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Tribological Properties and Thermal Stability of Various Types of Polyimide Films

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TRIBOLOGICAL PROPERTIES AND THERMAL STABILITY OF VARIOUS
TYPES OF POLYIMIDE FILMS

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ABSTRACT

E-710 Thermal exposure experiments at 315° and 350° C were conducted on seven different types of polyimide films to determine which was the most thermally stable and adherent. The polyimides were ranked according to the rate of which they lost weight and how well they adhered to the metallic substrate. Friction and wear experiments were conducted at 25° C (room temperature) on films bonded to 440C HT stainless steel. Friction, film wear rates, wear mechanisms, and transfer films of the seven films were investigated and compared. The polyimides were found to fall into two groups as far as friction and wear properties were concerned. Group I had lower friction but an order of magnitude higher film wear rate than did group II. The wear mechanism was predominately adhesive, but the size of the wear particles were larger for group I polyimides.

INTRODUCTION

It has been shown in previous investigations (refs. 1 and 2) that polyimide and polyimide-bonded graphite fluoride films have potential for solid lubricant applications (like foil bearings) where long thermal soaks are encountered. Low thermal weight loss rates, good adhesion and good friction and wear properties were obtained for films thermally aged at temperatures up to 315° C.

The word polyimide is a generic designation and refers to a class of long-chain polymers which have recurring imide groups as an integral part of the main chain. By varying the monomeric starting materials, polyimides of different chemical composition and structure can be obtained. The polyimide chains consist of aromatic rings alternated with heterocyclic groups and due to the multiple bonds between these groups the polyimides are characterized by a high thermal stability (400° C in air, 500° C in inert atmospheres (refs. 3, 4, and 5)). At the decomposition point, they crumble to a fine powder without melting. They also have a high radiation stability (refs. 5, 6, and 7) and can withstand high exposure to neutrons, electrons, ultraviolet light, and gamma radiation. They are resistant to most common chemicals and solvents, but are attacked by alkalis (refs. 6 and 7). For a more detailed discussion of the physical properties, see references 5 to 10.

Previous studies on polyimide type PI-4701 (refs. 11, 12) indicated that there was a transition temperature, above which the friction coefficient and film wear rate dropped considerably. Moisture in the atmosphere was found to raise the temperature at which this transition occurred. Observations of the sliding surfaces above and below the transition temperature, indicated that the reason for the change in tribological properties was due to a change in the flow properties of the polyimide. Below the transition the polyimide tended to wear in a brittle manner and very fine powdery wear particles were produced. Above the transition, a very thin surface layer of the film was found to plastically flow. Similarly, a thin plastically flowing transfer film was found on the rider as opposed to the thick, heavy compacted films found below the transition.

Moisture in the atmosphere was found to raise the transition temperature, although it acted as a plasticizer to lower the friction at tempera-

tures below the transition, but it did not affect the wear. It was postulated the reason for the transition was due to some segment of the molecule obtaining an additional degree of freedom, which enabled the polyimide to plastically flow on the surface. Moisture is known to hydrogen bond to polyimide molecules; it was postulated that this put a further constraint on the molecules ability to plastically flow and the transition was increased to a temperature at which H_2O molecules were removed (or at least their presence was negligible).

Since most applications for polyimides would be where there is an environment of moist air, this investigation was conducted to determine if any one particular polyimide had better tribological properties in moist air at 25° C. The objectives were threefold. First, to determine which of these polyimides was the most thermally stable and most adherent at elevated temperatures; second, to determine if the different types of polyimide films had different tribological properties; and third, to attempt to achieve a better understanding of the lubricating and wear mechanisms by studying the film wear surfaces and the transfer films.

Seven different commercially available polyimides were evaluated. They were designated PIC-1 through PIC-7. PIC-1 (PI-4701) was the polyimide used in previous investigations. The films were applied to AISI 440C HT stainless steel disks and evaluated on a pin-on-disk friction and wear apparatus. The pin material was 440C HT (high temperature) stainless steel and was slid against the film under a 1-kg load at a speed of 1000 rpm (2.6 meters per second). In addition to sliding a hemispherically-tipped pin (as is normally done), riders with 0.95 mm-diameter and 1.20 mm-diameter flats on them were also slid against the film. This was done to investigate the

effect of a controlled, lower, constant contact stress on the tribological properties.

MATERIALS

The polyimides used were obtained as precursor solutions. In most instances a thinner of N-methyl-pyrrolidone was added to the polyimides to make them sprayable. Seven different types of polyimides were evaluated. The chemical composition and structure of four of the polyimides were proprietary. They are designated in Table 1 as polyimide types PIC-1 to PIC-4. The structures of the other three polyimides are known and are shown in figures 1(a), (b), and (c). They are designated as polyimide types PIC-5 to PIC-7 in this investigation. The polyimide used in previous work by this investigator (refs. 1 to 4 and 11 to 14) is designated as PIC-1 (PI-4701). The films were applied to AISI 440C HT (high temperature) stainless steel disks (1.2 cm thick by 6.3 cm diameter) that had a Rockwell hardness of C-60. The riders used were made of AISI 440C HT stainless steel of Rockwell hardness C-58. The films were also applied to 304 stainless steel foils (6.3 by 5.1 by 0.015 cm) that had a hardness of Rockwell B-87.

APPARATUS

A conventional type of pin-on-disk friction and wear apparatus was used in this study (fig. 1). The riders were either hemispherically tipped pins with a radius of 0.475 cm or the same hemispherically tipped pins with 0.95 mm or 1.20 mm-diameter flats worn on the hemisphere (see insert fig. 2). They were loaded with a 1-kilogram deadweight against the film which was applied to a flat, 6.3 cm-diameter disk. The disk was rotated at 1000 rpm, and the rider slid on the disk at a radius of 2.5 cm which gave it a linear sliding speed of 2.6 m/sec. The friction specimens were enclosed in a chamber to obtain a controlled air atmosphere of 10 000 ppm H_2O (approximately

50 percent relative humidity), dry air and dry air bubbled through water were mixed. Humidity was monitored continuously.

PROCEDURE

Surface Preparation and Cleaning

The 440C HT stainless steel disk surfaces were roughened by sandblasting to a centerline average (CLA) roughness of 0.9 to 1.2 micrometers. The 304 stainless steel surfaces were roughened by sanding with number 150 wet sandpaper to a cla roughness of 0.25 to 0.36 micrometers. After surface roughening, the steel surfaces were scrubbed with a brush under running tap water, rinsed in distilled water, and then clean, dry compressed air was used to quickly dry the surfaces. The specimens were stored in a dessicator until they were ready for coating with the polyimides.

The rider (surface roughness, $0.09 \pm .02$ micrometer, CLA) was lightly scrubbed with ethyl alcohol and with levigated alumina. It was next rinsed in distilled water and dried with compressed air. Polyimide was not applied to the riders.

Film Application and Cure

An artist's airbrush was used to apply the polyimide films to the disks. The films did not dry rapidly; thus, only a thin layer was applied at one time to prevent "running". Each layer was completely cured before the next layer was applied. The cure was to slowly raise the temperature from ambient (25°C) to 320°C at a rate of approximately $1\frac{1}{2}$ degrees centigrade per minute. The temperature was then held at 320°C for 1 hour. The film thicknesses evaluated in this study were from 20 to 25 micrometers. Since each layer applied was from 8 to 13 micrometers thick, up to three applications were needed to achieve the desired thickness.

Friction and Wear Tests

The procedure for conducting the friction and wear tests was as follows: A rider and disk (with applied polyimide film) were inserted into the friction apparatus and the test chamber was sealed. Moist air (10 000 ppm H_2O) was purged through the chamber for 15 minutes. Moist air was used as a controlled atmosphere. The flow rate was 1500 cubic centimeters per minute, and the volume of the chamber was 2000 cubic centimeters. After purging for 15 minutes, the disk was set into rotation at 1000 rpm and a 1-kilogram load was gradually applied. The 1-kilogram load applied to the 0.95 mm-diameter flat (0.0071 cm^2 area) gave a projected contact stress of 13.8 MPa (2000 psi); while the 1-kilogram load applied to the 1.20 mm-diameter flat (0.011 cm^2 area) gave a projected contact stress of 8.7 MPa (1250 psi). Measurements of the transfer area on the hemispheres after 1/4 kc of sliding indicated that the initial contact stresses were greater than 105 MPa (15 000 psi). The test temperature was 25° C (room temperature).

Each test was stopped after 1 kilocycle of sliding (160 m). After the rider and disk were removed from the friction apparatus, the contact areas were examined by optical microscopy and photographed. Surface profiles of the disk wear tracks were also taken. Rider and disk were placed back into the apparatus and the previous test procedure was repeated. The rider was not removed from the holder, and locating pins in the apparatus insured that it was returned to its original position. The same was true for the disk.

