surface oxides is the amount of oxygen dissolved into the oil. Hong [30] has found that deaeration of oils and conducting the test under an inert test environment reduce wear. Klaus and Bieber [31], on the other hand, have found an optimal value for the oxygen concentration into the oil at which the lowest wear occurs.

The oxide layers may also react chemically with water and active groups from the lubricant. This suggests a very complex interaction of mechanical and chemical effects on the surface of the specimens. In essence, the results obtained in this study probably cannot be explained by a single mechanism. In addition to the mechanical tractions during the sliding process, chemical reactions are taking place on the surfaces. The presence of water, surface active groups in the lubricant, dissolved gases from the test atmosphere, and the high local temperature due to frictional heating may produce a complicated picture of corrosive, abrasive, and adhesive friction and wear phenomena.

4.3 Discussion of the Results

As mentioned above, it is unlikely that a single mechanism is responsible for all the variations in the friction and wear observed. Several possible mechanisms which may explain some of the results are discussed below.

4.3.1 Discussion on the Wear Results Obtained in R134a Environment and PE Oils

The major questions discussed in this section are: (a) why is the wear in R134a environment and PE oils almost two orders of magnitude larger on the cast iron plates than the aluminum plates? (b) why is the wear practically unaffected by the amount of water into the oil?

The following scenario is suggested:

1. The preexisting oxide layers on the surface of both the aluminum and the cast iron plates are worn out in the first few minutes of the test.

2. There is very little oxygen dissolved into the oil to form new oxides or to effectively compete with the wear process. Consequently a bare metal surface is created. The lack of oxygen is due to: (a) Purging the test chamber, and (b) the much higher solubility of R134a in the oil compared to oxygen.

3. The pentaerythriol esters attack the pure metal surface with their active polar groups. At this instant the large difference in the affinity of these active groups to aluminum and iron
comes into play. Hotten [18] and Laemmle et al. [32] have proven that aluminum is able to form strong bidentate bonds with some polar organic compounds such as pentaerythriol partial esters (see Appendix D for details). The molecules orient vertically, thus forming a layer which protects the surface. In fact esters have proved to be very effective lubricants for aluminum surfaces [33, 34, 35]. Iron, on the other hand, fails to form such strong chemical bonds with the active polar groups. Groszek [36] has shown that the affinity of pure iron towards the active polar groups is several times lower than the affinity of iron oxides towards the same compounds. The esters fail to effectively cover the surface and the molecules do not have vertical orientation. This surface film is not very strong and does not offer adequate protection. Whenever the oil was able to form a protective layer on the metal surface, the corrosive wear mechanism was predominant (Fig. 11b). On the other hand, when the oil failed to protect the surface, other mechanisms such as adhesion and abrasion were dominant, which lead to higher wear.

4. The water present into the oil is not able to oxidize the surface of the cast iron plates fast enough in order to compete with the wear process. Hence there is little oxide on the surface which results in a low affinity of the surface toward polar compounds. Therefore, the wear on the cast iron plates is high, although some beneficial effect of the water was detected.

4.3.2 Effect of Viscosity of the PE Oils on Friction and Wear

Here the question is why the PE1 and PE2 oils which have a viscosity difference of almost five times produce very similar wear and friction results? The comparison of the friction and wear results for these oils is shown in Fig. 12. A possible explanation follows:

1. Viscosity is not a critical factor under boundary lubricated conditions. What counts is the ability of the lubricant to form a strong bond with the metal surface. Since the ester oils studied had the same chemical composition and differed only by the length of the molecular chain, the reaction with the metal surfaces were probably the same.

2. The slight improvement of the wear results obtained with the more viscous oil over the less viscous oil is due to the larger thickness of the surface layer formed, the better vertical alignment of the oil molecules and the stronger chemical bond with the surface [32].
Fig. 12 - Friction and Wear of PE1 and PE2 Oils
(a) Wear Results, and (b) Coefficient of Friction
4.3.3 Effect of the Oxidizing Environment on Friction and Wear of Aluminum Lubricated by PE Oil

Water seems to have no effect on the friction and wear of aluminum when the test is conducted in PE oil and a R134a environment. In air, however, the amount of water is very important. The combination of air plus low water content produces the highest wear. The addition of water reduces wear drastically. The suggested mechanism is as follows:

1. There is sufficient amount of oxygen dissolved into the oil to quickly oxidize the surface. Tao [22] has shown that, in most cases, the oxidation process proceeds at a higher speed than the wear.

2. The aluminum oxide formed is brittle and easily penetrated and fractured even under light loads, as suggested by Whitehead [29].

