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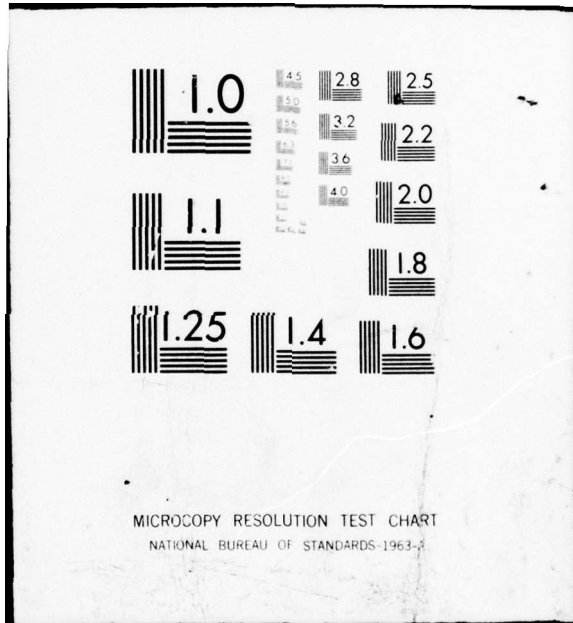
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POLYMER WEAR MODES

FINAL REPORT

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Professor of Mechanical Engineering

October, 1977

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13. ABSTRACT This work originated with frequent observation that polymers wear less under severe conditions of sliding than under mild conditions of sliding. An investigation was conducted with a view to deriving mathematical models for the wear behavior of polymers. It was found that the physics of the wearing process is not sufficiently understood to write mathematical models at this time. The investigation included rubbing various polymers against steel surfaces in a circular track while continuously monitoring the gases in the vicinity of rubbing. The following conclusions were reached: 1. The conventional equations for temperature rise on rubbing surfaces are of limited value. This was found by comparing the gases evolved from the sliding process with gases evolved from polymers heated to various temperatures. 2. The wear rate is controlled primarily (if not exclusively) by the tendency to form or not form a stable transfer film on the metal surface. Severe wear always occurs if there is no transfer film or if the transfer film is readily removed, and the wear rate is proportional to rubbing severity. 3. Where a stable transfer film forms, very little wear occurs until a surface temperature is reached that is 50°C above the temperature at which severe wear begins in the case where no transfer film forms or is retained. 4. The nature of the transfer film depends upon the severity and time (number of passes) of sliding, and severity excursions through all ranges of severity. The exact nature of this dependence has not been explored. 5. Surface cleanliness influences wear rate far more than surface finish does. The wettability of molten polymer to metal may be the most important factor in controlling the tenacity of a transfer film at severe conditions of rubbing.			

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Polymer Wear Modes

K.C. Ludema

University of Michigan

(U.S. Army Grant DAHCO4 74 C 0011)

The motivating force for study of the details of polymer wear is our inability to design sliding surfaces with a desired wear life. Much progress has been made by iterative methods, but many mysteries remain. Instances regularly appear where wear rate predictions are in error by a factor of 100, and there are numerous instances where the wear rate is much lower in severe rubbing severities than in light duty. There is also a continuing uncertainty of the general influence of surface roughness of a metal counter surface on the wear rate of polymer. Finally, the observation that some polymers wear metals away requires more attention to the metal surface than simply to regard it as a rigid and inert bystander to the wear process.

The specific objective of this work was to develop wear models for polymers that are more appropriate than the well known P.V. Limit. The assumption at the beginning of the work was that wear in the mild regime is well understood and is adequately described as involving transfer of polymer to the counter surface, followed by the fatigue of fragments from the counter surface. The fatigue of fragments constitutes wear. It was also assumed that when severe rubbing conditions were applied the polymer might either melt at the sliding surface or char. In the case of melting, it was thought possible to derive a mathematical model including such factors as the formation and expulsion of molten species, so that the influence of slider shape (i.e., length to width ratio) and rubbing states (i.e., single pass versus repeat pass sliding) could be predicted.

The work is reported under three major headings. The first conclusions were reported in a paper entitled, "Transfer Films and Severe Wear of Polymers," by S.H. Rhee and K.C. Ludema, a paper presented at a conference at Leeds University (U.K.) in September 1976 and soon to be published by Mechanical Engineering Publications, Ltd., (P.O. Box 24, Northgate Avenue, Bury St. Edmunds, Suffolk IP32 B.W. England). This paper discusses the difficulties in calculating a realistic temperature rise on sliding surfaces and describes a method for measuring surface temperature. It involves ana-

lyzing the gases evolved from a polymer-metal sliding interface and comparing these gases with those from the same polymer heated to various temperatures. By comparison of these results with thermo-gravimetric analysis and differential thermal analysis realistic estimates were made of the actual temperatures on sliding surfaces.

The first paper concentrated on the conditions that produced severe wear, working with polymers that produced an adhering transfer film. The major finding was that severe wear did not occur at the softening temperature of the polymer (often erroneously referred to as the melting point) but at about 50°C higher. This finding shifts attention from supposing that severe wear occurs when the polymer softens. It is proposed that the important phenomenon is the behavior of the transfer film. If the transfer film remains flat behind the slider it provides or becomes a "lubricant" film upon which the slider rides on later passes. If the transfer film is hot enough to have low viscosity and if the polymer does not wet the metal counter surface the transfer film agglomerates into spheres which are removed by the next slider to pass the area. The transition to severe wear there is strongly influenced by the adherence of a transfer film to the metal counter surface.

The second phase of the study is reported in a paper entitled, "Mechanisms of Formation of Polymeric Transfer Films," by S.H. Rhee and K.C. Ludema, and published in *Wear*, v. 46, p. 1, 1977. In this paper it was shown that in the absence of a stable transfer film severe wear occurs, and it takes place by plucking out fragments of polymer when the polymer becomes sufficiently softened by heating. Attention was then turned to finding the conditions that control the degree of adhesion of, or likelihood of formation of a stable transfer film. For example, when sliding a polymer on smooth quartz a stable transfer film was not formed and wear was high, whereas on abraded quartz the transfer film was stable and the wear rate of the polymer was very low. On some surfaces the method of cleaning strongly influenced the stability of the transfer film. It is possible that a model could be developed, using the shear strength properties of the polymer with the viscous properties of the surface contaminants and the average slope of surface roughness by which predictions could be made on the likelihood of

the formation of a transfer film. To date only the physics of the problem have been studied and insufficient data are in hand to develop the model.

Since the second paper was submitted the work has turned to an investigation of those conditions preparatory to severe wear. In the previously reported work, conditions near to or in the severe wear regime were imposed upon the specimen immediately. It was usually found that some time was required for a stable transfer film to form and for the substrate to heat sufficiently to produce severe wear. In later work it was found that the mode of operation in the mild wear regime strongly influenced the manner in which the transition to severe wear occurred. This was suggested by the finding that a transfer film was difficult to establish on smooth quartz but easy to establish on lightly abraded quartz. A less dramatic difference was seen when using stainless steel counter surface but often a time ranging from ten minutes to twenty minutes was required to establish an equilibrium coefficient of friction, which was taken as an indication of a change in the nature of the transfer film. Thus two further experimental sequences were done in the mild wear regime. In both instances the tests were done in order to confirm steady state behavior of the transfer film under steady state conditions of rubbing. It was expected that this would serve as the basis for later studies of the transient behavior of transfer films by changing rubbing conditions after a transfer film is established at one condition.

The two test series are as follows:

1. The first was the rubbing of Nylon 6-6, Nylon 11, Delrin 500, Delrin AF, and ultra-high molecular weight polyethylene (UHMWPE) against 440C stainless steel. All surfaces were prepared by dry #600 abrasive paper followed by vigorous cleaning with isopropanol and a paper towel. The evidence of adequate removal of abrasive was that there was no scratching of the metal surface during the wear test. The apparatus used and geometric configuration of the specimen is the same as shown in the papers referenced above. The data for each polymer are summarized in tabular form in Table I at the end of the report. It should be noted that in every case the wear rate as measured by weight loss is linear with speed and load after

an initial transient. Interestingly, the initial transient does not involve a higher wear rate than in the equilibrium period. Rather the wear rate is lower which is indicated by the fact that the data curves do not extrapolate to zero wear at either zero load or zero sliding speed. This finding may support the conclusion of Lancaster that wear in the mild regime is a fatigue mechanism, which is further described in this work as an intermittent flaking off the transfer film. Perhaps at low load and sliding speed, conditions for fatiguing flakes from the transfer film are not reached. An attempt was made to study this transfer film using Nylon 6-6. By the use of polarizing optics in a microscope, the transfer film in one location was observed during the test. No conclusions were reached concerning the loss of material from the transfer film, mostly because with each pass of the polymeric slider, there was forward movement of the transfer film even at times of virtually no wear loss. Thus the mechanism of break-in or initial transient wear was not confirmed.

2. A second series of tests was done with Nylon 6-6. Plain carbon steel surfaces were prepared by circumferencial grinding of one set of counter-faces and by radial grinding of another set of counter-face using again the configuration of the apparatus described above. Four surface finishes were obtained in each case, 5 μ -in, 12 μ -in, 20 μ -in, and 80 μ -in. Again the surfaces were prepared by abrasive operation followed by cleaning with isopropanol and a clean paper towel. Some difficulty was experienced in cleaning sufficiently to prevent later scratching of the plate by residual abrasives. Abrasive particles were never observed but abrasion could be prevented by adequately vigorous rubbing of the surface with an isopropanol soaked paper towel. The lack of scratching was taken to indicate adequate cleaning. In these tests, again the amount of wear was measured by weight loss of the polymer. In the case of Nylon 66 it is usually found that the materials must be stored and the experiments must be run in a dry atmosphere to prevent absorption of water by the polymer, which confuses weight changes due to wear. Table 1 at the end of the report shows the data for these tests. In the table it may be seen that there is no significant difference in the wear rate for the two surface finish orientations. This appears to be contradictory with the information in the literature. However

the information in the literature is internally contradictory in that some authors report an optimum surface finish of approximately 12 μ -in, and others find the optimum to be at much smoother surface finishes. It is possible that the major factor in all of these variations is the different methods of surface cleaning.