Each test was stopped and the test procedure repeated after selected sliding times. Film wear was calculated by measuring the cross-sectional area of the wear track on the polyimide film (from the surface profiles) after each sliding interval. At least four traces were taken and averaged.

Thermal Aging Tests

The thermal aging tests were conducted at temperatures of 315° C (599° F) and 350° C (662° F). At various intervals the foils with applied films were taken out of the oven, let cool for 15 minutes, and weighed to obtain a weight loss. Cooling time was 15 minutes, to insure water absorption rates had stabilized. The foils were aged for as long as 766 hours at 315° C and 213 hours at 350° C.

Adherence Tests

The adherence tests were performed on the films applied to the foils before and after thermal aging. They consisted of simple bending and flexing tests of the foils. The foils with applied films were repeatedly flexed and bent by hand to various degrees and then observed by optical microscopy for cracking. In many instances thermal exposure alone caused the films to spall.

Analysis of Sliding Surfaces

Optical microscopy techniques were used to study the lubricating films, the transfer films, and the wear particles in this investigation. The surfaces were viewed at magnifications to 2000x. At these high magnifications, the depth of field was very small (approximately 1 μ m); thus the focusing distance was used in measuring various features on the sliding surfaces such as film thickness, and wear track depth.

The thin films (1 μ m or less) of polyimide were transparent. Since illumination and observation of the surfaces were normal to the surfaces, interference fringes could be seen in the films both on the disk wear track and on the rider. Interference fringes indicated that solid lubricant films were present and that the films were smooth and continuous.

RESULTS AND DISCUSSION

Thermal Exposure Effects

Film Weight Loss Rates. - The weight loss rates at constant temperatures of either 315° or 350° C were determined for at least four different film weights for each polyimide. The film weights ranged from 0.1946 gm to 0.0276 gm. It was found that the rate of film weight loss was linear with time for all the films regardless of film weight. Figure 3 gives a representative example of how the different weight films lost weight as a function of time at a constant temperature. Plotted in figure 3 are PIC-7 films of weights, 0.1200, 0.1000, 0.0764, and 0.0346 gm.

A linear regression fit (least squares) of the film weight loss data points (for each exposure test) was made to obtain weight loss rates. As a general rule, for any particular type of polyimide, the heavier the film, the greater the film weight loss rate. However, if the weight loss rate is calculated in terms of percent total film weight lost per hour, then it is found that percent of the film lost per hour is either constant or decreases slightly as a function of increasing weight. Thus, it appears that the weight loss of polyimide films is bulk oriented as well as surface oriented, since the surface area was constant.

The fact that most of the weight loss curves (fig. 3) did not pass through the zero of the y-axis indicates a considerable amount of water or other volatile constituent was liberated from the films during initial exposure at 315° or 350° C. In general, the heavier the film, the greater the amount of volatile released. For most of the films, the volatile tended to be released in less than 24 hours of exposure; but for polyimide type PIC-5, it took up to 100 hours at 315° C.

Table 2 compares the percent film weight loss rates for the seven different polyimides evaluated at 315° and 350° C. For all the polyimides the weight loss rates at 350° C were about 5 times greater than at 315° C; but the relative ranking of the polyimides, as far as thermal stability was concerned was about the same at 315° and 350° C. The most thermally stable polyimide was PIC-7, it was followed respectively in decreasing order of stability by PIC-2, PIC-3, PIC-5, PIC-1, PIC-6, and PIC-4.

Film Adherence. - The adherence of the films was evaluated by simple bending tests both before and after thermal exposure to temperatures of 315° and 350° C. The bending tests did not cause the films to spall; however the long thermal soaks did cause some of the films to blister and spall, both at 315° and 350° C.

Table 3 gives the exposure times when cracking and spalling of the films occurred at 315° and 350° C for weights >.0500 gm and <.0500 gm. No cracking or spalling at 315° C was observed for 4 of the films: PIC-2, PIC-3, PIC-5, and PIC-7. The other 3 showed some form of cracking or spalling. In general, the thicker the film, the sooner these cracks and spalls occurred.

At 350° C, cracks were found to occur in each type of polyimide; however in some individual cases no cracks were found. The most adherent polyimide at 350° C was PIC-5. Of the six PIC-5 films evaluated at 350° C, only a small amount of cracking was observed in one corner of one foil after 184 hours of exposure. The next best was PIC-2. Of the six PIC-2 foils evaluated at 350° C only two showed fine cracking. No spalls were observed to occur in either PIC-5 or PIC-2.

Even though PIC-7 gave the lowest weight loss rates, it was not the best as far as adherence was concerned. Only one of the four PIC-7 films

evaluated at 350° C did not crack or spall and that was the thinnest film. Equivalent results were found with PIC-3. Two of the four PIC-3 films evaluated at 350° C cracked and spalled. The other three polyimides evaluated, PIC-1, PIC-4, and PIC-6 all experienced severe cracking and spalling at 350° C, and are not considered good candidates for use when long thermal soaks at this temperature are encountered.

TRIBOLOGICAL PROPERTIES

Friction coefficient. - A comparison of the friction traces using three different contact areas during the initial stages of sliding on a PIC-3 polyimide film applied to a 440C HT stainless steel substrate is shown in figure 3. The results are typical of all seven polyimide films. The friction coefficient for the hemisphere sliding against the film is lower than either flat area; and the friction coefficient, in general, was lower for the 0.0071 cm²-area flats than for the 0.011 cm²-area flats. According to Amonton's law and the adhesion theory of friction, the friction coefficient should be independent of the apparent area of contact. Bowden and Taber (ref. 16) have shown that Amonton's law breaks down when hard surfaces slide on thin metallic films. It could be that a similar effect occurred for thin polyimide films applied to a hard substrate.

To ascertain if apparent area of contact was responsible for the increase in friction, shear strength was calculated for each contact area from the relationship: friction force (F) is equal to the apparent area of contact (A) times the shear strength (S). The contact area for the hemisphere was calculated by measuring the area of the transfer film on the rider (after 1 Kc of sliding). The area was found to be 9×10^{-4} cm². The shear strengths calculated for the hemisphere, the 0.0071 cm²-area flat, and the 0.011 cm²-area flat were respectively: 2500 N/cm², 520 N/cm², and 370

N/cm^2 . Since the calculated shear stress increased with decreasing apparent area of contact, it implies that the real area of contact may have been greater for the smaller apparent contact areas, however, this does not explain why friction force increased with increasing apparent area of contact. It thus appears that the calculated shear stress is higher for the smaller contact areas because the friction force is also dependent on the plowing component of friction or on the viscoelastic properties of the polyimide. Plowing is dependent upon the contact stress. The contact stresses on the hemisphere, 0.0071 cm^2 -area flat and 0.011 cm^2 -area flat were respectively: 105 MPa (15,000 psi), 13.8 MPa (2000 psi), and 8.7 MPa (1250 psi).

The friction coefficients for longer sliding durations are plotted in figure 4 as a function of sliding duration for all seven polyimide films. The results for the hemisphere sliding on the film are plotted in figure 4(a). The lowest friction coefficients were obtained with polyimide films PIC-1, PIC-4, and PIC-7, however as the figure indicates the wear lives (time taken to wear through films) were very short. Lower friction coefficients and short wear lives for these three films were also found for the other two contact areas (figs. 4(b) and (c)).

There are no clear differences between the friction coefficients of the other polyimides. The values obtained depended on the sliding duration and the type of rider contact which was slid against the film. Table 4 gives values for the average friction coefficient obtained for each film and the variation which occurred with sliding duration for a particular individual experiment. The sliding duration is given.

Film wear. - Figure 5 plots the average cross-sectional areas of film wear for each polyimide as a function of sliding duration for (a) the hemi-

sphere, (b) the 0.0071 cm^2 -area flat, and (c) the 0.011 cm^2 -area flat, respectively.

The general trend was that the wear for each individual film increased in a linear manner (from zero) as a function of sliding duration. A linear regression fit (least squares) of the data (from each test) was made and an average film wear rate determined. Table 4 gives the average wear rates (and the variation obtained) for each film and for each type of rider contact in terms of cm^2/kc and m^3/Nm .

The table indicates that the three films that gave the lowest friction coefficients (PIC-1, PIC-4, PIC-7) also gave the highest wear rates. It is also seen that for these three films, as the area of contact increased (or contact stress decreased) longer wear rates were obtained. The wear rates found for these three films varied from $360 \pm 150 \text{ m}^3/\text{Nm} \times 10^{-15}$ to $40 \pm 8 \text{ m}^3/\text{Nm} \times 10^{-15}$.

The other four films (PIC-2, PIC-3, PIC-5, and PIC-6) gave much lower wear rates; and as the contact stress was reduced from that of the hemisphere to that of the flat, the film wear rate decreased. The film wear rates obtained for the 0.0071 cm^2 -area flat and the 0.011 cm^2 -area flat were nearly equal.