3. The wear particles thus formed are very hard and abrasive.

4. The PE oil does have strong affinity towards pure aluminum but not towards aluminum oxide [37]. Hence it fails to form protective films on either the surface of the aluminum plate, or the wear particles.

5. The wear particles then abrade the surface thus increasing the friction and wear. A record of the coefficient of friction given in Fig. 6a shows a relatively high friction throughout the test. The worn surface in this case was much rougher (0.9 µm Ra) than the worn surface obtained in R134a (0.27 µm Ra). This also suggests that abrasion may have occurred.

Thus the mechanism responsible for the increase in wear under oxidizing environment may be a corrosion initiated abrasive wear. When water is added to the oil, a different chemical reaction which produces protective surface layer probably occurs. This reaction occurs between aluminum oxide and water. It has been proven [18] that the oxide formed on the aluminum surface due to exposure to air is metastable γ-Al₂O₃. The latter is known to react with water to form aluminum trihydroxide known as Bayerite or Gibbsite [37]. This reaction product is soft and has layered structure which suggests that it is an effective solid lubricant.

4.3.4 Effect of the Oxidizing Environment on Friction and Wear of Cast Iron Lubricated by PE Oil

The results shown in Fig. 4b indicate that a large reduction in wear occurred when the test environment was changed from R134a to air. The tests conducted in argon also showed a reduction in wear, especially when water was added to the oil. The reason for this behavior may be the higher affinity of esters towards iron oxides compared to the pure iron. The suggested mechanism is as follows:

1. In the air environment there is sufficient oxygen to oxidize the surface completely no matter how much water is present in the oil. When argon is the test environment, addition of water is necessary in order to achieve complete oxidation of the surface.
2. The ester molecules attach to the iron oxide surface and form a protective film. They fail to form such protective film on the pure metal surface [36].

3. The addition of water has a beneficial effect on wear because it facilitates the formation of iron oxides which have stronger affinity towards the polar organic compounds.

4.3.5 Discussion of the Friction and Wear Results from the Tests Conducted Lubricated by PAG Oil

The variation of the water content in the PAG was about ten times larger than the variation of the water content in the PE's. This is due to the much higher water saturation limit which is typical for the PAG oils [39, 40, 41]. The PAG's have strong affinity toward water. Two water molecules attach to each oxygen atom in the PAG chain [40]. This bonding may significantly affect the polar activity of the PAG molecule [40].

The PAG's have both hydroxyl and ether groups which are polar and have affinity towards metal surfaces [42]. Pure PAG's however do not offer very good protection for aluminum. Montgomery [43] reports that an order of magnitude larger wear is obtained with pure polyglycols compared to the wear obtained with alkanes and alcohols. The reason is that the reaction products of the lubricant with the metal surface are easily removed from the surface. How water will affect this processes is unclear.

The results for the friction and wear of aluminum in PAG oil are the most consistent with respect to the effect of water. In all test environments, the addition of water reduced the wear by an order of magnitude, as shown in Fig. 4a. It is suggested that water is responsible for an activation of the PAG molecule which then reacts more readily with the metal surface to form a protective film. The effect of water may also facilitate the vertical orientation of the PAG molecules [40]. Further research, however, is necessary to characterize this process.

5 SUMMARY

Friction and wear tests of two material contact pairs lubricated with three different oils and three different test environments are conducted using the HPT. The material contact pairs are M2 tool steel against 390 aluminum and M2 tool steel against gray cast iron. The three oils are a polyalkylene glycol (PAG) and two polyolester (PE1 and PE2) oils. The test environments are R134a, air and argon. The results can be summarized as follows:

1. The wear on the aluminum plates for the tests conducted with the PAG oil in all three environments was greatest at the lowest moisture content levels. From the standpoint of friction and wear, it is beneficial to have a water content level of 5000 ppm or greater in the PAG oil when the plate material is 390 aluminum.
2. The wear on the cast iron plates, when using a PAG oil as the lubricant, showed a slight increase with water content in a R134a environment. This trend is opposite when air is the test environment.

3. Both ester oils lubricated aluminum much better than the cast iron. The difference in the amount of wear can be as high as two orders of magnitude. This is probably due to the ability of the esters to form bidentate bonds with aluminum. Esters do not form such bonds with iron.

4. The plate wear is greater for the PE1 tests than for the PE2 tests for both material contact pairs. This is most likely due to the difference in the viscosity of the oils.

5. In PE2 oil, water does not seem to significantly affect the friction and wear of both aluminum/steel and cast iron/steel contacts when R134a is the test environment. On the contrary, for the aluminum/steel contacts, the water content significantly influences wear when argon or air is the test environment. For the cast iron/steel contacts, the wear is strongly influenced by the water content when the test is conducted in argon, but it is not influenced by the water content when the test is conducted in air.