Conclusions

In the mild wear regime;

- a. If a transfer film forms it does so progressively with each pass of rubbing, requiring hundreds of passes,
- b. The behavior in the high severity regime is dependent on the time and sequence of operation in the low severity regime, e.g., longer operation in the low severity regime postpones severe wear when severity of rubbing is increased. This study was not completed.
- c. Surface roughness does not strongly influence wear rate when surfaces are very carefully cleaned.
- d. Surface cleanliness is the most important factor in wear rate, e.g., adherent transfer films form on clean surfaces and result in low wear rate.

In summary the transfer film is the most important factor in determining the wear rate of polymers. Further work is required to better establish the mechanics of transfer film formation. The most important future study should be on the role of adsorbed species on the adhesiveness of a transfer film to a metal substrate. When control of surface species is established it would be useful to explore the influence of the geometry of surface roughness on establishing the transfer film. When these details are in hand it should be possible to write mathematical models for the wear of polymers.

<u>Polymer</u>	<u>k</u>	<u>a</u>	<u>b</u>
Nylon 6-6	5.3×10^{-9}	1.43	1.43
Nylon 11	1.1×10^{-11}	1.84	1.66
Delrin 500	2.5×10^{-13}	1.9	1.4
Delrin AF	$\approx 2.5 \times 10^{-14}$		1.2
UHMWPE	5×10^{-15}		

Table I Constants in equation $\gamma = kP^a V^b$ where γ = wear rate in $\mu\text{g/s}$, k is constant, P is the contact pressure (N/m^2), V is the sliding speed (m/s), a and b are constants. V ranges from 0.1 to 0.5 m/s, P ranges from .7 to $7 \times 10^6 \text{ N/m}^2$.

<u>Surface finish</u>	<u>Circumferential</u>	<u>Radial</u>
u-in	(Wear rate $\mu\text{g/m}$ (of sliding))	
≈ 5	0.69	0.94
≈ 12	0.59	0.58
≈ 20	0.90	0.72
≈ 80	0.93	0.71

Table II Wear rate of Nylon 6-6 with a load of 150N and a sliding speed of 0.40 m/s, sliding on circumferential lay and radial lay of four surface roughness values.

In the conduct of this research a number of research personnel gained valuable experience. They were:

Mr. Tim Adama-MSME-Dec. 1974.

Mr. Beyer-MSME-1975.

Dr. S.H. Rhee-post doctoral fellow in polymer science.

Mr. H. Vete-MSME in June 1976.

Mr. P. Bareman-MSME in December 1976.

Mr. J. Deibler-BSME in December 1977.

The bibliography used in this entire project may be found listed at the ends of the two papers derived from this work.

MECHANISMS OF FORMATION OF POLYMERIC TRANSFER FILMS

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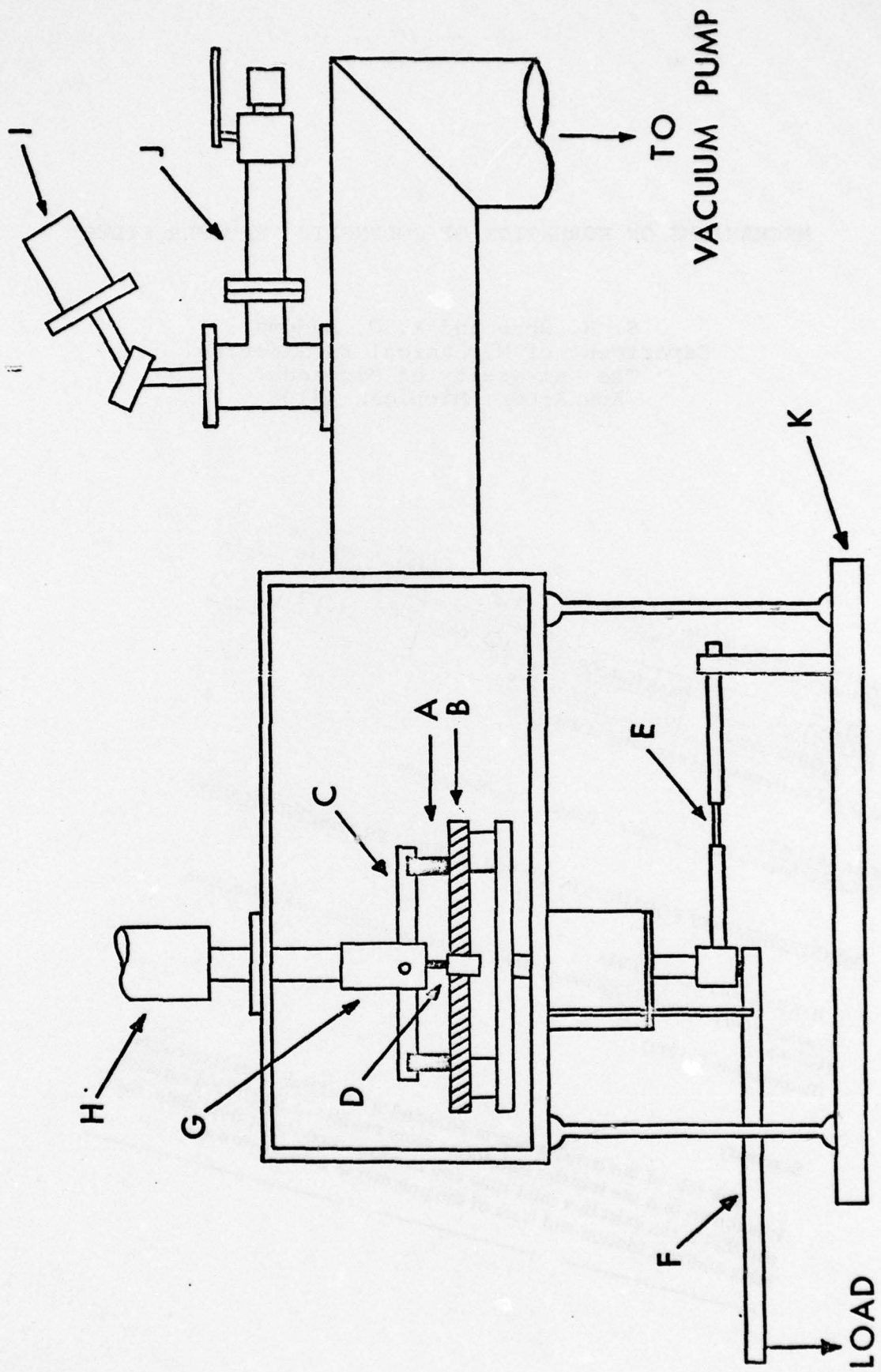
S. H. RHEE and K. C. LUDEMA

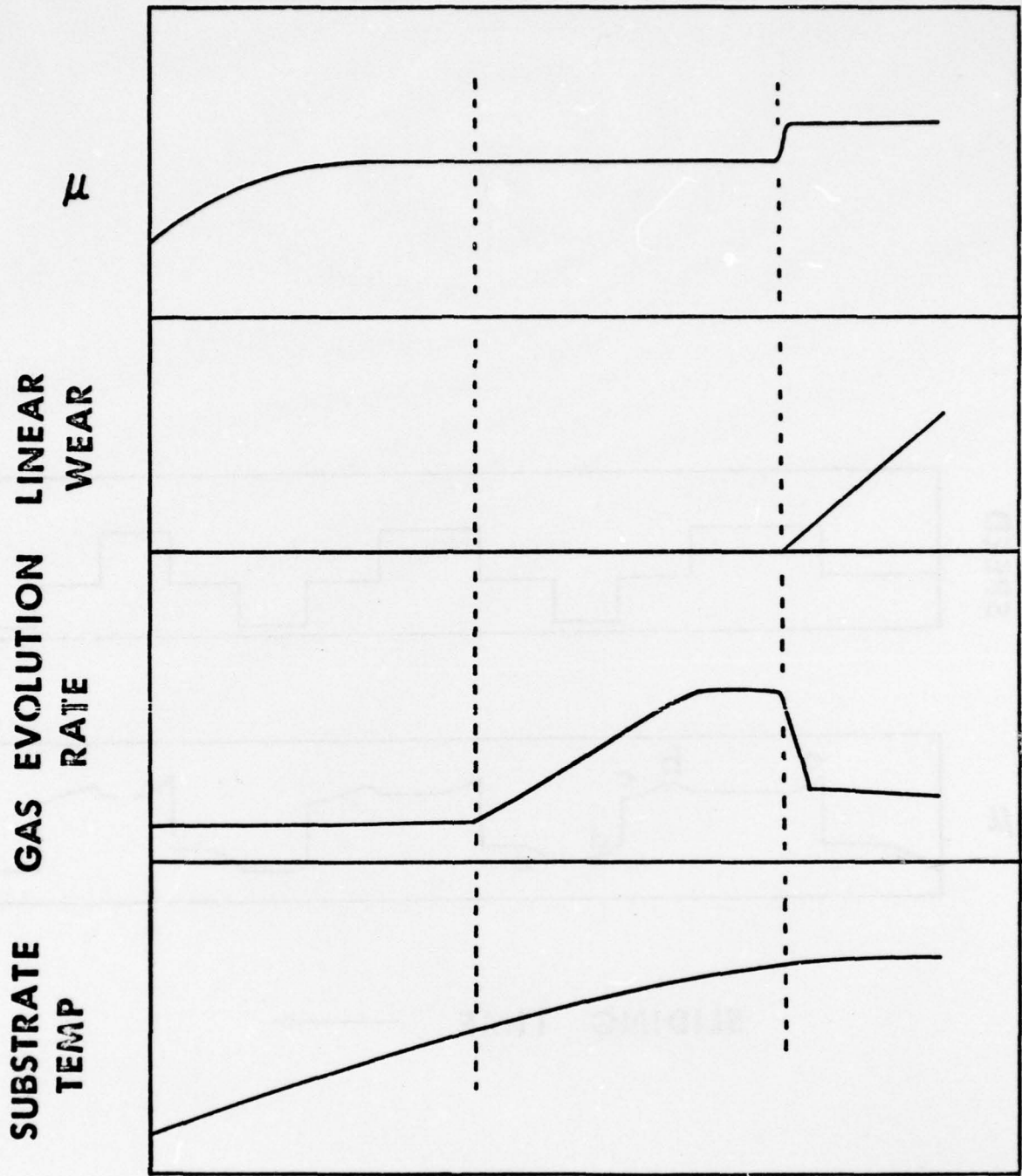
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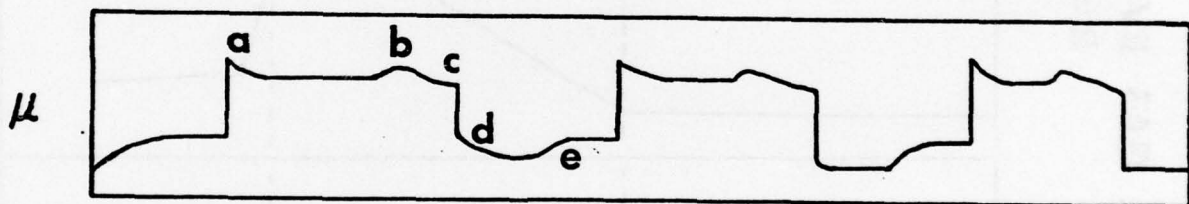
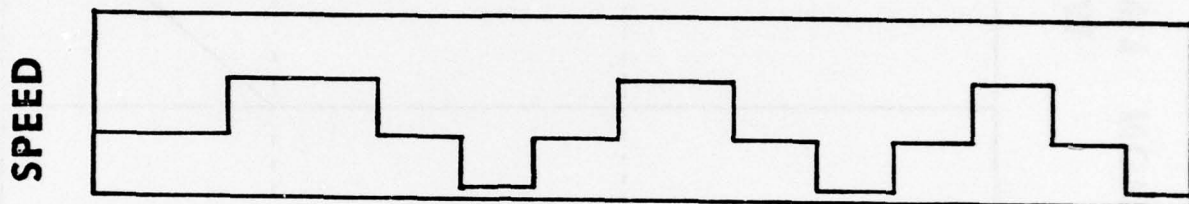
Summary