The lowest overall wear rates were obtained with the PIC-3 film. The next best film wear rates were obtained with the PIC-5 films. The wear rates for the PIC-2 film were very similar to the PIC-5 film for the two flat areas, however the wear rates for the hemisphere sliding on the film was a little higher. The PIC-6 film was the fourth best.

Film wear mechanisms. - Wear mechanisms of the polyimide films were studied by using an optical microscope to magnifications of 2000x. It was found that the appearance of a particular polyimide wear track did not de-

pend on the type of rider contact (whether it be a hemisphere or flat) which slid against it. The wear tracks of some of the polyimides looked very different, however.

Photomicrographs of the film wear tracks on a PIC-2 film and on a PIC-3 film are shown in figures 6 and 7, respectively. The appearance of the PIC-3 film wear track is also typical of the wear tracks on PIC-5 and PIC-6 polyimide films. As figure 6(a) illustrates, the surface of the wear track on the PIC-2 film was very smooth and shiny. Striations can be seen in the sliding direction and the film wear track is transparent enough that the metallic asperities of the substrate can be seen through the film at high magnifications (fig. 6(b)). In localized areas, however, non-smooth regions are seen as shown in figure 6(b). The areas tend to be wedge-shaped and the material appears to be in the process of spalling.

At low magnification, the wear track surface of the PIC-3 film (fig. 7(a)) is darker and not as smooth as the PIC-2 film. At high magnification, it is seen that the wear track surface on the PIC-3 film (fig. 7(b)) was completely covered with the wedge-shaped textured material that was found to occur only in localized areas in the PIC-2 film wear track. The wear rates and friction coefficients obtained for these two films were not very different, so apparently this difference in wear track appearance was not significant.

Photomicrographs of the PIC-4 film wear track surface is shown in figure 8 after 5 kc of sliding. These photomicrographs (characteristic of high wear) also typify the film wear track surfaces found for PIC-1 and PIC-7 films. Bright areas are seen on the wear track at low magnifications (fig. 8(a)), but in general the film wear track is very dark colored. High magnification photomicrographs of these bright areas (fig. 8(b)) indicate that

they are agglomerated wear particles which are still adhering to the wear track.

The texture of the film wear track surfaces for all the films (with the possible exception of PIC-2 films) indicates that the wear process taking place is adhesive, since the wear particles appear to have been pulled out of the surface. The wear particles from polyimides PIC-1, PIC-4, and PIC-7 were produced at a faster rate and in general were larger than those produced on the other polyimides.

In addition to adhesive type of wear, two of the films (PIC-4 and PIC-7) tended to spall in localized regions around the film wear track. These spalls were found regardless of the type of contact (hemisphere or flat-area) which was slid on the film. When the film spalled it did not make a clean break with the substrate. This indicated that the spall was due to the brittleness of the polyimide and not due to poor adherence of the film to the substrate.

A few small spalls were also observed to occur after long sliding durations in the PIC-2 polyimide films. The tests were stopped when the spalls were observed. Thus the test duration times, given in Table 4, specify the time when spalling was observed.

Rider wear and transfer. - Two different types of polyimide transfer to the rider were observed to occur for the different polyimides. The first type was a very adherent, plastically flowing thin film type of transfer, and could be found for all polyimides after short sliding intervals. The thin, flowing type of transfer (from PIC-2 films) did not seem to be affected by contact geometry. Transfer to the hemisphere and the flat areas looked very similar. Figure 9 gives photomicrographs of the transfer film to a 0.0071 cm^2 -area flat after sliding on a PIC-2 film for 300 kc. The

polyimide tended to build-up in the entrance region of the contact area, but in the contact zone the films were very thin and broad interference bands were seen (fig. 9(b)). An occasional clump of polyimide material (fig. 9(a)) was found on the flat area, but for the most part these were rare occasions. As sliding distance increased, all polyimides except PIC-2 tended to produce transfer of the second type.

The second type of transfer film appeared on the remaining polyimides. The transfer was powdery in nature and although it adhered to itself to form "clumps", good adherence to the rider did not occur. In general, either clumps (compacted powdery material) or loose powdery polyimide was found in the contact area. Figure 10 gives photomicrographs of the transfer to a 0.011 cm^2 -area rider flat after sliding on a PIC-3 film for durations of 1 kc and 300 kc, illustrating this type of transfer.

When the first type of transfer occurred no measurable wear was observed on the metallic rider. When the second type occurred, some rider wear did occur, especially for the PIC-3 film. Figure 10(b) gives a photomicrograph of the 0.011 cm^2 -area flat which slid on the PIC-3 film for a sliding duration of 300 kc. The wear is most noticeable at the sides of the contact area (fig. 10(b)), and is in the form of grooves on the rider flat. A "clump" of polyimide material lies in one of the grooves. It appears the groove was worn in the flat by the polyimide clumps. Apparently the polyimide "clumps" are forced through the contact area; and instead of shearing, they slide at the metal interface causing the metal to wear.

Figure 10(c) gives high magnification photo micrographs of the transfer to the 0.0011 cm^2 -area rider flat which slid on the PIC-3 film. The transfer consists of powdery material and "clumplike" material. Hardly any thin lamellar-like transfer is seen. Initially the clumps are thin but as

the sliding time increases they grow thicker. The thickness of the clumps after 300 kc of sliding in figure 10(b) is 3 to 4 μm .

Cylinder or Roll Formation

Aharoni (ref. 17) has proposed some rigid polymers can wear by a process termed roll formation. This type of wear particle was also observed for most of the polyimides in this study; however, they were only observed to occur during the initial stages of sliding (less than 1 kc). Figure 11(a) shows polyimide cylindrical wear particles in the exit region of the rider, figure 11(b) in an area within the film wear track, and figure 11(c) shows them in a region outside the wear track. Figure 11(c) was taken between crossed polaroid filters and shows the cylinders are birefringent, indicating they have an anisotropic crystal structure. Thus, the polyimides are either crystalline to begin with or the sliding process orders them.

Figure 11(a) indicates one source of cylinder production is the transfer film on the rider. As the transfer leaves the contact area, it tended to break off and roll up to form a cylinder. Figure 11(b) indicates another source of cylinders is the surface of the cured polyimide film. Initial passes over this film induced the polyimide to roll up into cylinders. However after very short sliding distances the surfaces changed (transfer films developed, the film surface losses its smooth character, etc.) and the conditions are not suitable for cylinder production.

CONCLUDING REMARKS

This investigation indicated that the different polyimides had markedly different tribological properties. The polyimides were divided into two groups; Group I: low friction, high wear and Group II: high friction, low wear. Even so, within each group differences in friction, wear and transfer were observed. This is not surprising since each polyimide has a different

chemical composition, and such parameters as degree of crystallinity, molecular weight, and whether they are linear or crosslinked are different.

It would be beneficial to correlate the tribological properties of the different polyimides with chemical structure, however this is difficult since four of the polyimides were proprietary and the other three were not well characterized as to crystallinity, molecular weight or degree of crosslinking.

What is known about the latter three polyimides is that the PIC-5 polyimide is a fully imidized, condensation copolyimide consisting of the two compositions in figure 1(a). PI-6 is an addition polyimide with a structure as shown in figure 1(b). The molecular weight, degree of crosslinking and crystallinity of these two polyimides are unknown. The most information available is for PIC-7. It is a condensation polyimide with the structure shown in figure 1(c). It is amorphous, linear, and essentially non-crosslinked with a high molecular weight. Some additional properties of these three polyimides are shown in Table 5.

Of the polyimides with known chemical compositions, PIC-5 gave the best wear results, while PIC-7 gave the worst. PIC-7 did give the lowest friction coefficient which indicates friction and wear are not directly related. Comparing the structures and physical properties of the two indicates that from a tribological viewpoint a linear non-crosslinked polyimide is not desirable, although there may be some other parameter influencing the results. Table 5 indicates PIC-7 has a higher tensile modulus than PIC-5 and that elongation at break is 10% for PIC-5 and 2-6% for PIC-7. These two properties indicate that PIC-5 is less brittle than PIC-7 and thus has a tendency to plastically flow rather than brittely fracture as did PIC-7.

The lower friction coefficients obtained with PIC-7 may have been due to wear particles being more easily adhesively "plucked" from the surfaces.

From a tribological viewpoint the best two polyimides were PIC-2 and PIC-3. PIC-3 gave the lowest film wear rates and had good thermal stability. PIC-2 had equivalent thermal stability, but slightly higher film wear rates. From surface morphological considerations PIC-2 had what one would desire, a very smooth, almost glasslike wear track surface (figure 10). Also the transfer films were very thin and tended to coalesce and plastically flow across the contact. The other polyimides formed transfer films of compacted polyimide films which slid across the rider and tended to wear it.