REFERENCES


A.1 Introduction

The design of the facility for the tribological evaluation of critical contacts in compressors, in pressurized refrigerant environments, centers on the development of a tribometer enclosed in a pressurized chamber. The tribometer was designed and manufactured by Advanced Mechanical Technology Inc. (AMTI) of Newton, Massachusetts. The data acquisition system, peripheral instrumentation and equipment were developed at the University of Illinois at Urbana-Champaign. The completed High Pressure Tribometer (HPT) system, shown in Figure A.1, is located in the Tribology Laboratory in the Mechanical Engineering Building (MEB) on the campus of the University of Illinois at Urbana-Champaign. A schematic of the HPT is given in Figure A.2.

![Figure A.1 - The High Pressure Tribometer (HPT)]
Central to the HPT design is a special pressure/vacuum chamber, which surrounds the tribo-contacts. This chamber is capable of testing any inflammable non-corrosive gas. Multiple thermal control loops are included to permit testing at temperatures typically found in compressors. Two separate servo motors provide motion and loading capabilities. The rotational (θ-axis) motor is capable of unidirectional rotation and oscillatory motion. The load (Z-axis) servo motor provides either static or oscillatory loads for the contact. A complex
transducer measures the applied load, frictional forces, and moments during a test. The feedback from this transducer, as well as other sensors, provide the HPT with an excellent control system.

The design of the HPT system consists of five sections: the HPT, a purging facility, a charging facility, a sampling facility and a data acquisition unit. A brief description of the apparatus follows. For an extensive description of the apparatus refer to reference [1].

A.2 Specimen Chamber

To adequately simulate a pressurized refrigerant environment, any test conducted must occur within the boundaries of a pressure chamber. The chamber of the HPT is rated at upwards of 250 psi operating pressure. A schematic of the pressure chamber is shown in Figure A.3. The chamber consists of two separate halves. The upper half of the chamber remains stationary while the lower half can be raised or lowered via the Z-axis servo motor. When the lower half engages with the upper half, a seal is formed and thus the unit may then be purged or pressurized.

Figure A.3 - The Pressure Chamber
The spindle serves as the mounting face for the upper specimen holder. The tribo-contact occurs inside the cup. The cup is a removable aluminum piece which serves two important functions. First, it serves as the mounting surface for the lower specimen holder. Secondly, the cup serves as the lubricant reservoir during the test. A Pyrex sleeve, sealed at the bottom by an O-ring, surrounds the cup. This permits the cup to be filled with a lubricant, completely submerging the contact to be tested. The cup contains a small hole (sampling hole) which communicates with the sampling port on the outside of the chamber and provides a means of injecting the lubricant into the cup of the pressure chamber after the chamber has been purged and pressurized.

The removable cup is bolted to a complex force transducer module. The transducer is outfitted with an intricate array of strain gages, which are used to measure the forces during a test. Frictional forces \( F_x, F_y \), load force \( F_z \), as well as moment \( M_z \) are of interest and are relayed to the control box outside the pressure chamber. There is also a thermal sensor installed in the transducer that is used to monitor the temperature of the lower specimen.

The transducer module is firmly mounted to an internal suspension system. This consists of a pair of diaphragm springs which provide compliance in the \( Z \)-direction while maintaining high stiffness in the \( x, y \), and \( \theta \) directions. These diaphragm springs are used to permit accurate loading while the chamber is pressurized. When the chamber is pressurized to 250 psi, it takes approximately 7000 lbf to hold the two halves closed. Most of this force is taken up by the suspension system, so that with proper strain gage amplifier configuration, tests loads as low as 1 lbf can be accurately applied and monitored.

A.3 Thermal Systems

Virtually all internal surfaces of the chamber can be heated. This is required to prevent condensation of refrigerant on these surfaces at the high test pressures. Both halves of the pressure chamber are outfitted with cartridge heaters that are used to heat the chamber walls above the condensation temperature. The upper half is outfitted with a 400 W cartridge and the lower half contains two 500 W cartridges. The temperature of each half can be controlled from the main control panel.

The temperature of the rotary spindle, and therefore the upper specimen, is controlled from -30 °C to 150 °C by an external recirculating unit. Due to the high value of the heat transfer coefficient and the unique design of the passages machined in the spindle, the upper specimen can be maintained within a couple of degrees of the fluid temperature.

The last thermal system to be discussed is the chiller. Similar to the recirculator, the chiller is an independent unit with its own controls. This unit pumps a 50/50 mixture of laboratory grade ethylene glycol/distilled water through passages machined into portions of the
HPT. It is set at ambient temperature and is used to cool critical parts of the tribometer.