The role of the transfer film in reducing wear of polymers is discussed. It is shown that the transfer film forms more readily on roughened surfaces and that it can exist in a solid state and in a low viscosity or fluid state. Each state controls friction and wear of the polymer in a different way.





SLIDING TIME →



SLIDING TIME \longrightarrow

ABSTRACT

The role of the transfer film in reducing wear of polymers is discussed. It is shown that the transfer film forms more readily on roughened surfaces and that the transfer film can exist in a solid state and in a low viscosity or fluid state. Each state controls friction and wear of the polymer in a different way.

INTRODUCTION

When polymeric solids slide against other solids such as steel there appears to be no way to predict either the friction of the system or the wear life of the polymer from handbook data. Friction and wear vary over wide ranges when sliding speed, applied load and system temperature are varied. Neither have thermal analyses of the sliding system produced satisfying results, partly because of the difficulty in measuring temperatures in the sliding interface.

There is some progress however in these studies. Dowson (1) reports a thermal analysis of sliding by extrapolation from temperatures measured by thermocouple in several locations within the metal counterface. Lancaster (2) reports wear at low rubbing severity and attributes it to a fatigue mechanism. Finally, a number of authors of both research papers and test reports note that in some cases a polymeric film is transferred and remains firmly attached to the metal counterface, with the apparent effect of reducing wear.

This paper reports the results of some work to measure the properties of the transfer film and proposes a model for transfer film formation and behavior. The research reported consisted in the measurement of friction and wear rate over a wide range of load and speed together with measurements of temperatures in the vicinity of the sliding interface. Transfer films were observed visually during the tests but the thickness and dynamic mechanical properties were not determined directly.

In view of the strong influence of the controllable variables in friction and wear the experimental apparatus and materials will be described in some detail, though it was also done in a previous paper (3). In the tests the severity of rubbing covered a range from well below conditions for severe wear to the conditions for severe wear. Severity of rubbing is defined in terms of the product $\mu W V$ where μ is the coefficient of friction, W is the applied load and V is the sliding speed. The product $\mu W V$ is taken as the input mechanical energy to the sliding interface.

EXPERIMENTAL

Materials

Commercially available nylon 66, poly (oxymethylene) (DuPont's Delrin) and PTFE-dispersed poly (oxymethylene) (DuPont's Delrin AF) were purchased from Cadillac Plastics, Detroit, Michigan in the form of extruded rods of 12.7 mm (1/2 inch) diameter. They were cut into 1 inch long cylinders, and the rubbing side of the cylindrical specimens was reduced to 6.35 mm (1/4 inch) diameter.

Apparatus

The experimental system used in this work is shown in Figure 1.

Fig. 1 Experimental test apparatus: A-polymer specimen; B-countersurface; C-pivoted specimen holding bar; D-LVDT wear transducer; E-friction force constraint arm; F-lever arm; G-input shaft; H-drill press spindle; I-mass spectrometer; J-solid sample probe; K-drill press support.

Two polymer specimens are held opposite to each other on ends of a bar (C) pivoted at its center; the center-to-specimen distance is 98 mm. The resulting contacting geometry is a dual-pin-on-disc configuration. One of the countersurface is a disc of 440C stainless steel of 25.4 mm diameter by 25.4 mm thick, finished to .254 μ m (10 μ -in) surface finish or better. The other countersurface is a disc of quartz 12.7 mm (1/2 inch) thick.

Friction force is measured by strain gage attached on a constraint arm (E) which limits rotation of the countersurface. The normal load is provided by pressing upward on the lower disc shaft and by limiting the vertical motion of the upper input shaft. The sliding system is enclosed in a vacuum chamber and a

mass spectrometer analyzing tube is connected to the vacuum chamber. A vacuum of 26.7 ~ 40 mPa (2.3×10^{-6} mmHg) is easily attained by a combination of a turbomolecular pump and a mechanical fore pump. Wear is measured by a linear variable differential transformer (LVDT) (D) located in the center of the countersurface disc. The bulk temperature of the countersurface is measured by an iron-constantan thermocouple, located 3 mm below the rubbing surface of stainless steel and 2 mm for quartz.

The mass spectrometer is an AVA-610 60° single focusing magnetic sector type manufactured by Aero-Vac Corporation. A pyrolysis probe (J) is located in the vacuum chamber. Its function is to heat a sample of polymer in a vacuum environment so that the products of thermal decomposition can be analyzed.

Procedure

The sliding surfaces of polymer specimens were prepared on 600 grit abrasive paper and cleaned with flowing water, acetone and isopropyl alcohol before inserting them into the specimen holder. The countersurface of stainless steel was polished with 600 grit abrasive paper and cleaned with acetone and isopropyl alcohol. The vacuum chamber was then closed and evacuated to a total pressure of 26.7 ~ 40 mPa (2.3×10^{-6} mmHg). A certain load and speed were decided for each test, and friction, wear, countersurface temperature and decomposed gases were monitored throughout the test.

Prior to the friction tests a small sample of polymer is heated progressively in the pyrolysis tube and a trace of the evolved gases vs. temperature is monitored by mass spectrometer. Then friction tests are run and gas analysis is done. Similar gas compositions are taken to mean that pyrolysis temperature and friction interface temperature are the same.

RESULTS

In the experimental program several polymers were made to slide on several substrates, but the most instructive were those done on a 440-C stainless steel plate finished with 600 grit Al_2O_3 abrasive paper, a fine polished quartz plate, and a quartz plate finished with 600 grit Al_2O_3 abrasive paper. Again tests were run at many combinations of load and speed but the most illuminating tests were run at a selected combination of load and speed, beginning with all components at room temperature. The speed and load were selected such that as the test progressed the rubbing elements heated and severe wear occurred within 600 to 3600 s from the beginning of the test. The proper speed and load are different for each polymer and depend to some extent on the coefficient of friction of the system. The difficulty in establishing equivalent states may be seen in the data for nylon 11 for two loads, as seen in Table I.

The difference between the two tests were that at the low load the transfer film was not properly established, and the severe wear debris probably included a large number of "fatigued" fragments. At the higher load the transfer film covered the steel surface more completely and was fully effective in suppressing wear until a high temperature.

The latter state was studied and reported here. The speed and load that produced "equivalent states"

in the several polymers tested are shown in Table II.

Tests were done on quartz, comparing two surface finishes. During the test the wear rate and rate of gas evolution were measured as well. For the smooth quartz the wear rate was high from the start of the test and the volume of gas evolved was always very low. On the abrasive finished quartz there was no wear but a large volume of gas was evolved from the sliding interface after some time. These observations are consistent with the formation of a stable and highly adherent transfer film to the abrasive finished surface but not to the smooth quartz. Since transfer films are difficult to observe by other than visual means another test was devised to detect a transfer film. It consisted in measuring the value of μ of Delrin, then of Delrin AF separately on the smooth and on the abrasive finished quartz. This was followed by sliding Delrin on the "track" of the test with Delrin AF as shown in Table III.

It may be inferred that a transfer film, perhaps predominantly of Teflon, is formed on abrasive finished glass and that the transfer film controls both friction and wear.