Since the friction coefficients for Group I polyimides were less than Group II polyimides, the question arises as to the effect of frictional heating. Frictional heating was determined by monitoring the temperature on the film wear track with an infrared pyrometer. It was found that it took about 60 kc of sliding before the temperature stabilized. Since Group I polyimide films were worn through to the substrate in less than 30 kc of sliding they never obtained a stabilized operating temperature; thus their temperatures, at the end of each test were less than for Group II polyimides. Table 4 gives film wear track temperatures at the end of each test. Higher friction produced higher temperatures but no correlation of temperature and wear was determined.

SUMMARY OF RESULTS

Tribological studies at 25° C and thermal exposure experiments at 315° and 350° C on seven different types of polyimides indicate that:

1. The polyimides fell into two groups according to friction and wear properties.

(a) Group I: Low friction, high wear, Polyimide types PIC-1, PIC-4, and PIC-7.

(b) Group II: High friction, low wear, Polyimide types PIC-2, PIC-3, PIC-5, and PIC-6.

2. The most thermally stable polyimide was PIC-7; PIC-2, PIC-3, and PIC-5 were the next best; then PIC-1; and finally PIC-6 and PIC-4.

3. The most adherent polyimides after long thermal soaks were PIC-5 and PIC-2; next came PIC-3 and PIC-7; finally PIC-1, PIC-4 and PIC-6.

4. The wear mechanism for the polyimides was of an adhesive nature, but the adhesive wear particles of Group I polyimides were larger than those of Group II polyimides. Group I polyimides tended to spall from the wear track which indicated they might be more brittle than Group II polyimides.

5. In general, film wear rates tended to increase with decreasing contact stress for Group I polyimides, but Group II polyimides tended to show a decrease in wear rate with decreasing contact stress.

6. Most of the polyimides produced thick transfer films that consisted of compacted polyimide wear particles. These wear particles tended to slide across the rider contact area rather than to plastically flow; and after long sliding durations they tended to wear the metallic rider. One exception, was the polyimide, PIC-2; it produced thin, plastically flowing transfer films.

7. During the initial stages of sliding (1 kc of sliding), birefringent cylindrical wear particles were observed. These may have been produced by the "rolling-up" of a thin surface layer of the polyimide film or from polyimide transfer "rolling-up" as it flowed across and out of the rider contact area.

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TABLE 1. - DESIGNATION OF TYPES OF POLYIMIDES
USED IN THIS INVESTIGATION

Designation	Type	Structure
PIC-1	Condensation	Proprietary
PIC-2	Condensation	Proprietary
PIC-3	Condensation	Proprietary
PIC-4	Condensation	Proprietary
PIC-5	Condensation	Figure 1(a)
PIC-6	Condensation	Figure 1(b)
PIC-7	Condensation	Figure 1(c)

TABLE 2. - SUMMARY OF FILM WEIGHT LOSS RATES
AT 315° C AND 350° C FOR THE SEVEN
DIFFERENT TYPES OF POLYIMIDES
EVALUATED

Type of polyimide	Rate of film weight loss, percent/hr	
	Exposure temperature	
	315° C	350° C
PIC-1	0.053 ± 0.014	0.26 ± 0.03
PIC-2	.042 ± .011	.20 ± .07
PIC-3	.042 ± .017	.20 ± .10
PIC-4	.087 ± .015	.34 ± .03
PIC-5	.043 ± .14	.27 ± .08
PIC-6	.079 ± .030	.40 ± .15
PIC-7	.025 ± .009	.13 ± .04

TABLE 3. - MINIMUM EXPOSURE TIMES AT 315° C or 350° C WHEN
CRACKING AND SPALLING OF SEVEN DIFFERENT
POLYIMIDE FILMS WAS OBSERVED

Polyimide type	Film weight, gm	Exposure temperature			
		315° C		350° C	
		Time cracks observed, hr	Time spalls observed, hr	Time cracks observed, hr	Time spalls observed, hr
PIC-1	>0.0500	214	447	94	94
	< .0500	523	None	184	184
PIC-2	>0.0500	None	None	None	None
	< .0500	None	None	146	None
PIC-3	>0.0500	None	None	47	94
	< .0500	None	None	None	None
PIC-4	>0.0500	100	170	47	94
	< .0500	115	334	47	94
PIC-5	>0.0500	None	None	184	None
	< .0500	None	None	None	None
PIC-6	<0.0500	47	47	20	20
	< .0500	214	334	50	80
PIC-7	>0.0500	None	None	47	97
	< .0500	None	None	None	None

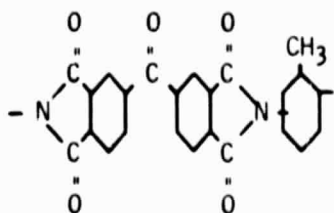
TABLE 4. - SUMMARY OF FRICTION AND WEAR RESULTS FOR THE POLYIMIDE FILMS BONDED TO 440C HT

STAINLESS STEEL SUBSTRATES

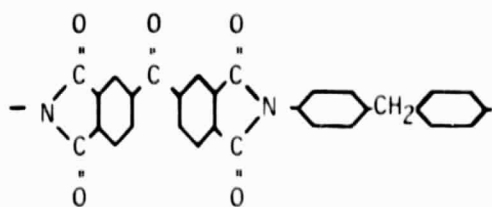
Type of polyimide	Area of contact, cm^2	Variation of friction coefficient	Average friction coefficient	Test duration, kc	Thickness of film worn through, μm	Film wear track temperature end test, $^{\circ}\text{C}$	Film wear rate cm^2/kc or m^3/Np $\times 10^{-15}$
PIC-1	Hemisphere 0.0071 .011	0.10 - 0.14	0.13	30	20	34	40±8
		.14 - .25	.20	30	16	39	60±10
		.19 - .29	.24	30	25	39	130±25
PIC-2	Hemisphere 0.0071 .011	0.18 - 0.25	0.23	120	16	39	10±2
		.36 - .43	.39	300	11	50	3±1.5
		.32 - .39	.33	280	12	53	4±1
PIC-3	Hemisphere 0.0071 .011	0.07 - 0.25	0.27	120	12	37	6±2
		.22 - .41	.37	350	9	51	2±1
		.32 - .42	.41	600	13	54	3±0.5
PIC-4	Hemisphere 0.0071	0.10 - 0.18	0.13	5	8	32	80±20
		.18 - .25	.21	1	5	30	350±150
PIC-5	Hemisphere 0.0071 .011	0.19 - 0.37	0.30	120	14	41	6±1
		.16 - .42	.35	300	12	49	3.5±.5
		.21 - .30	.29	500	16	46	4±.5
PIC-6	Hemisphere 0.0071 .011	0.21 - 0.37	0.28	120	18	44	12±.5
		.20 - .36	.34	150	18	49	12±2
		.22 - .29	.27	300	15	45	7±2
PIC-7	Hemisphere 0.0071	0.07 - 0.15	0.10	15	13	33	40±11
		.18 - .25	.22	1	6	--	50±30

TABLE 5. - PROPERTIES OF POLYIMIDE RESINS GIVEN BY MANUFACTURER

Property	Polyimide type		
	PIC-5	PIC-6	PIC-7
Tensile strength	120 MPa	83 MPa	110 - 140 MPa
Tensile modulus	2100 MPa	3900 MPa	4700 MPa
Flexural strength	200 MPa	130 MPa	120 MPa
Flexural modulus	3300 MPa	4500 MPa	-----
Compressive strength	210 MPa	170 MPa	-----
Compressive modulus	2000 MPa	-----	-----
Elongation at break	10%	2%	2 - 6%
Density	1.4 g/cc	1.37 g/cc	1.42 g/cc
Thermal expansion coefficient	$5.0 \times 10^{-5}/^{\circ}\text{C}$	$8.0 \times 10^{-5}/^{\circ}\text{C}$	-----
Glass transition	310° - 315° C	-----	350° - 371° C

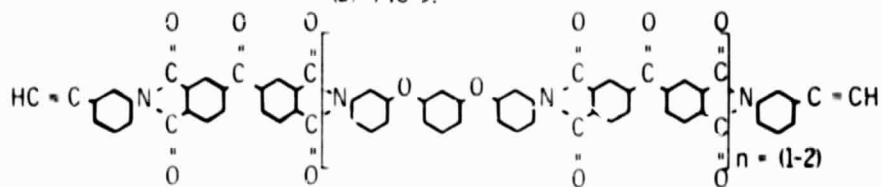


20 PERCENT OF THE RECURRING UNITS.

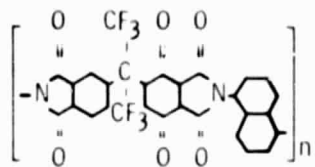


80 PERCENT OF THE RECURRING UNITS.

(a) PIC-5.



(b) PIC-6.



(c) PIC-7.

Figure 1. - Structure of polyimide types PIC-5, PIC-6, and PIC-7.