A.4 Rotational and Axial Motions

Motion in the tribometer is generated by two independent dc servo motors. A large θ-axis servo motor provides rotational motion for the upper specimen, while a second, somewhat smaller, Z-axis servo motor provides axial motion and loading during the test.

The θ-axis dc servo motor (3 kW) is controlled through a pulse width modulated (PWM) amplifier. The low inertia motor coupled with the high performance amplifier provides excellent response and permits complex motion. The shaft of the motor is attached through a flexible helical coupling to the short shaft entering the chamber. The position of the θ-axis is monitored by a differential optical encoder that is used to control spindle motion.

The Z-axis dc servo motor is controlled separately through its own PWM amplifier. This fast response motor-amplifier combination supplies both Z-axis motion, up to 0.07 in./sec, and test loads, up to 1000 lbf. This motion is transmitted by a lead screw which is driven through a backlash-free 100:1 harmonic drive. An encoder feedback loop supplies a means to monitor the location of the lower half of the chamber, while the transducer acts as the force feedback loop that controls the applied axial load.

A.5 Instrumentation and Controls

There are four strain gage amplifiers: F_x, F_y, F_z and M_z. Each consist of an amplifier board that plugs into the control box and interfaces with panel controls and switches as shown in Figure A.4. Also shown in Figure A.4 are the front panels of the two motor circuit boards and the front panel of the temperature control board. The motherboard, with a microprocessor, interfaces with the control circuits and provides a wide variety of functions. It interfaces with a four line LCD display and eight panel switches. In addition to interfacing with the front panel, the microprocessor can perform control, limit and alarm features. It also has the ability to interface with a personal computer, via an RS-232c port, to allow for external configuration and data acquisition.

Feedback for the loads is provided by the transducer in the form of F_x, F_y, F_z and M_z. Each of the force (torque) directions has its own independent amplifier that excites the strain gages and is used to condition the load to equivalent engineering units.

The Z-axis motor control board permits axial loads to be applied during the test as well as providing motion to open and close the chamber. The force can be static, up to 1000 lbf, or oscillatory from 0-1000 lbf at frequencies of up to 5 Hz.
The θ-axis motor control loop, with optical encoder feedback, permits the θ-axis servo motor to be precisely controlled. The motor is capable of simple unidirectional rotation (0-2000 rpm) and oscillatory motion with amplitudes of up to 180° and frequencies of up to 5 Hz. Presently, the tribometer controls permit oscillatory motion with either sinusoidal or triangular waveforms. The controls also permit a constant torque to be applied to the test.

The on-board temperature controllers are used to control the temperatures of the cartridge heaters. The upper and lower heaters can be independently set from ambient to 95 °C. Thermal sensor feedbacks from the chamber allow the temperatures to be accurately controlled to ±1 °C.

The last tribometer control is the microprocessor. The Intel 80C188EB 16-bit microprocessor, located on the motherboard, is capable of independently controlling nearly all tribometer functions. It can be used to control the two cartridge heaters as well as θ-axis and Z-axis motions. The interface to the microprocessor consists of a frontal panel keypad with eight switches and a 4 line x 40 character LCD display. This display is used to set test parameters and monitor data values.

A.6 Peripheral Equipment

The HPT has also been outfitted with apparatuses for purging, charging and sampling, as well as, a data acquisition system. A vacuum pump is used to purge the system, more specifically the pressure chamber. An external pressure vessel is used to charge the chamber with refrigerant. A silicone heating blanket placed around the pressure vessel is used to
generate the required refrigerant pressure to charge the pressure chamber. A 30 lb refrigerant tank (in most cases), attached to the pressure vessel, is used to supply the refrigerant to the chamber. Data acquisition is made possible through the use of a personal computer linked to the motherboard by an RS-232c connector.

Reference

APPENDIX B

EXPERIMENTAL PROCEDURE

B.1 Cleaning of Specimens

Prior to testing and specimen installation, the specimens must be thoroughly cleaned. The specimens, specimen holders, screws, and cup are all ultrasonically cleaned for 10 minutes in a solution of mineral spirits followed by a rinsing with 2-propanol to remove any residues. Gloves are worn, and the specimens are handled with clean forceps during the installation process to prevent the transfer of any contaminants to the specimens which may result in inaccurate wear measurements. The same procedures are followed upon completion of testing, after which the wear is measured.

B.2 Installation of Specimens

In order to effectively test the equivalent geometries of the critical compressor contacts, a specimen holder was designed and made and is shown in Figure B.1. The lower specimen is mounted into its holder, which in turn is mounted into the cup. The upper specimen is mounted directly onto the spindle by four 10-32 machine screws. The hole pattern in the cup allows the specimen holder to be mounted in an orientation which permits the specimen to be near one of the sight ports.