Tests were also done to compare quartz and stainless steel, both finished in the same way with abrasive paper. They both produced the same results showing, for example, that there are no chemical effects in the formation and degradation of transfer films due to the elements in the steel (or quartz) substrates although the surfaces may be activated due to abrasion. The only difference between the tests using the stainless steel and quartz is that the product of applied load and sliding speed for the tests on quartz is 1/6 that on stainless steel to achieve the same results. This experimental finding agrees with expectations gained from calculations using the thermal properties of the two materials, as shown in Table IV.

The calculated quantities are given in the form used in equations (4) for the temperature rise in the polymer ($\propto 1/k$) and temperature rise in the substrate ($\propto (1/k)(k/\rho C_p)^{1/2}$) where k is the thermal conductivity, ρ is the density and C_p is the specific heat at constant pressure.

The data for the tests on abrasive finished stainless steel and quartz are shown in Figure 2 in schematic form. It may be seen that the friction increases at the beginning of the test. The reason is not clear. For very carefully cleaned countersurface material the coefficient of friction begins at a slightly higher value, suggesting that the first few passes of the slider promotes desorption of adsorbed gas. Such gases were never detected but possibly because the quantity of gas evolved is too low for the gas analyzer system to detect. There is always some rise in pressure during sliding however, even in cleaned and previously degassed counterface surfaces. The largest change in friction with time finally may be due to the formation of the transfer film. It is interesting that the value of μ does not change significantly at a later time when the temperatures are higher. At higher temperatures the transfer film becomes liquid-like, which may be inferred from the rate of gas evolution which always occurs at temperatures in the sliding region above the melting point of the crystalline phase of the polymer. When the latter temperature is reached the viscosity of the amorphous phase of the polymer is in the range of 1 kPa·s (10^4 poises) or less.

TABLE I
Conditions for Wear of Nylon 11 on Stainless Steel Plate

Sliding speed	Load	μ	LWV	Time to severe wear	Temperature in steel substrate at beginning of severe wear
1.47 m/s	222 N (50 lbs)	.7	228.4	300 s	44°C
1.47 m/s	444 N (100 lbs)	.5	326.3	1 020 s	110°C

TABLE II
Conditions for Equivalent States of Rubbing Severity for the Polymers

Polymer	Shear strength at* room temp.	T_m	T_d	Speed	Load	Measured μ	Time to severe wear	Temperature of counterface substrate
UHMWPE	24.1 MPa (3 500 psi)	140°C	400°C	1.47 m/s	444 N (100 lbs)	0.55	2 100 s	140°C
Delrin	65.5 MPa (9 500 psi)	170°C	220°C	1.47 m/s	444 N (100 lbs)	0.65	600 s	100°C
Delrin AF	55.2 MPa (8 000 psi)	170°C	220°C	1.47 m/s	888 N (200 lbs)	0.20	1 800 s	130°C
Nylon 66	70.5 MPa (10 500 psi)	254°C	370°C	1.47 m/s	444 N (100 lbs)	0.66	3 600 s	200°C
Nylon 11	41.4 MPa (6 000 psi)	190°C	350°C	1.47 m/s	444 N (100 lbs)	0.50	1 020 s	110°C

TABLE III
Coefficient of Friction in Sequence of Tests with Delrin and Delrin AF on Quartz

	Delrin on clean glass	Delrin AF on clean glass	Delrin on track of Delrin AF
Smooth quartz	0.5	0.4	0.5
Abrasive finished quartz	0.5	0.2	0.2

TABLE IV
Thermal Properties of the Stainless Steel and Quartz Used in the Tests

	$\frac{1}{K}$	$\frac{k}{\rho C_p}$	$\frac{1}{k} \left(\frac{k}{\rho C_p} \right)^{1/2}$	Calculated ratio	Experimental ratio
Stainless Steel	0.04	7.1×10^{-3}	0.107×10^{-3}	6	6
Quartz	0.723	0.84×10^{-6}	0.663×10^{-3}	1	1

* Modern Plastics Encyclopedia, Vol. 52, No. 10A, 1975-1976, McGraw-Hill.

Fig. 2 Schematic data for polymer sliding continuously on quartz and stainless steel.

An interesting observation during the tests on the stainless steel counterface is that with all of the polymers except the polyethylenes, Fe and Cr was found attached to the polymer at the end of tests that were stopped before severe wear occurred, however, less was found attached to Nylon 11 than to the others. In tests with 222 N (50 lb) of load per pin, and a value of $\mu = 0.5$, with a cross sectional area of $31.7 \mu\text{m}^2$ (0.05 sq. in.), the average shear stress at sliding surface is about 3.45 MPa (500 psi). This may be compared with the shear strength (at room temperature) shown for the polymers in Table II. Little can be inferred from this observation since the actual shear strength of the polymer at the temperature of operation is not known. However, the observations indicate that a transfer film is not laid down by successive and simple shear from the polymeric slider. Rather there is a considerable turbulence or rolling of polymer within the transfer film, at least in the early solid state of the transfer film.

A final test sequence is reported which shows the dual nature of the transfer film. In this test nylon 66 slid against abrasive finished quartz at three speeds: 0.03 m/s (3 cm/sec), 0.2 m/s (20 cm/sec), and 0.4 m/s (40 cm/sec); with a load of 222 N (50 lb). Figure 3 shows schematically the sliding speed cycle and also shows smoothed data of the values of μ for the tests. The high speed always produces gases which usually accompanies viscous shear of the transfer film. The low speed produces no gas.

At the beginning of the test, at a speed of 0.2 m/s (20 cm/sec) a transfer film builds up in the conventional manner, and it is relatively discontinuous and hard. When the speed increases the value of μ increases, which is characteristic of the solid state film. However, at "a" in Figure 3 the transfer film changes character and μ decreases.

Fig. 3 Schematic illustration of speed cycle and corresponding data of the coefficient of friction for nylon 66 sliding at 3 cm/sec, 20 cm/sec, 40 cm/sec and a load of 50 lbs on 2 pins of 1/4 inch diameter.

When speed is decreased, μ increases because the transfer film cools, but then μ decreases, probably because the transfer film solidifies. Before the value of μ settles to its original value the speed in these tests is decreased to 0.03 m/s. The value of μ decreases gradually, probably because the transfer film cools and fragments. When the speed is again increased the value of μ increases gradually again to the previous value.

DISCUSSION

When sliding begins some particles of polymer are torn from the surface of the polymer, leaving pockmarks. The tearing is done by local shear stresses and by softening of regions of the polymer surface due to heating. The disposition of the removed particles is now the most important event. If some polymer becomes attached to the substrate such that shearing in the polymer seldom dislodges polymer attached to the substrate then a transfer film is beginning to form. This condition seems to apply to abrasive finished surfaces using the polymers listed in this paper. More particles continue to be torn from the polymer and most of these particles adhere to the previously formed film.

In some materials some of the particles may become detached resulting in mild wear. Where few particles are retained there is severe wear. This occurred when sliding several polymers on a polished quartz surface.

As rubbing continues in systems that form transfer films, particles continue to be torn from the polymer and add to the thickness and coverage of the sliding track. During this stage the value of μ increases to approach a particular maximum value. At some point the film thickness ceases to increase. At low rubbing severities the film is not continuous, allowing for rolling and turbulence of semi-solid particles under the slider with some loss. In this stage the value of μ increases with increase in speed. At higher sliding severity the film heats up and the viscosity decreases so that the film behaves more as a viscous liquid. The film becomes continuous. In this state the value of μ is high because of large contact area and μ is nearly independent of sliding speed. Wear is usually minimal in this state.

Transfer films build up to a maximum and a constant thickness which is probably characteristic of each rubbing pair. This may be explained as follows. At the beginning of sliding the highest temperature and the lowest shear strength is at the polymer—countersurface interface. As particles of polymer become attached to the countersurface that end of the particle farthest removed from the countersurface is at the highest temperature and it shears most readily in a narrow shear band. As the film increases in thickness the shear occurs over a thicker shear band and the temperature in the outer layers of transfer film decreases. Thus, the tearing of new particles from the polymer is discouraged and eventually ceases. The inner strata or sandwich of transfer film is the highest temperature region in the system. At high severity of rubbing it exceeds 50°C above the melting point of the crystalline phase of the polymer as seen by the rate of gas evolution from the transfer film.

The existence of a stable and uniform transfer film thickness brings up the interesting problem of the flow pattern of material "under" the slider. In the case of the viscous flow at high sliding severity the flow cannot be laminar. The highest temperature in the film is probably near the center of the thickness and at that point the viscosity should be the lowest and the shear gradient would be the largest. This material may flow to the surface at the rear of the slider, which may be the site of gas evolution. In any case the evolution of gases results from heating and not from mechanical shear.

CONCLUSIONS

The following findings are reported:

1. Severe wear is not due to melting but rather due to tearing out of polymer particles which have been softened due to heating. Severe wear following the formation of a transfer film begins with the agglomeration of the transfer film into loosely attached spheres.
2. The region of highest temperature in a sliding system with a transfer film is near the mid section of the transfer film.
3. In some (perhaps most) systems some surface roughness is required to establish a transfer film.
4. When a transfer film is formed, severe wear is postponed to 50°C higher temperature than in the system without the transfer film. When a transfer film is formed the wear rate is lower at high severity of sliding than at low severity. At the lower severity, the film is composed of semi-solid particles and the value of μ increases with increasing sliding speed (and vice versa). At higher sliding severity the film is continuous and composed of viscous liquid. The value of μ is high and nearly independent of sliding speed.

It is obvious from the above results that there are many options available in the coefficient of friction and wear rates of polymers. Simple change in generic family of polymers assures very little in achieving a design goal. Surface finish of counterface, sequences of operating conditions and thermal properties of system materials are also important. Doubtless slider geometry and gaseous

environment will also emerge as necessary considerations in designing for wear resistance.