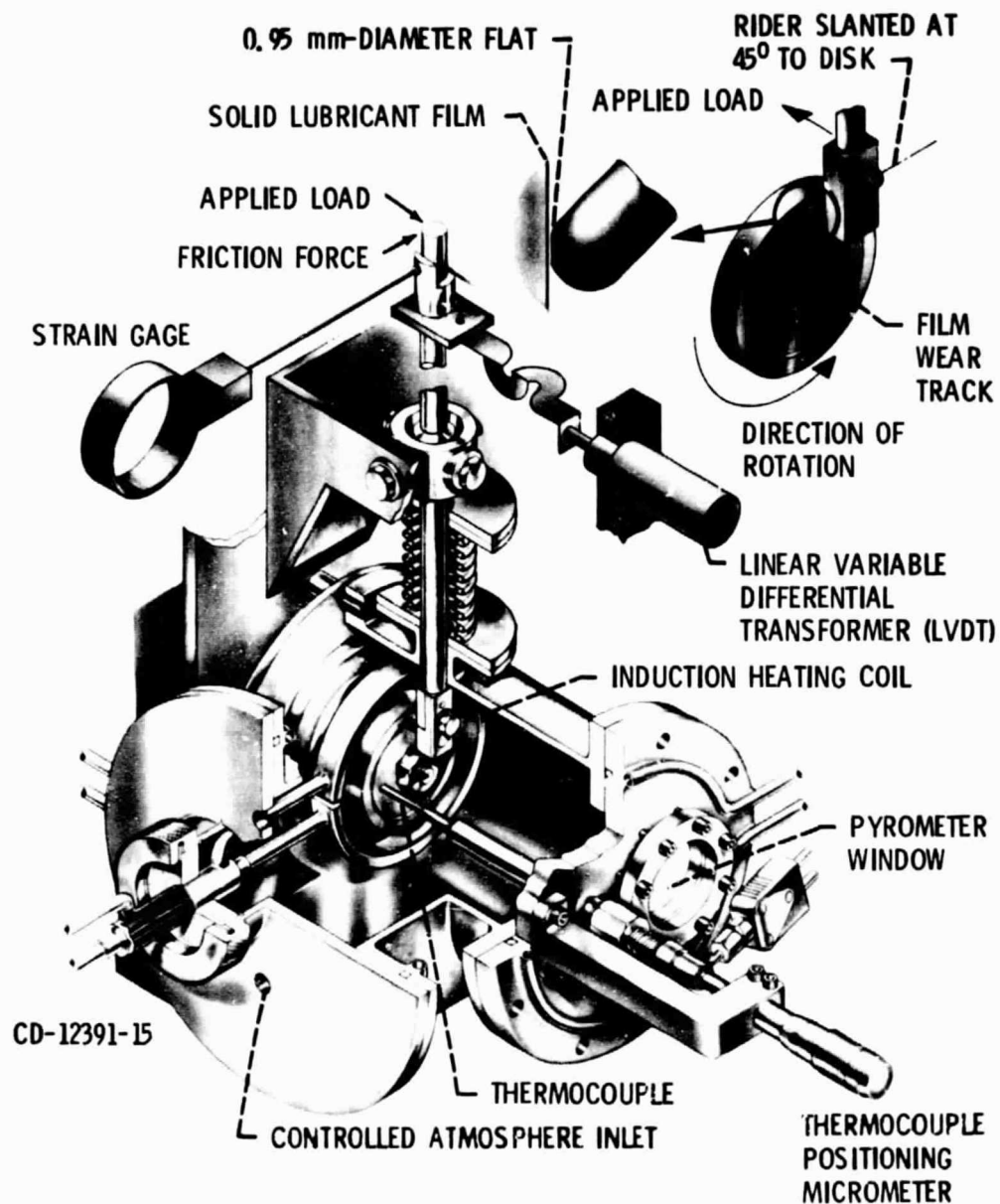


Figure 2. - Friction and wear apparatus.

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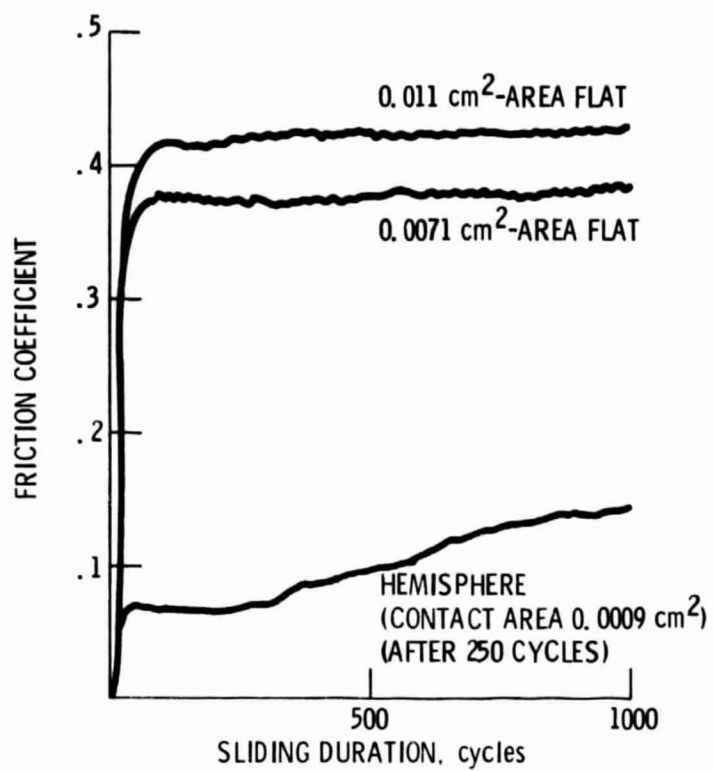
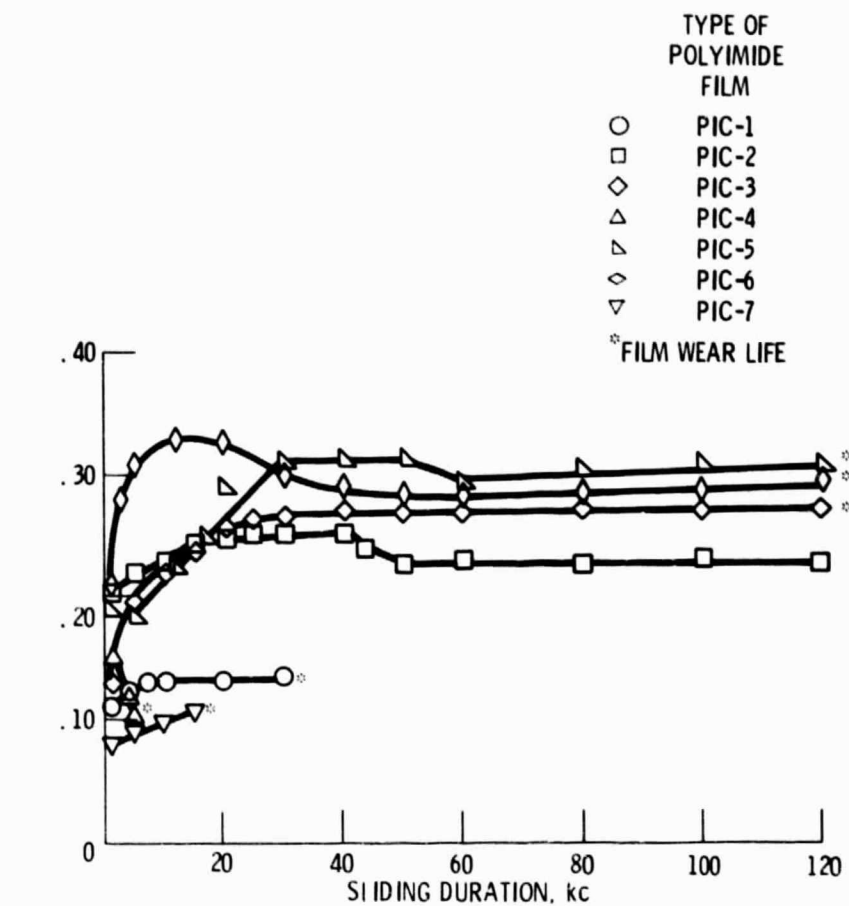
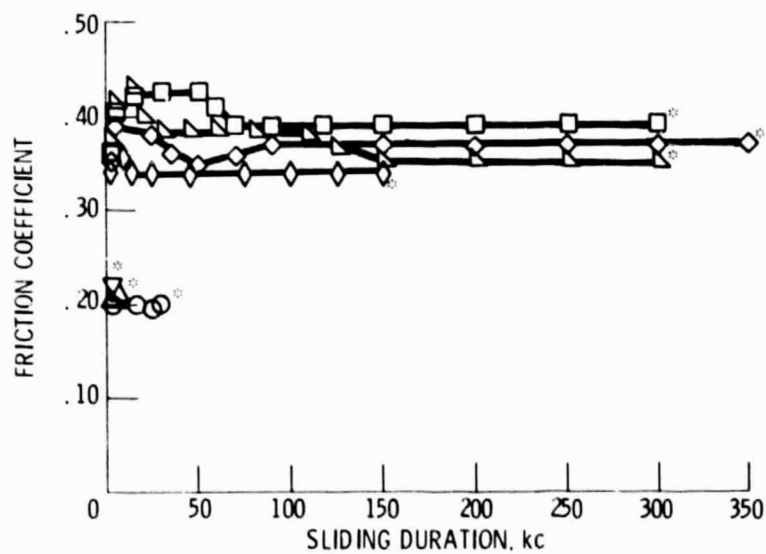


Figure 3. - Comparison of the friction traces during the initial stages of sliding on a PIC-3 film applied to a 440C HT stainless steel substrate by using three different rider contact areas.