The cup is assembled with the glass sleeve. The cup is installed into the chamber by carefully pressing the unit into position. Care must be taken to align the sampling hole in the cup with the sampling line in the top of the transducer. The six steel locator pins on the top of the transducer assure alignment as well as providing resistance to torsional buckling. The cup is secured to the transducer by tightening three 10-32 machine screws. The chamber is closed to the point just before the upper and lower specimens contact each other.

Once the specimens are in close proximity, the system is heated to the test temperature. Both the cartridge heaters and the recirculator are set to the desired test temperature. They help to heat the oil/refrigerant mixture and promote a uniform chamber temperature, thus minimizing thermal gradients.
In order to obtain a higher moisture content than what the oil in the original container has, a small amount of tap water is mixed with the oil from the container. Oil is taken from its container and approximately 250 ml is poured into a beaker. A small amount of tap water is then mixed with the oil. The oil/water mixture can now have its moisture content measured. In order to get a moisture content less than what the oil from the container has, a special procedure must be used as explained in section B.3.1.
B.3.1 Low Moisture Content Oil Preparation

In order to obtain a lower moisture content than that of the oil coming from its original container, the water must be extracted from the oil. Water is extracted from the oil by running an inert gas, argon, through the oil at an elevated temperature which boils out the water from the oil. An apparatus was constructed to perform this task and is shown in Figure B.2.

![Figure B.2 - Low Moisture Apparatus](image)

Approximately 250 ml of oil is poured into a beaker which contains a magnetic stirring bar. A hose which contains many small holes is fed into the beaker. The holes are needed to release the argon gas into the oil. The hose is connected to the pressure regulator on the pressure vessel containing argon gas. The beaker is placed on a magnetic stirrer/heater. The speed of the stirrer and the temperature of the heating plate can be controlled. The heater is set to 100 °F which is high enough to extract the water out and low enough so that the oil does not degrade. The three valves which regulate the flow of the argon gas are opened, and the argon gas flows into the oil. By regulating the flow rate of the gas, the speed of the magnetic stirrer,
the temperature of the oil, and the length of time of the process, the amount of water extracted from the oil is controlled.

**B.3.2 Measurement of Moisture Content**

Because some moisture may exist in the HPT and the hydraulic cylinder, the water concentration in the oil may change during a test. The moisture content is measured both before and after each test. In general, the moisture content of the oil varies only slightly before and after a test.

The measurement of the water concentration of the oil is determined by the Karl Fischer (Aquametry) Method using a "Dead-Stop" Technique [1]. In this technique KFR (Karl Fischer Reagent) is titrated into a solvent until the stop point is achieved. Figure B.3 shows the Karl Fischer apparatus used, which was purchased from Labindustries, Inc. First, KFR is pumped into the self-zeroing buret, which contains a scale in milliliters, so that the amount of KFR used can be measured. Enough solvent, methanol, is poured into the jar so that the meter-electrode tips are submerged in the solvent. KFR is then poured into the jar from the self-zeroing buret through the valve. The KFR is mixed in with the solvent by means of a magnetic stirrer until the meter-electrode reads approximately 4.7 which is the stop point. This indicates that the KFR is saturated in the solvent. The Karl Fischer Apparatus is now ready to be calibrated.

In order to calibrate the Karl Fischer Apparatus, a known quantity of water is added to the saturated KFR/methanol solution through the sample port and is mixed by the magnetic stirrer. The quantity of water used is $15 \times 10^{-3}$ ml, causing the meter on the meter electrode to drop to a lower level. KFR is then added again to the mixture, through the valve on the buret, until the reading on the meter-electrode is once again 4.7. The amount of KFR added to the solution is 3.4 ml. This amount of KFR is proportional to the water content in the solution. Specifically, for this Karl Fischer Apparatus and the Karl Fischer Reagent used, 1 ml of KFR is equivalent to $4.41 \times 10^{-3}$ ml H$_2$O, which gives the calibration constant, $k = 4.41 \times 10^{-3}$ ml H$_2$O/ml KFR. The Karl Fischer Apparatus is now ready to measure the moisture content in the oil.