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Transfer Films and Severe Wear of Polymers

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1. Introduction

Design engineers have some difficulty in obtaining reliable information on the wear rate of polymers. Perhaps one reason is that there are more variables influencing wear rate than one ordinarily expects. The same problem exists in attempts to physically model the wear process.

Consideration of the mechanism of polymer wear often involve either abrasive species, material fatigue or thermal quantities. In this paper the question of abrasive wear will be avoided and the focus shall be on linear polymers sliding against steel, since these were the conditions applying in the experiments described below.

Thermal criteria for severe wear of polymers seem attractive because heat is thought to be the cause of polymer bearing failure. One expression of this concept is the PV limit for bearings which states that beyond a particular product of the contact pressure, P , and the sliding speed, V , the wear rate will change from mild to severe wear. The product PV together with the coefficient of friction, μ , constitute the energy input into the sliding interface. Presumably if the input energy is not removed at a sufficient rate then the polymer will reach a temperature at which severe wear occurs. There is no general agreement on what the crucial temperature is. Matsubara and Watanabe (1) believe it to be the melting point of the polymer and Awatani and Kimura (2) assume the same.

Tanaka (3) finds evidence of melting by observing morphological change at the rubbing surface of a polymer and goes on to suggest that at higher sliding speed the molten film becomes thicker and is the cause of a higher rate of wear. Lancaster suggests melting in one paper (4), but avoids connecting the crucial temperature with the melting of the polymer in another paper (5) and he furthermore leaves open the possibility that mild wear is "fatigue limited". The latter point is not readily apparent since fatigue in the conventional sense of the word is less likely to occur at the high temperatures associated with high values of μ PV.

There are three compelling reasons for doubting the melting hypothesis. The first reason is that there is not a step decrease in μ when severe wear occurs as one might expect if molten species were to suddenly appear in the contact region. The second reason is that the published PV limits are not in the same order as are melting points for a group of polymers. For example, the limiting PV at 100 fpm for unmodified Acetal (M.P. 171°C) is 3000, and that for Teflon (M.P. 327°C) is 1800 (6). Finally, for some polymers gas is evolved from the region of sliding when operating in the regime of mild wear and these gases are known to form at temperatures well above the melting point of the polymer.

A number of attempts have been made to thermally model a sliding pair. Most calculations are based on models of continuous contact between idealized asperities. The equations of Jaeger (7) assume a rigid material. The equations of Tabor (8) allow for plastic flow of asperities, and the equation of Lancaster (4) allows asperities to deform in response to the expected thermal softening of the asperities. It is not likely that these simple models are universally useful for polymer sliding however, and for two reasons. The first is the case where hot spots appear randomly over the surface of a hard polymer sliding on glass. In such cases the temperature rise in the asperities due to rubbing can best be estimated by a stochastic

method such as that proposed by Ling (9). Unfortunately even this method begins by assuming domain sizes which may not be realistic and does not adequately reflect the visco-elastic nature of the polymeric material.

The second reason is that many polymers when sliding repeatedly over the same path leave a "transfer film" of polymer attached to the metal. Many authors report the existence of these films but apparently most assume the film to be too thin to alter surface geometry. For several softer linear polymers however the transfer film is important because it is thicker than the expected height of asperities. In essence, in such cases there are no asperities in contact. Neither is there a random distribution of heating where the transfer film covers the entire contact area. Thus thermal analyses are inadequate at this time because of the inadequacy of good physical models of surfaces.

In order to develop good physical models of sliding surfaces, it is useful to measure surface temperature experimentally, and from these data develop good physical models. This paper reports results of and conclusions from experiments in which friction, wear and temperatures were measured for polymers rubbing on steel. The conventional temperature measuring devices were not used for obtaining surface temperature. Rather the surface temperature was inferred from the analysis of gases emitted from the contact region. It is often noted when rubbing polymers in a vacuum that the pressure rises various amounts during the various stages of wear. A gas analyzer in the vacuum system was used to determine the source of the evolved gases and insure against reaching erroneous conclusions due to vacuum leaks or the baking out of the counter surface. A similar method has been previously used by Wilkins and Kranz (10), and by Buckley and Johnson (11) but they made different observations than those reported here.

2. Experimental

2.1 Apparatus

The experimental system used in this work is shown in Figure 1.

The polymer samples are 6.3 mm diameter cylinders and are held in a bar pivoted at its center. The two samples are located opposite to each other on the bar at a radius of 98 mm. By pivoting the support bar at its center, the polymer pins are self-leveling. The resulting contact geometry is a dual-pin-on-disc configuration. The support bar is attached to the input shaft which passes through a double O-ring vacuum seal. The input shaft terminates in a standard Morse taper, fitting into a large drill press output shaft which provides the rotational motion. The sliding speeds available range from 0.2 mm/s to 14.6 m/s.

The counter-surface is a disc of 440-C stainless steel of 0.28 m diameter by 25.4 mm thick, finished to 10 μ -in surface finish or better. It is attached to a shaft that passes through a single O-ring vacuum seal. Rotation of the counter surface is limited by a constraint arm which is instrumented for friction force measurements.

The normal load is provided by pressing upwards on the lower specimen disc shaft and by limiting the vertical motion of the upper input shaft. Normal loads as high as 1.35 kN (300 lbs) can be achieved by way of a lever arm and dead weights, as illustrated in Figure 1.

The supporting structure consists of a rectangular steel vacuum chamber, 0.38 m deep by 0.60 m wide by 0.30 m high. The vacuum chamber is connected to a pump by a 0.15 m tube. Connected to the wall of the tube is a mass spectrometer analyzing tube.

Wear is measured by a linear variable differential transformer (LVDT) located in the center of the countersurface disc.

The bulk temperature of the countersurface is measured by an iron-constantan thermocouple, located 3 mm below the rubbing surface.

The mass spectrometer is an AVA-610 60° single focusing magnetic sector type manufactured by Aero-Vac Corporation. It separates gas molecules in a high vacuum according to the ratio of atomic mass to charge and records the partial pressure contribution of each mass weight from atomic mass unit (amu) 12 to 300. Changes in total pressure of 3.4×10^{-4} Pa (10^{-7} mmHg) are easily identified on the mass spectral scans.

Near the mass spectrometer analyzing tube a pyrolysis probe is located. Its function is to heat a sample of polymer in a vacuum environment so that the products of decomposition can be analyzed.

The vacuum equipment consists of the following:

A Sargent Welch-Turbo-Molecular Pump, Model 3102 C with a pumping speed of .260 m^3/sec ,

A Sargent-Welch Due-Seal Model 1397 Mechanical Fore-Pump.

An NRC 836 ionization gauge control with a NRC 536 Bayard-Alpert type ionization gauge and two NRC 531 thermocouple gauges, located in the foreline and the vacuum chamber.

2.2 Materials

Three different polymer groups were selected for this study; they were Nylon 66, polyoxymethylene (Delrin 500 by DuPont), PTFE-fiber dispersed polyoxymethylene (Delrin AF by DuPont). High density polyethylene (HDPE) and polytetrafluorethylene (PTFE) were used in the preliminary stage of this study but they did not produce gases during the sliding process within the range of experimental conditions. This means that either

severe wear proceed without melting or else the decomposition temperature of the polymers is not reached in the contact region.

2.3 Procedure

Each polymer was subjected to two types of tests. One test series included Differential Thermal Analysis, Thermo-Gravimetric Analysis and pyrolysis. The first two tests were done in standard commercial devices from which many results are quoted in the literature. The pyrolysis was done in the apparatus used for the wear tests to provide perspective on the sensitivity and range of detection of various species of the system used for wear tests.

The second test series was a sliding of polymer against the stainless steel where the mass spectrometer was available to detect pressure rise due to gas evolution and to analyze the evolved gases. Direct comparison was then made of the gaseous species evolved from the pyrolysis tests with those from the sliding tests.

The test samples were machined to proper size (6.3 mm diameter cylinders) using standard machine shop practice. The sliding surfaces were prepared on 600 grade emery paper and cleaned with flowing water and isopropyl alcohol before inserting them into the specimen holder. The counter surface, experienced virtually no wear during tests. It was polished with 600 grade abrasive paper and washed with isopropyl alcohol before each test. The vacuum chamber was then closed and evacuated to a total pressure of 7 to 10 mPa (2 to 3×10^{-6} mmHg).

The mass spectrometer, visicorder, and chart recorder were all turned on well in advance of each test for stability of the instruments. During each test under a specific load and speed the subsurface temperature of the counter surface and the total system pressure were recorded whenever mass spectra were taken. Each test was continued until either sufficient amounts of decomposed gases were detected, or severe wear occurred.

The pyrolysis samples were prepared by using a hacksaw to produce fine particles of the polymers, which were then loaded into the glass capillary tubes. The glass sample tubes were then inserted into the sample holder. A sufficient time was given for outgassing during the initial warm-up period of the heater chamber, and mass spectra were taken at wide temperature intervals below the decomposition temperature of each polymer and at narrow intervals at or above the decomposition temperature.

3. Results

3.1 Differential Thermal Analysis (DTA) and Thermo-Gravimetric Analysis (TGA) of Specimen Materials

The melting points and decomposition temperatures of the three specimen polymers that produced gases during wear tests are shown in Table 1.

Table 1. The melting points and decomposition temperatures of Delrin 500, Delrin AF, and Nylon 66 determined by DTA and TGA.

	Melting Point	Decomposition Temperature	
		In Air	In N ₂
Delrin 500	170°C	246°C	246°C
Delrin AF	170°C	246°C	300°C
Nylon 66	254°C	295°C	400°C

3.2 Pyrolytic Decomposition

Mass spectra of the gases evolved from the specimen polymers taken at the starting point of decomposition are shown in Figure 2 for Delrin 500, Figure 3 for Delrin AF, and Figure 4 for Nylon 66. Each polymer has characteristic decomposition products as summarized in Table 2.