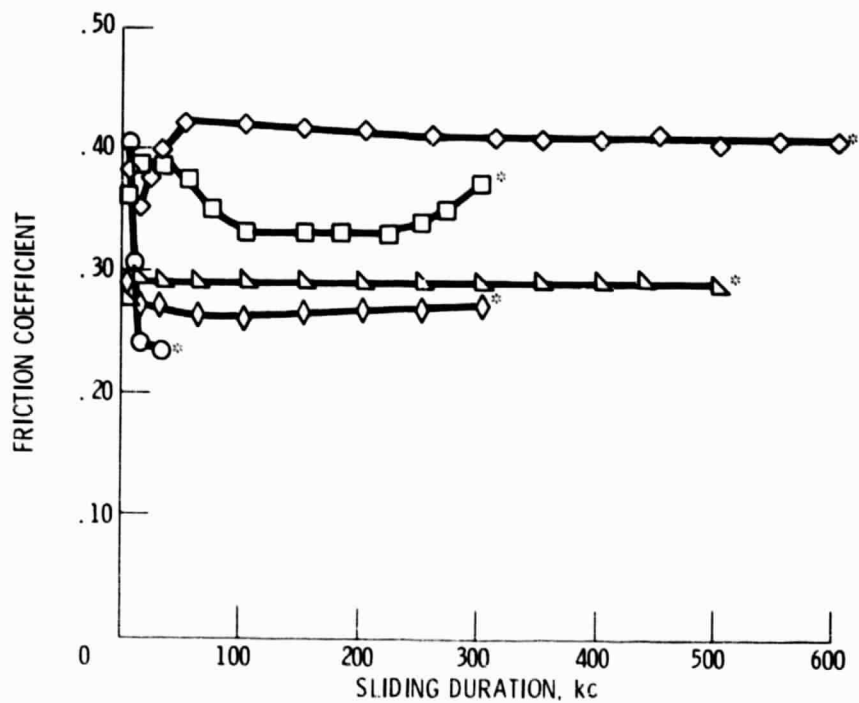


(a) Hemisphere.



(b) 0.0071 cm²-area flat.

Figure 4. - Average friction coefficient as a function of sliding duration for films applied to 440C HT stainless steel substrates.



(c) 0.011 cm²-area flat.

Figure 4. - Concluded.

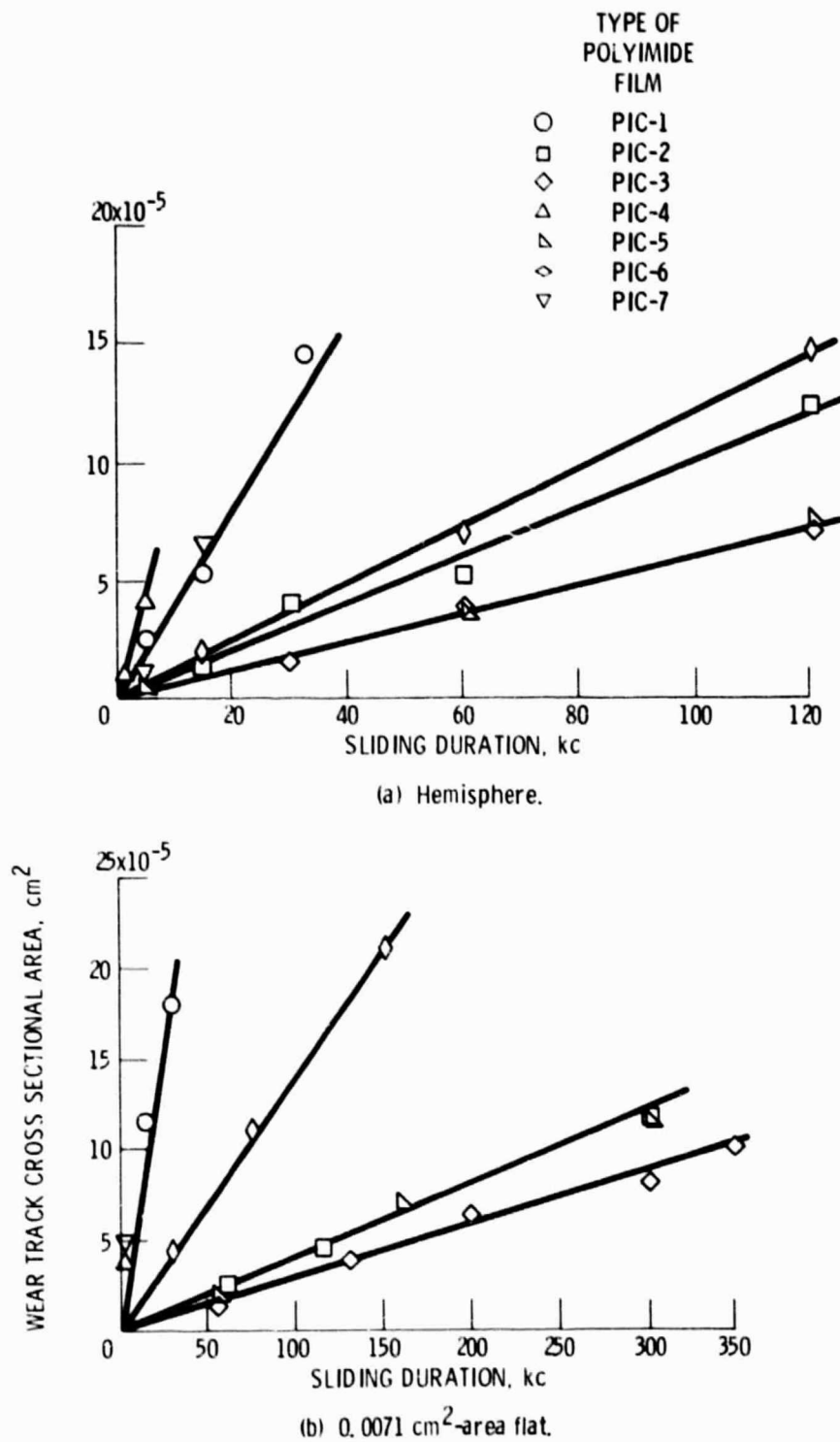
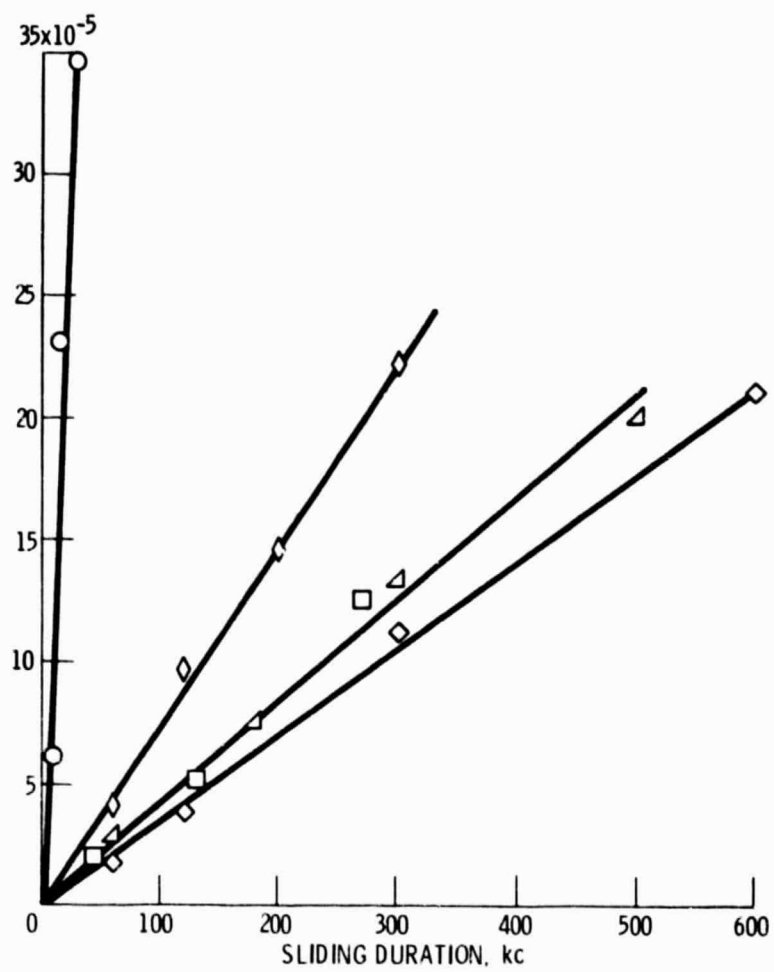
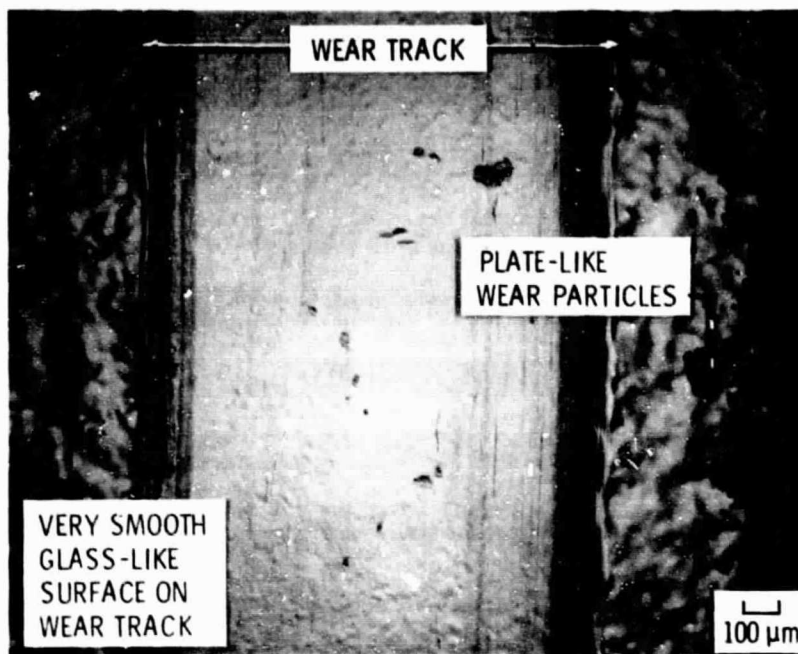