The weight of the oil and its container is initially measured. Approximately 10 ml of oil is poured into the KFR/methanol mixture through the sample port, and the weight of the oil and its container is measured again. KFR is then added to the mixture through the valve on the buret until the reading on the meter-electrode is once again 4.7. The scale on the self-zeroing buret indicates how much KFR was added to the mixture. By knowing the weight of the oil used, the density of the oil, and the amount of KFR used, the moisture content of the oil can be found using the following equation.
\[ MC = \frac{Rk\rho}{W}(10^6) \]

- **MC** = moisture content (ppm)
- **R** = amount of KFR (ml)
- **k** = calibration constant (ml H₂O/ml KFR)
- **\( \rho \)** = density of oil (g/ml)
- **W** = weight of oil used (g)

Figure B.3 - Karl Fischer Apparatus
B.3.3 Hydraulic Cylinder

The apparatus shown in Figure B.4 is used to inject the oil into the tribometer. This apparatus is a hydraulic cylinder which contains two separate compartments, one of which will contain the oil.

Hook up to vacuum pump or air compressor

Figure B.4 - Hydraulic Cylinder

B.3.3.1 Cleaning

The hydraulic cylinder must first be cleaned before it can hold the oil. Methanol is used to clean the oil compartment. First, a container which holds 250 ml of methanol is connected to valve #3 of the hydraulic cylinder as shown in Figure B.4. A vacuum pump is then connected to valve #1 which is opened. Valve #3 is opened, and the vacuum pump is turned on thus allowing the methanol to enter the cylinder compartment. After the compartment is filled, the vacuum pump is turned off and disconnected from valve #1. The air compressor is then connected to valve #1 and turned on so that the methanol leaves the hydraulic cylinder and returns to its original container. The cylinder is flushed with methanol twice in order to be thoroughly cleaned. The vacuum pump is then connected to valve #2 which is opened. With valve #1 and valve #3 closed, the vacuum pump is turned on for five minutes, so that any vapors that still exist in the cylinder are removed.

B.3.3.2 Injection of Oil into the Hydraulic Cylinder

After the moisture content of the oil has been measured as described in section B.3.1, the oil can be placed into the hydraulic cylinder. First, the beaker of oil is connected to valve #3 of the hydraulic cylinder, which is opened. A vacuum pump is then connected to valve #2. The vacuum pump is turned on so that the oil is sucked into the hose. Valve #3 must then be closed.
once the oil has reached it. Valve #2 is closed, and the vacuum pump is shut off. This procedure is necessary to insure that no air enters the hydraulic cylinder. The vacuum pump is then connected to valve #1 which is opened. Valve #3 is opened, and the vacuum pump is turned on thus allowing the oil to enter the cylinder compartment. The hydraulic cylinder can hold 225 ml of oil which is used for two tests. The hydraulic cylinder is then hooked up to the tribometer so that the oil can be injected into the cup within the pressure chamber. Before the oil can be injected into the pressure chamber, the chamber must be purged and pressurized with refrigerant. The reasoning behind injecting the oil into the chamber after purging and pressurizing is that purging would extract moisture from the oil if it were under vacuum.

B.4 Purging Procedure

Before purging, the charging facility, the drain facility, and the hydraulic cylinder are connected to the HPT so that their lines may be evacuated at the same time. By turning on the Welch vacuum pump, the entire chamber can be evacuated (Figure B.5). The pressure in the chamber is monitored by the thermal vacuum gage connected to the chamber. The chamber can be purged to below 300 μin. Hg.

![Diagram of HPT Purging Facility](image)

Figure B.5 - HPT Purging Facility
B.5 Charging Procedure

Before the HPT can be charged with a refrigerant vapor, the 8.0 lb pressure vessel (Figure B.6) must contain a sufficient amount of the desired refrigerant. The refrigerant in the pressure vessel is transferred to the HPT chamber by proper temperature control of the vessel to generate sufficient pressure. After the chamber has been purged, the chamber is now ready to be charged with refrigerant vapor. By opening valves attached to the pressure vessel and then using the valve attached to the chamber to throttle the flow of refrigerant, the desired pressure is easily obtained. A pressure of 50 psig was used for all the tests.

B.6 Injection of Oil

Once the chamber is purged and pressurized with R134a refrigerant to 50 psig, the oil is then injected into the chamber through the sampling hole on the tribometer. An air
compressor is connected to valve #1 of the hydraulic cylinder (Figure B.4). Valve #2 and the valve which connects the sampling hole to the hydraulic cylinder are opened. The air compressor is turned on and places a high pressure on the right compartment of the hydraulic cylinder forcing the oil into the pressure chamber of the tribometer. When the oil reaches the desired level in the cup, the valve which connects the sampling hole to the hydraulic cylinder is closed, and the air compressor is turned off. The reasoning behind injecting the oil into the chamber after purging and pressurizing is that purging would extract moisture from the oil if it were under vacuum. Once the oil has filled the cup inside the tribometer, at least one hour is needed to allow the refrigerant to dissolve into the oil to reach equilibrium, a state in which the refrigerant is fully saturated into the oil.