Table 2. Major decomposition products of the three polymers at the start of decomposition.

	Decomposition Temperature	Identity & Atomic Mass Units of the Decomposition Products
Delrin 500	220°C	HCHO (amu = 30) CHO (amu = 29)
Delrin AF	220°C	Same as Above
Nylon 66	350°C	Co ₂ (amu = 44) H ₂ O (amu = 18)

The data in Table 2 confirm those found in the literature for thermal degradation of the same polymers (12). It should be noted here that the lowest temperature of decomposition by pyrolysis in a high vacuum are lower than those determined by TGA. Since the pyrolysis method was considered more sensitive than TGA, the former were used as reference temperatures only throughout this study.

Gases evolved during heating of an empty glass capillary are shown in Figure 5. The gases are mainly O₂ and N₂.

3.3 Decomposition of Polymers Due to Frictional Heating

A typical mass spectrum taken during a sliding test of Delrin 500 is shown in Figure 6. The sliding conditions were such that decomposed gases were detected as soon as the sliding began. During this period of gas evolution, temperature rise in the counter surface was negligible. It was also possible to detect similar amounts of gases from the sliding surface at different combinations of speed and load as shown in Table 3.

Table 3. Several combinations of load and speed for Delrin 500 at which gas evolution rates were about the same, and the total linear wear of polymer was less than 0.01mm during the test.

Load N	Speed cm/sec	μ	T _{sub} °C	T _{surface} , inferred °C
111	50	0.44	18	220
111	100	0.38	22	220
222	30	0.38	25	220
444	30	0.32	26	220

Since this mass spectrum (Figure 6) matched that obtained in pyrolysis (Figure 2) the temperature of the sliding surface was inferred to be at least 220°C in some locations of the contact area.

Delrin AF evolved gases at higher combinations of speed and load than those for Delrin 500 mainly because of low friction of Delrin AF. The minimum conditions of speed and load at which the sliding surface of Delrin AF reaches the decomposition temperature of 220°C are given in Table 4, and a typical mass spectrum in such a test is shown in Figure 7. The individual peaks in the spectrum are of the same height as shown in Figure 2 (pyrolysis of Delrin 500) and Figure 6 (frictional decomposition of Delrin 500).

Table 4. Several combinations of load and speed for Delrin AF at which gas evolution rates were about the same and wear was negligible.

Load N	Speed cm/sec	μ	T _{sub} °C	T _{surface} inferred °C
333	147	0.20	30	220
444	147	0.19	30	220
666	100	0.15	30	220

The test conditions for Nylon 66 were somewhat different from those for Delrin 500 and Delrin AF in the sense that it was not possible to have severe enough loads and speeds to ensure gas evolution from the sliding surface as soon as sliding began because of physical limitations of the testing system and the high decomposition temperature (350°C) of Nylon 66. The sliding surface temperature of Nylon 66 reached the decomposition temperature only when the bulk temperature of the counter surface was raised appreciably by frictional heating. This requires no different

interpretation of the test results than of the results for Delrin 500 and Delrin AF. The reason is that a high severity of sliding can be achieved by any combination of temperature rise in the sliding region due to μ , W and V and temperature in the substrate. Interface temperature is, after all, the sum of the temperature of the substrate and the temperature rise above that of the substrate.

The decomposition products detected in the sliding test of Nylon 66 are shown in Figure 8. As noted in the figure the subsurface temperature of the countersurface was 92°C the friction coefficient 0.76, and the time to reach the decomposition temperature 16 min. In this test a film of 3 μ m thick was formed on the wear track soon after sliding began, and the film was stable until and even after the sliding surface reached the decomposition temperature of Nylon 66. Linear wear of 0.05 mm was recorded for the first 5 minutes and then there was no more wear until severe wear occurred when the counter surface temperature reached 200°C. Similar results were found at different combinations of speed and load as listed in Table 5.

Table 5. Conditions for decomposition of Nylon 66 in Sliding Tests.

Load N	Speed cm/sec	μ	Countersurface Temp °C	Time To Reach Tc	"Initial" Wear
444	147	0.7	80°C	11 min.	0.05 mm
222	231	0.76	92°C	16 min.	0.025 mm
444	231	0.66	102°C	7 min.	0.05 mm

Under the same conditions listed in Table 5, decomposition of Nylon 66 did not always occur; sometimes the major decomposition product CO₂, was not detected at all, but only H₂O vapor pressure was increased. It is very

likely that the water content in Nylon 66 may influence the friction and wear behavior of Nylon 66 since Nylons are known to absorb water. A further study in this subject would produce a better understanding of the mechanism involved.

The friction and wear behavior of the three polymers with time of sliding are shown in Figure 9 for Delrin 500, in Figure 10 for Delrin AF, and in Figure 11 for Nylon 66. The subsurface temperatures of the countersurface are also plotted in the figures. A common and interesting observation was that even though the sliding surface temperature was appreciably higher than the melting points of the polymers, and actually reached the decomposition temperatures no measureable wear occurred until destruction of transfer film began at a "certain subsurface temperature" as shown by the arrow in Figure 11. Catastrophic loss of material from the sliding surface occurred simultaneously with destruction of transfer film. The volume of evolved gas does not increase in this latter stage of wear, probably indicating a limited temperature of molten material in the interface region.

In general, the friction for repeat-path sliding follows the same general trend for all polymers. At the beginning of the test the value of μ was the lowest, presumably because one or both surfaces were not sufficiently clean. The main contaminant may have been water but it was not confirmed. The gas analyzer readily identified water from a number of sources including from the decomposition of Nylon 66, but it may not be sufficiently sensitive to detect water that is desorbed from a friction track.

After only a few meters of sliding, the value of μ increased, coinciding with some transfer of the polymer to the steel. With continued

sliding the value of μ continued to increase and a transfer film progressively covered the steel in the sliding track. When the transfer film became continuous the value of μ reached a maximum. It then either stabilizes quickly as with Delrin 500 or levels off gradually as with Nylon 66.

If sliding conditions become more severe three changes occur simultaneously. The value of μ increases slightly but quickly, the transfer film detaches to become globules and ridges of polymer, and the loss or wear of polymer increases considerably often by a factor of 2000. Wear of the polymer proceeds intermittently as if by progressive removal of layers of polymer on the order of 1 mm.

For each condition of sliding where gas is evolved there is an equilibrium film thickness as may be surmised from friction data. A sudden increase in sliding speed causes a sharp rise in friction force followed by a more gradual reduction to a value higher than the original. A decrease in speed has the opposite effect. A change in load does not have a significant effect on the coefficient of friction. Finally, if sliding is stopped from a speed that causes evolution of gas, the resumption of sliding requires a force at least 50% higher than the previous sliding force. All of these observations are consistent with the melting of polymer under the slider. In fact, as noted above, gas is not evolved unless the polymer decomposes and this occurs at temperatures well above the crystalline melting point of the polymer.

4. Conclusions

There are three relevant ranges of severity of sliding of polymer against a smooth steel counterface. These three ranges are shown schematically in Figure 12a in terms of the log of the wear rate versus the severity of

sliding. In severity range "a" the friction is lowest and there is a low wear rate. In this range there is some lubrication by surface contaminants. The wear is probably due to local adhesion of polymer to the countersurface, producing a fragment that is easily displaced from the contact region because of the preponderance of the contaminants on the surfaces.

In severity range "b" the friction is increased but the wear rate is negligible for repeat path sliding. In this range a persistent transfer film forms, in time, up to an equilibrium thickness and sliding proceeds by shearing of the thin film. At the lower severity end of range "b" the film is solid but in a few polymers, such as Delrin and Nylon 66, the film melts in the contact region at higher severities. In the polymers used in the experiments reported above, the rate of gas evolution increased as sliding severity increased indicating increasing surface temperature as shown in Figure 12b. The transfer film for the Nylon 66 was about 3 μm thick and somewhat thinner for the other polymers tested.

In severity range "c" the rate of wear is very high, about 2000 times that in range "b". In this range there is no stable transfer film so that all molten polymer comes from the slider rather than from the transfer film ahead of the slider. The temperature in the contact area appears not to increase as severity increases in this range.

The transition from the low wear rate in range "b" to the high wear rate in range "c" is the most interesting phenomenon seen in the experiments and it may be explained as follows. In the middle of range "b" a film of polymer melts under the slider and this film cools very quickly when the slider moves on. As the sliding severity increases the film temperature

becomes higher, requiring a longer time to cool. Finally at the highest temperature the viscosity of the polymer is low and the cooling time is increased so that the polymer agglomerates into globules and ridges rather than to form an energetically less favorable thin film. These globules and ridges leave the contact region as wear debris. Thus the criteria for severe wear should include consideration of polymer viscosity, thickness of polymer film and wettability of the molten polymer to the counter surface.

Modelling of the events in the contact region is made difficult by the intermittent nature of severe wear. It appears that wear occurs in steps about 1 mm at a time. This suggests that the shape of the molten film may change with time and it grows until the proper hydrodynamic condition is reached. The molten polymer then flows out of the contact region and becomes wear debris.

Several practical consequences follow from the above conclusions. If the transition from low wear rate to high wear rate is controlled by the hydrodynamics of a molten film then slider surface geometry, i.e., contact shape and orientation as well as surface finish will influence wear life of sliders. Since wettability of molten polymer to a counterface may be an important variable, materials could probably be selected and/or altered to increase the wear life of sliders operating near the point of severe wear.

Another practical consideration is whether or not polymers slide repeatedly over the same path. Single path sliding cannot benefit from a transfer film. Thus in range "b" in Figure 12a it can be seen that wear rate for single path sliding increases with increase in severity of sliding. In fact the wear rate for single path sliding exceeds that for repeat path sliding by orders of 10^4 to 10^6 .