Figure 5. - Wear of seven different types of polyimide films as a function of sliding duration.



(c) 0.011 cm²-area flat.

Figure 5. - Concluded.



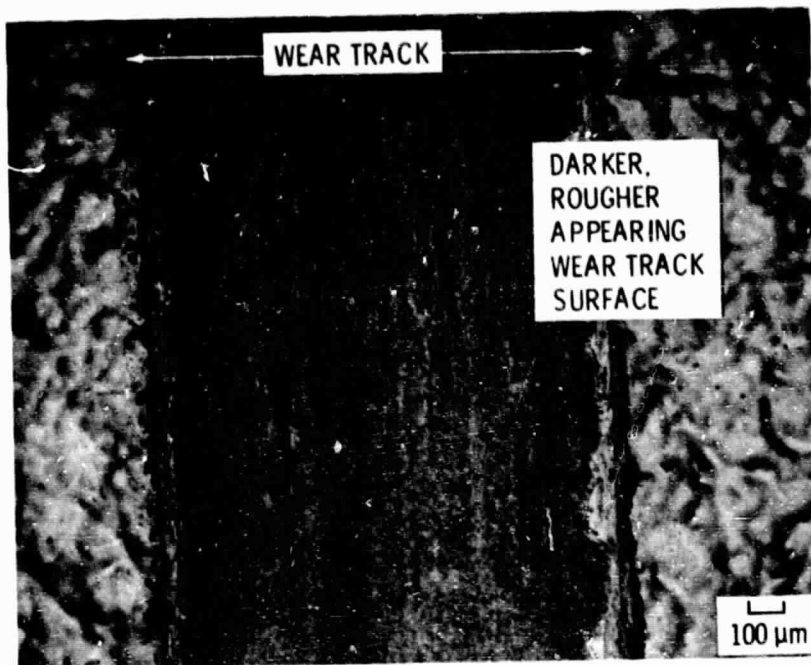
(a) OVERVIEW OF FILM WEAR TRACK.



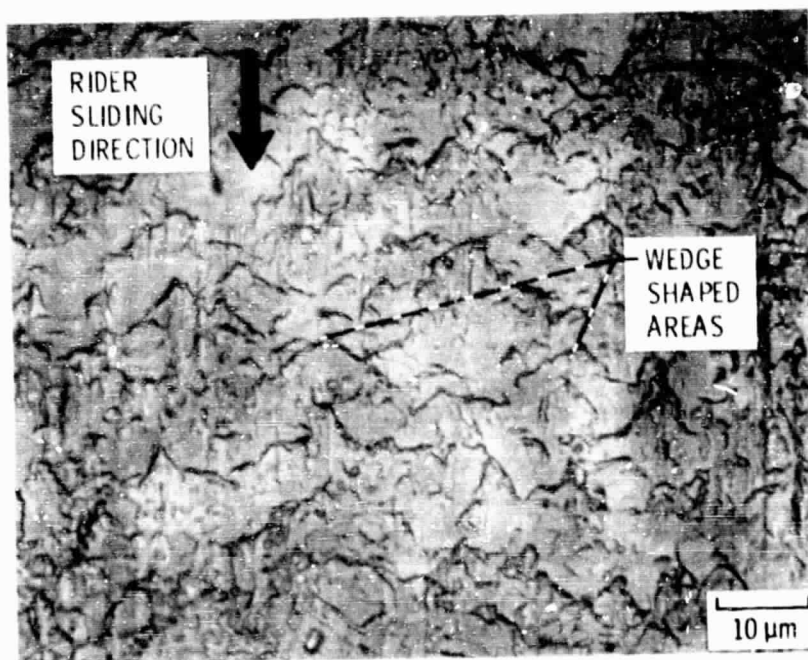
(b) HIGH MAGNIFICATION VIEW OF THE PIC-2 FILM WEAR TRACK SURFACE AFTER 300 kc OF SLIDING.

Figure 6. - Photomicrographs of the PIC-2 film wear track surface after 300 kc of sliding.

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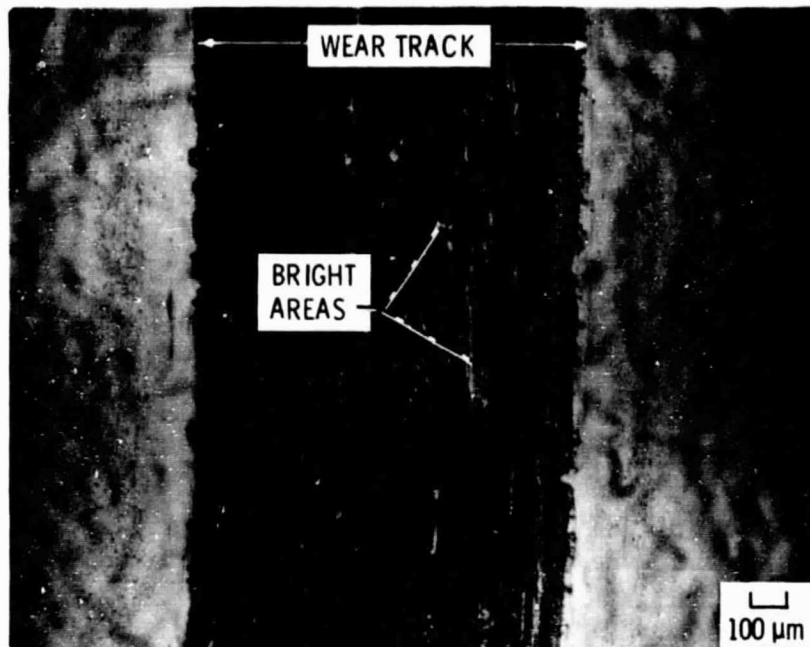


(a) OVERVIEW OF FILM WEAR TRACK.

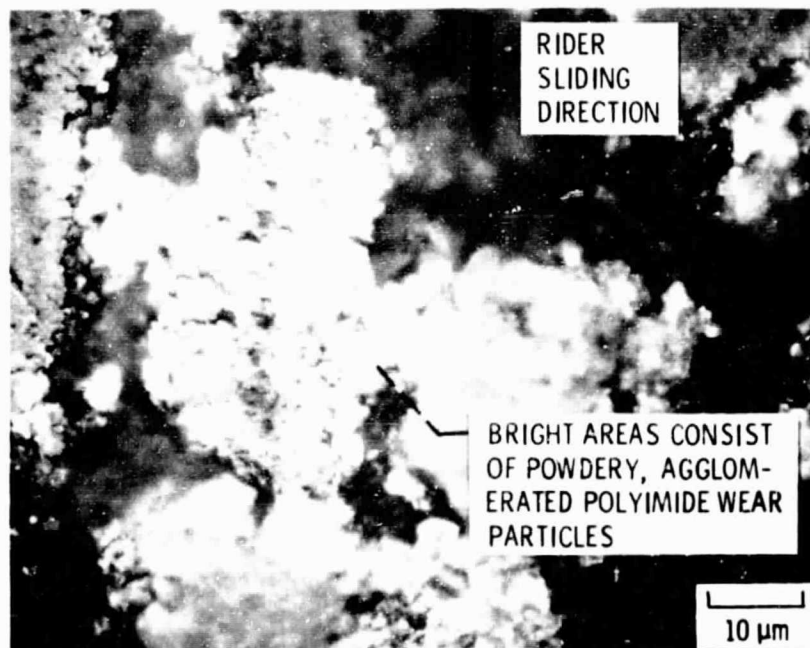


(b) HIGH MAGNIFICATION VIEW OF CENTER OF CENTER OF FILM WEAR TRACK.