B.7 Running a Test

Once the chamber has reached a steady state condition, the upper and lower specimen are fully engaged and the test can begin. Each test is conducted for one hour. Once the test has begun, the data acquisition system collects instantaneous information, and from these data computes an average coefficient of friction. The coefficient of friction (μ) and the upper (T1) and lower (T2) temperatures of both halves of the pressure chamber are displayed graphically as shown in Figure B.7.

![Figure B.7 - Graphic Representation of Computerized Data Collection](image-url)
Reference

Some common data collection schemes are used throughout this study. These include wear, surface roughness, and hardness measurements. The procedures for collecting these data are subsequently discussed in detail.

C.1 Wear Measurement on Plates

C.1.1 Dektak 3030 Stylus Surface Profilometer

Upon completion of a unidirectional test, the wear on the plate specimen is determined quantitatively by analyzing the wear scar depth via the Dektak 3030 stylus surface profiler. The Dektak stylus surface profilometer can measure wear scar depths from few nanometers up to 100 μm. A sample printout of the trace of a wear scar from the Dektak is shown in Figure C.1.

![Figure C.1 - Surface Profile of Plate Wear Scar](image)

The wear depth is determined by computing how far below the virgin (unworn) surface the average wear scar depth falls. The trace of the Dektak begins on the unworn surface, moves on the wear scar in the direction perpendicular to the wear scar, and then goes back to the unworn surface on the other side of the wear scar. After the trace is made, the plot is leveled by pressing the level key on the control pad. The first and last point of the trace are taken as the reference points and are lined up. Using the Dektak control pad, the reference cursor is moved to the initial point of the wear scar and the measurement cursor is moved to the last point of the
wear scar as shown in Figure C.1. The wear depth is determined by pressing the average height key on the control pad. The Dektak uses the first and last points of the trace as a zero reference. The distance between the zero reference and each data point located between the reference and measurement cursors (the data points on the wear scar) are determined, and an average value is calculated and displayed as the average height. The value of the average height is negative since the wear scar falls below the reference line. Four measurements were taken on the wear scar at different locations of each plate as shown in Figure C.2. An average value of these four measurements was taken to be the wear depth for each individual plate.

A micrometer was used to measure the wear on the plates which have wear scar depths greater than 100 μm.

![Diagram of wear scar and plate specimen with measurement traces labeled I, II, III, IV.]

**Figure C.2 - Plate Wear Measurements**

**C.2 Surface Roughness Measurements**

Surface roughness is an important parameter in friction and wear tests. Each pin and plate specimen is measured prior to testing, and the surface roughness of the wear scar is determined for each plate after testing. All the measurements were made with the Dektak stylus surface profiler. A load of 40 mg on the stylus was used for all the data obtained.

One of the most important parameters that has to be defined when measuring the surface roughness is the cut-off length (trace length). The accuracy of the measurement and the repeatability of results depend strongly on this parameter. It is common practice to choose a
length one to three times larger than the characteristic peak spacing of the surface in the direction of the traverse. Cut-off distances of 800 were used for the measurements.

C.2.1 Surface Roughness of the Plate

The surface roughness is taken for each plate prior to testing. When a trace is made, the surface roughness is obtained by pressing the Ra button on the key pad. Each surface roughness value is obtained as an average of four measurements taken at different locations on the plate, approximately equidistant from each other as shown in Figure C.3. A typical example of a trace of the surface roughness of a plate is shown in Figure C.4.

![Figure C.3 - Surface Roughness Measurements](image)

![Figure C.4 - Trace of the Surface Roughness of a 390 Aluminum Plate](image)
C.2.2 Surface Roughness of the Pin

The surface roughness is taken for each pin prior to testing. A trace is made on the cylindrical pin by placing the pin in a holder so that the pin does not move. Care must be taken, when placing the pin under the stylus, to insure that the curvature of the cylinder does not affect the movement of the stylus. An example of a trace of the surface roughness of a pin is given in Figure C.5. Each surface roughness value is obtained as an average of two measurements taken at different locations on the pin.

![Figure C.5 - Trace of the Surface Roughness of a M2 Tool Steel Pin](image)

C.3 Surface Hardness Measurements

C.3.1 Vickers Hardness Tester

The surface hardness of the M2 tool steel pins and the gray cast iron plates was measured using a Buehler Micromet II digital micro-hardness tester (Vickers), according to the standard procedures. All surface hardness values used in this study are averages of at least two separate readings per specimen. An indentation on the order of microns is made with a Vickers diamond indentor depending on the load used and the hardness of the material. The hardness measurement can be taken before or after running a test, as long as the indentation falls on the unworn surface.