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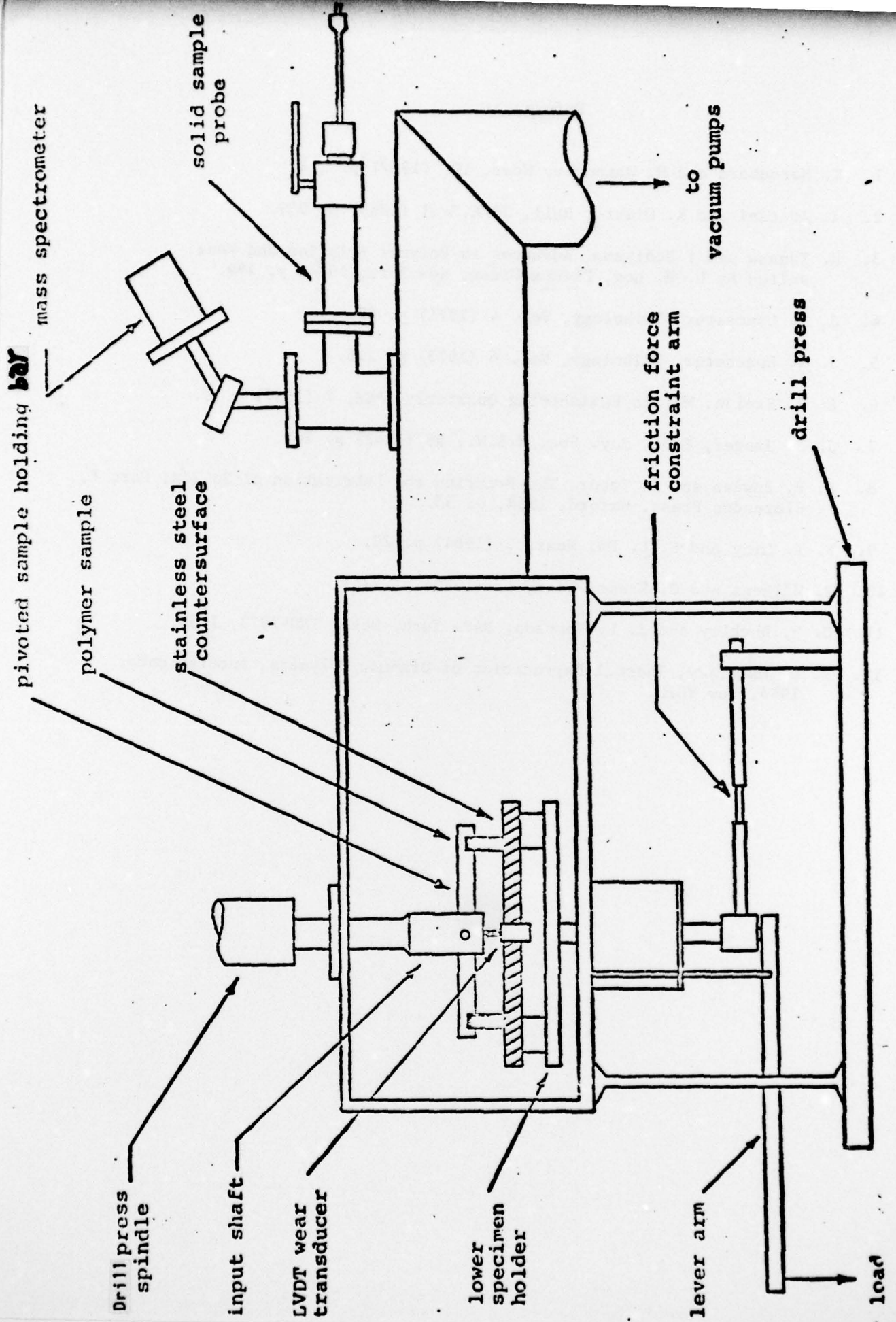


Figure 1. Experimental Test Apparatus.

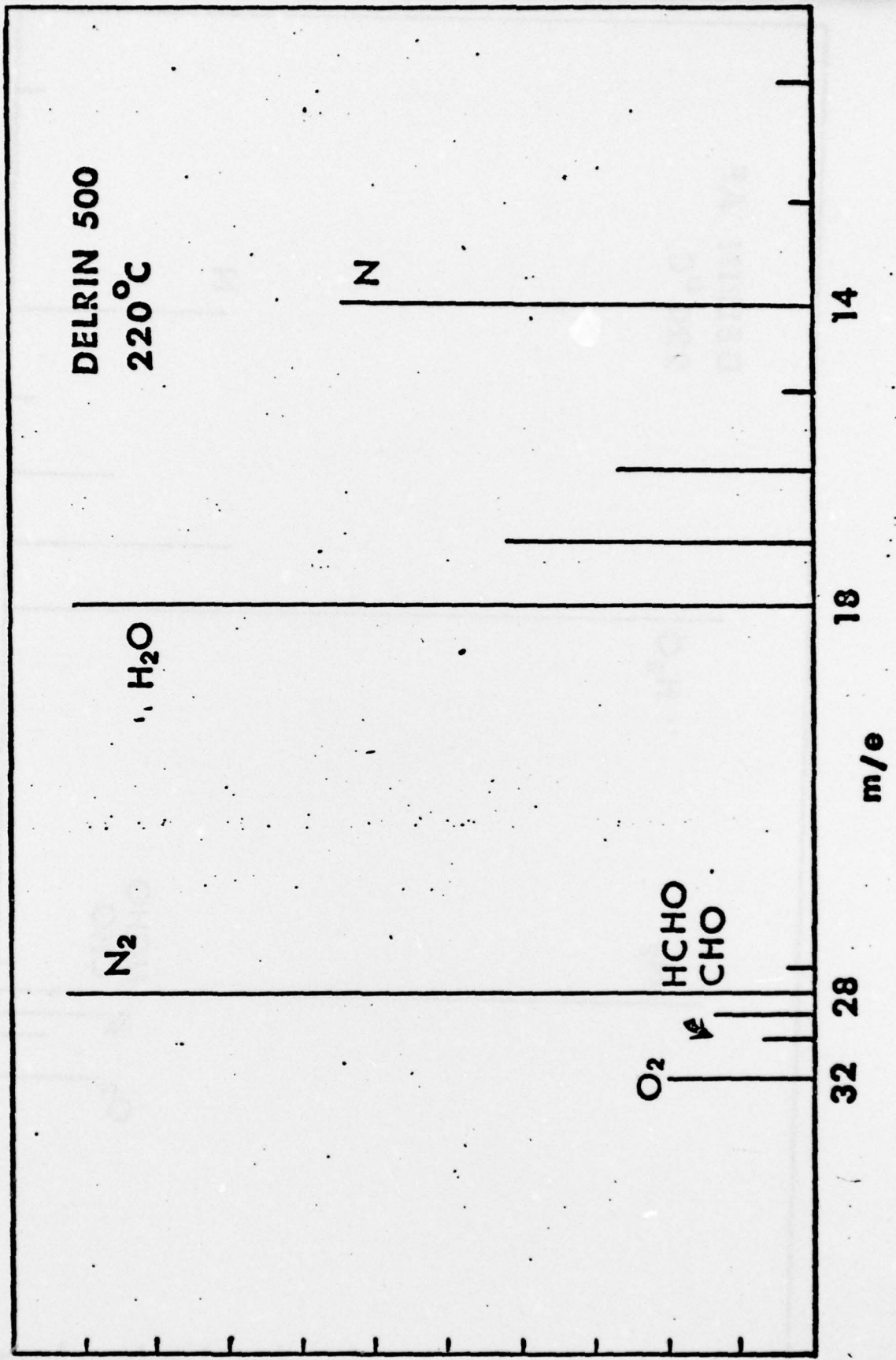


Figure 2. Mass spectrum of products of pyrolysis of Delrin 500 at 220°C.