Figure 7. - Photomicrographs of the PIC-3 film wear track surface after the 0.011 cm^2 -area flat slid on the surface for 300 kc. These photographs also typify the other contact areas and the wear track surfaces found for PIC-5 and PIC-6 films.



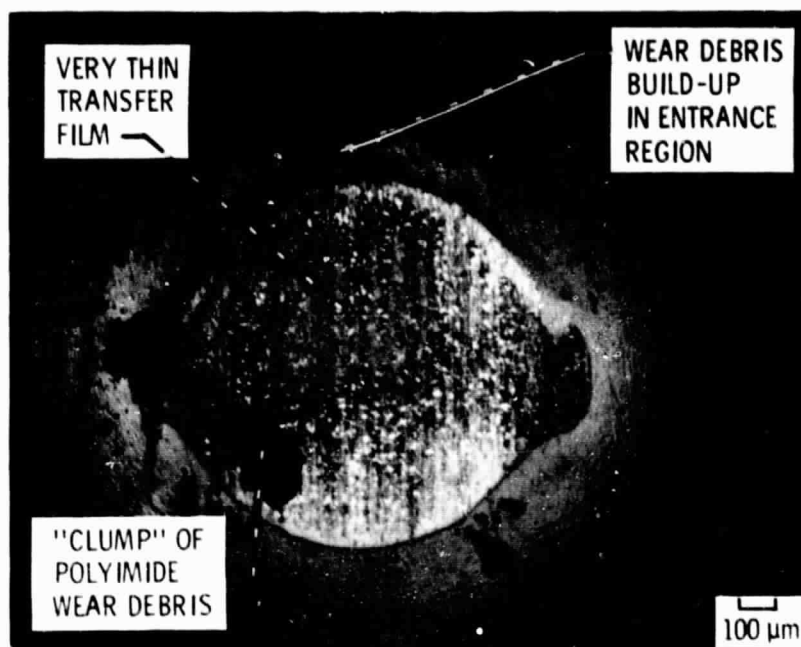
(a) OVERVIEW OF FILM WEAR TRACK.



(b) HIGH MAGNIFICATION VIEW OF CENTER OF FILM WEAR TRACK.

Figure 8. - Photomicrographs of the PIC-4 film wear track surface after 5 kc of sliding. These photomicrographs also typify the film wear track surfaces found for PIC-1 and PIC-7 films.

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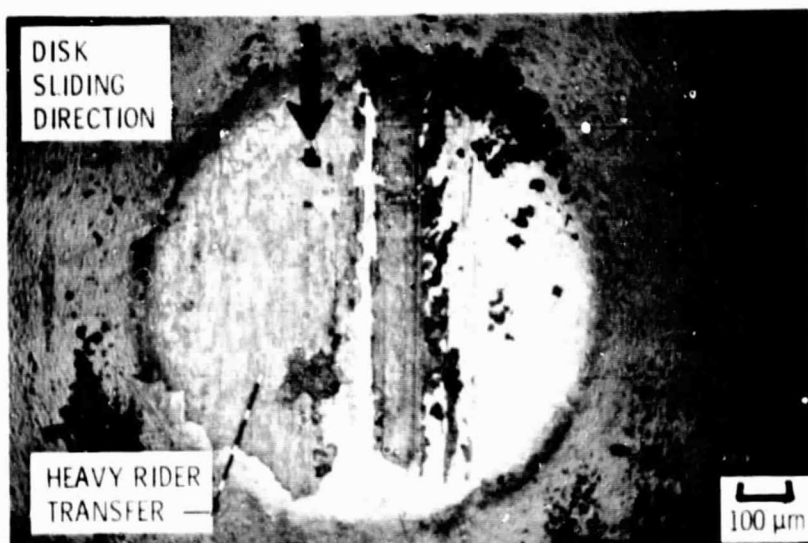


(a) OVERVIEW OF RIDER CONTACT AREA.



(b) HIGH MAGNIFICATION VIEW OF TRANSFER FILM IN CENTER OF CONTACT AREA.

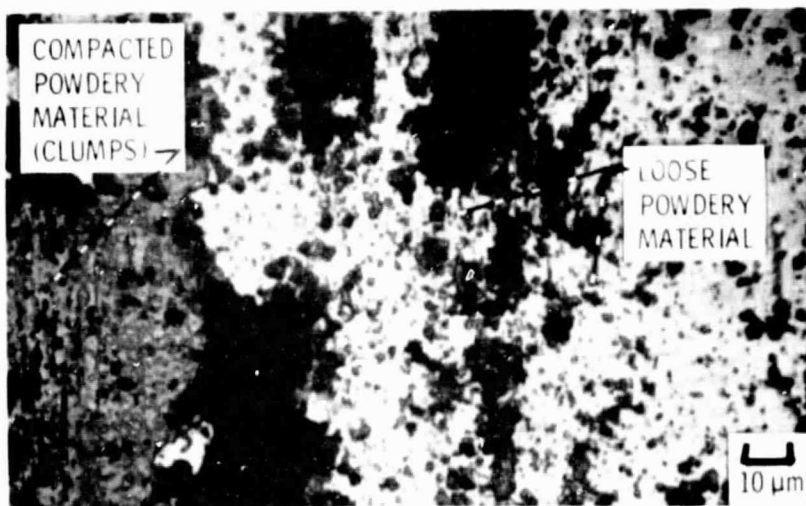
Figure 9. - Photomicrographs of the transfer film to a 0.0071 cm^2 -area rider flat after sliding on a PIC-2 film for 300 kc.



(a) OVERVIEW OF RIDER CONTACT AREA AFTER 1 kc.

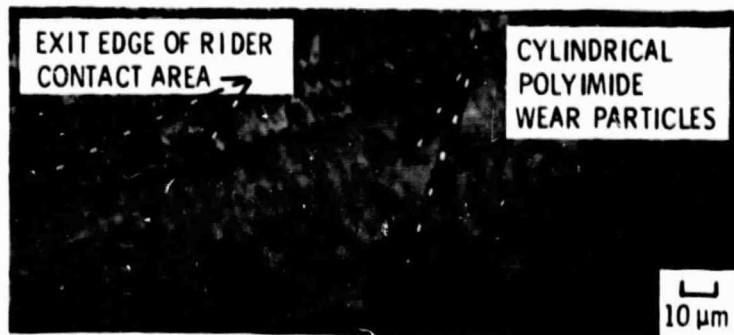


(b) OVERVIEW OF RIDER CONTACT AREA AFTER 300 kc.

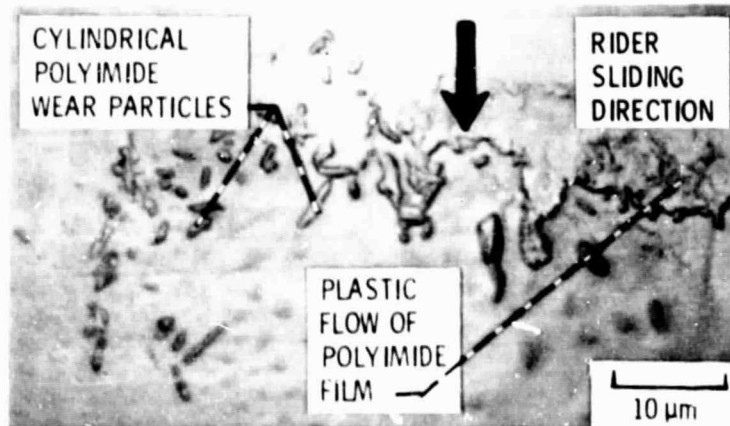


(c) HIGH MAGNIFICATION VIEW OF RIDER TRANSFER.

Figure 10. - Photomicrographs of the transfer and wear to the 0.011 cm^2 -area rider flat which slid on the PIC-3 film for sliding durations of 1 kc and 300 kc.



(a) EXIT REGION OF RIDER CONTACT AREA.



(b) AREA WITHIN FILM WEAR TRACK.



(c) AREA OUTSIDE FILM WEAR TRACK.

Figure 11. - High magnification photomicrographs of various areas on the friction and wear specimens showing cylindrically shaped wear particles that were produced during the initial stages of sliding on most of the polyimides.