C.3.2 Brinell Hardness Tester

The surface hardness of the 390 aluminum plates was measured with a Brinell hardness tester which uses a 3000 kgf 10 mm carbide ball. These hardness measurements can only be done on the plates after the tests have been conducted with the HPT due to the large
indentations which are produced on the specimen by the Brinell hardness tester. The indentations are made on the virgin surface of the specimens. The 390 aluminum plates contain silicon grains in its composition, and for this reason the Brinell tester must be used to get a more accurate measurement for the hardness than the Vickers tester would give. The indentation of the Vickers tester may land on one of these silicon grains giving a high hardness; whereas, the Brinell indentor is much larger than the silicon grains and covers a larger surface area thereby giving more accurate average hardness measurements. All surface hardness values used in this study are averages of at least two separate readings per specimen.
Appendix D

STRUCTURE OF VARIOUS CHEMICAL COMPOUNDS

D.1 Structure of the PAG Oil

PAG's are made from the reaction of alkylene oxide monomers with a nucleophilic starter, usually an alcohol. PAG’s can be represented by the following structure:

\[ R' \quad RO-(CH_2-CH-O)_n-R'' \]

where \( R, R'' = H \) or alkyl group; \( R' = H, CH_3, \) or alkyl group. The oil tested had methyl alcohol as the starter. The active polar groups are the hydroxyl and the ether groups.

D.2 Polyolester Oils

The polyolester tested were from the pentaerythriol family. The structure of the oil is shown in Fig. D.1

Laemmle et al. [2] and Hotten [3] suggest that polyolester may form bidentate bonds with the aluminum surface. The partial esters are more active and form chemical bonds with metal surfaces more readily [4]. Possible bonds with the aluminum surface formed by an unsaturated and a saturated ester are shown in Fig. D.2.
D.3. Oxides and Hydroxides of Aluminum

The description of the oxides and hydroxides of aluminum is based on the information provided by the work of Gates and Klaus [5]. Aluminum oxide (Al₂O₃) exists in many forms. The most common form is alpha (α) alumina (corundum) which is hexagonal. Other forms of Al₂O₃ occur less frequently: gamma (tetragonal), delta (orthorhombic, tetragonal), eta (cubic spinel), theta (monoclinic), chi (cubic hexagonal), kappa (hexagonal), and iota (orthorhombic). All alumina are transition except alfa. The hydroxides of aluminum are presented in Table D.1 and the structure of aluminum trihydroxides is given in Fig. D.3.

![Diagram of Bidentate Bonds](image)

**Fig. D.2 - Formation of Bidentate Bonds**
(a) Unsaturated Ester, and (b) Saturated Ester

<table>
<thead>
<tr>
<th>Chemical Name</th>
<th>Chemical Formula</th>
<th>Nomenclature</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminum Oxide Hydroxide or Alumina Monohydrate</td>
<td>AlO(OH) or (Al₂O₃ • H₂O)</td>
<td>Boehmite or Diaspore</td>
</tr>
<tr>
<td>Aluminum Trihydroxide or Alumina Trihydrate</td>
<td>Al(OH)₃ or (Al₂O₃ • 3H₂O)</td>
<td>Gibbsite (Hydrargillite) Bayerite Nordstrandite</td>
</tr>
</tbody>
</table>
Fig. D.3 - Structure of Aluminum Hydroxides
(a) Top View, (b) Side View, and (c) Stacking Sequence
Gibbsite, bayerite, nordstrandite and boehmite are layered structures with relatively weak bonding between the layers. Hence these hydroxides act as solid lubricants. All three trihydroxides have identical structure within each layer and differ only in the stacking of the layers (Fig. D3). Wefers and Bell [6] give approximate Moh's hardness values for the aluminum oxides and hydroxides which show that the layered structures have much lower hardness. For example, gibbsite is 2.5 to 3.5 on the Moh's scale; Boehmite is 3.5 to 4; Diaspore is 6.5 to 7; and α-Al₂O₃ is 9.

Gates and Klaus [5] have shown that chemical reactions occur between gamma alumina and water (and at reasonable rates), however, no reaction was observed between alpha alumina and water. The oxides formed on a fresh metal surface when it is exposed to an oxidizing environment are almost never alpha alumina. Usually the formation of gamma alumina is favored [7].

Which hydroxide will be formed depends on the environmental temperature. Low temperatures of up to 100°C seem to favor the trihydroxide. Between 100°C and 330°C, Boehmite is formed. At highest temperatures, alpha alumina is formed.

REFERENCES