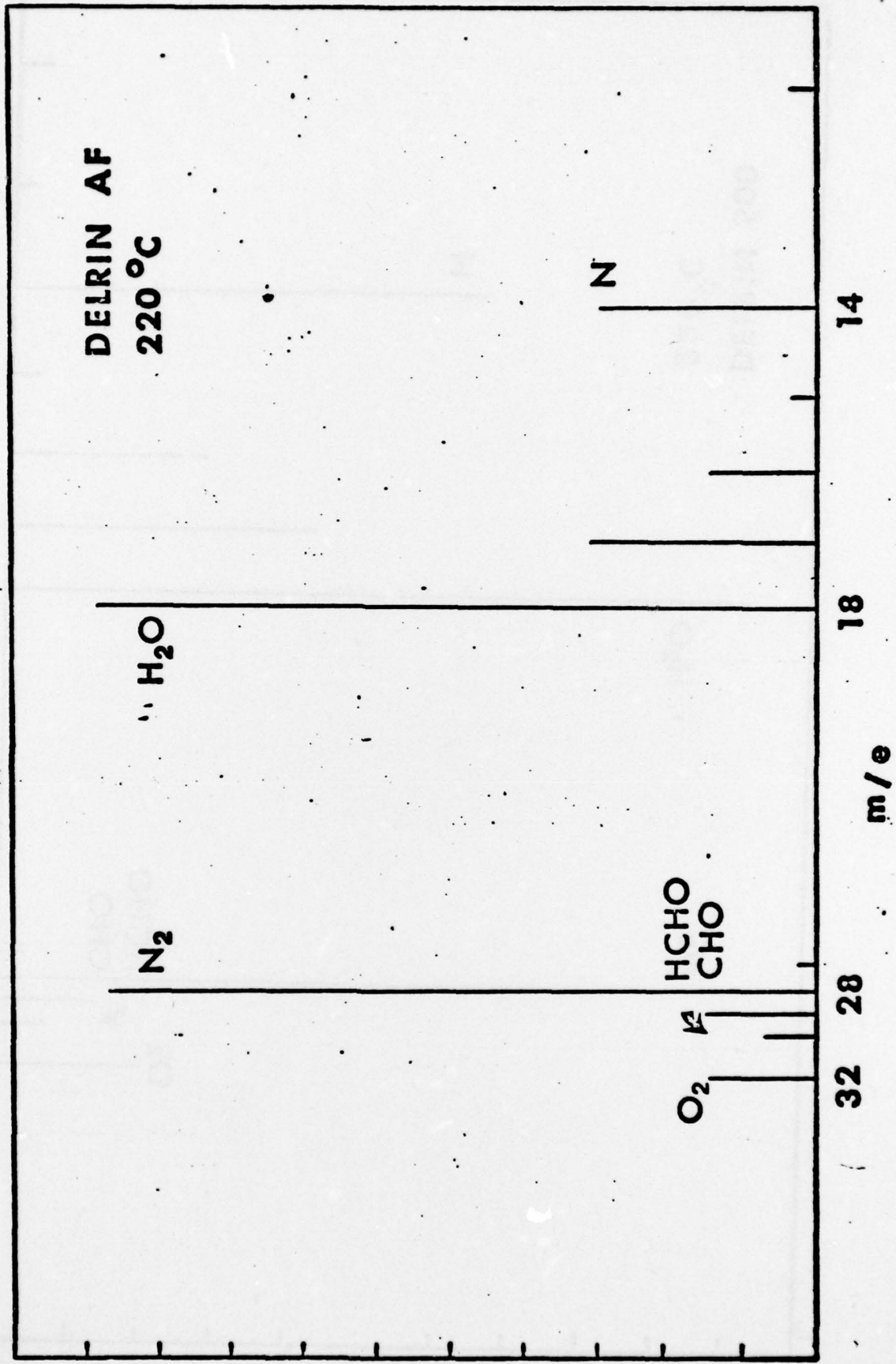


Figure 3. Mass spectrum of products of pyrolysis of Delrin AF at 220°C.

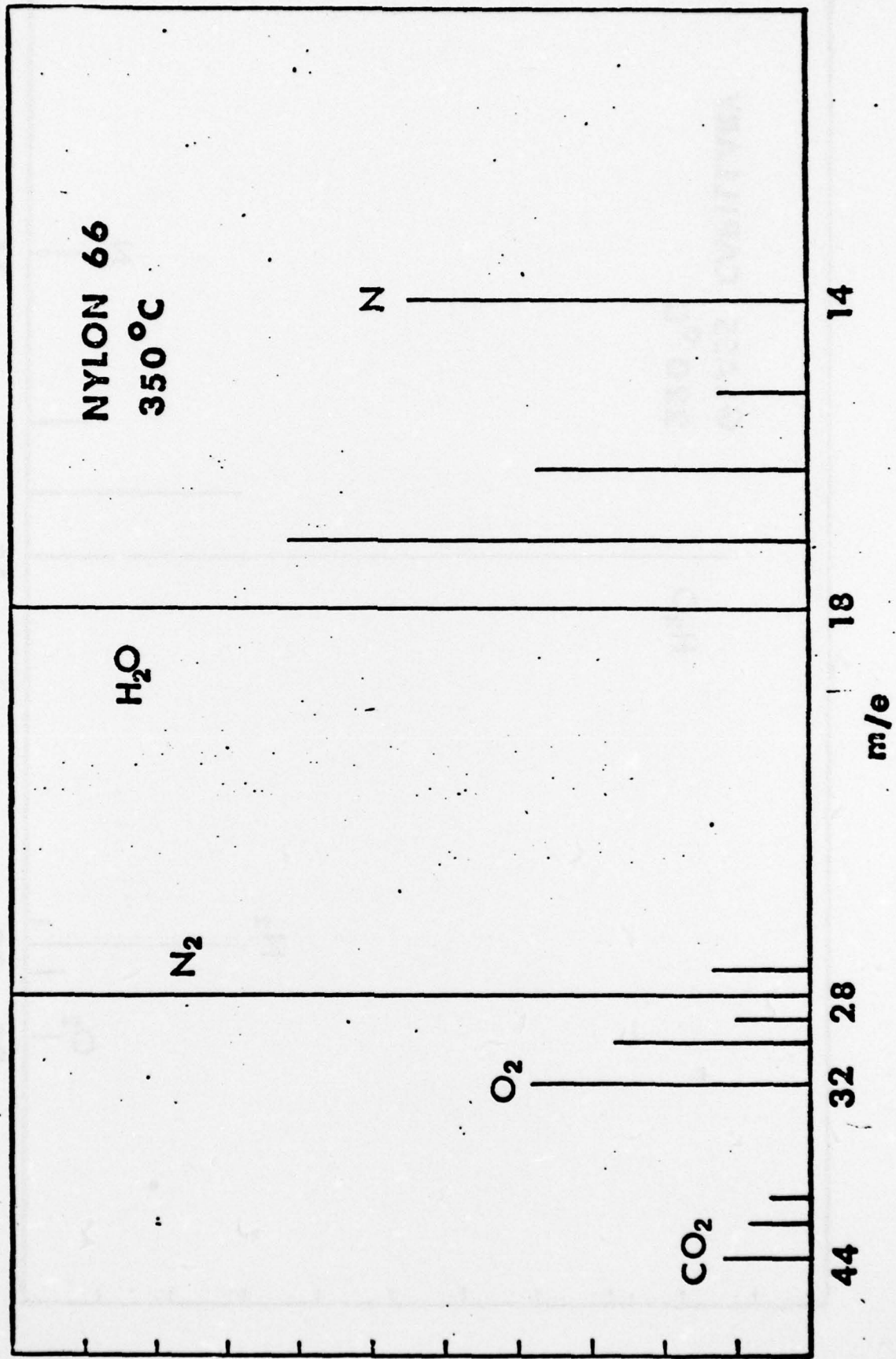


Figure 4. Mass spectrum of products of pyrolysis of Nylon 66 at 220°C.

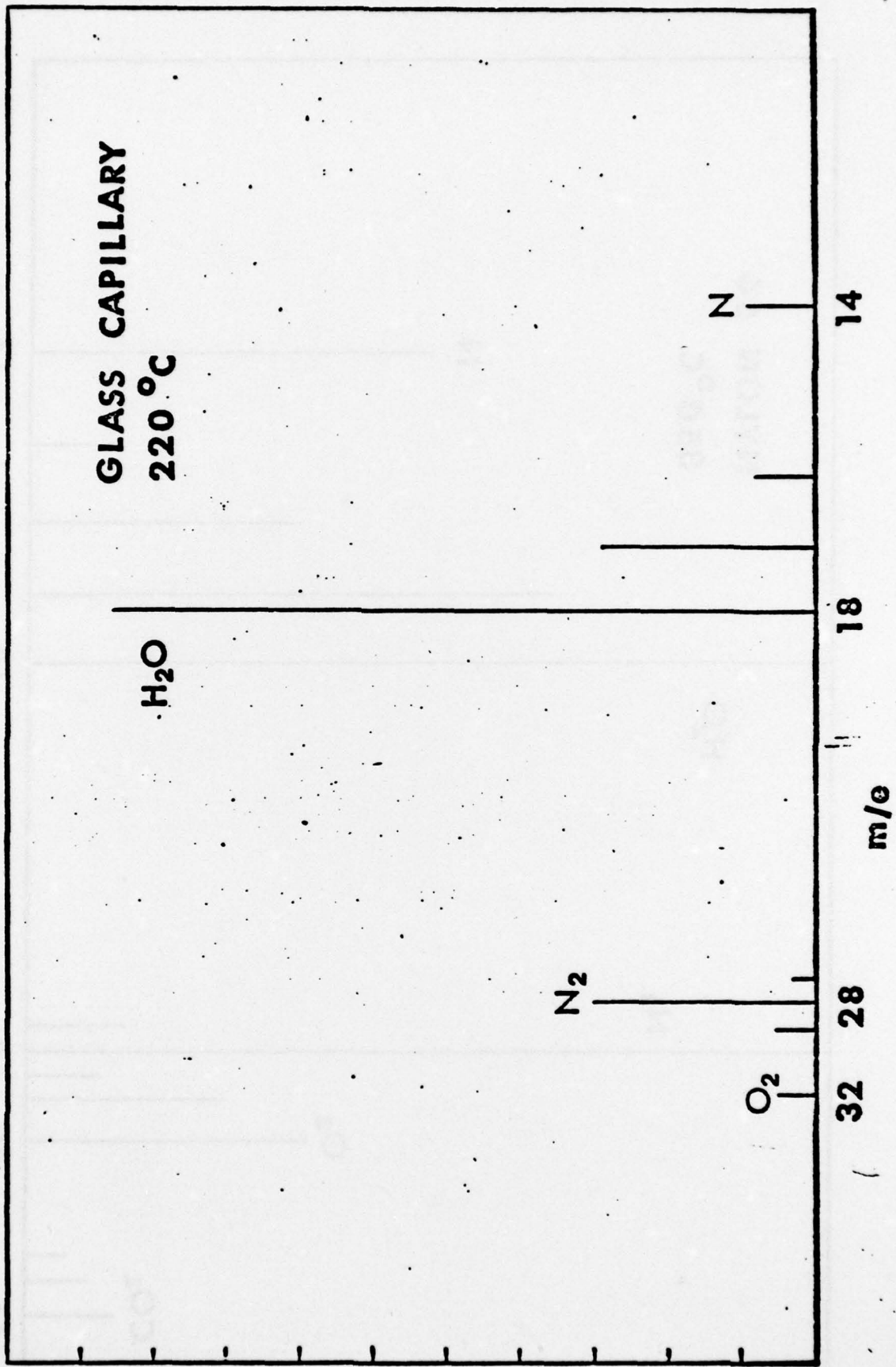


Figure 5. Mass spectrum of gases evolved from the glass capillary at 220 °C.

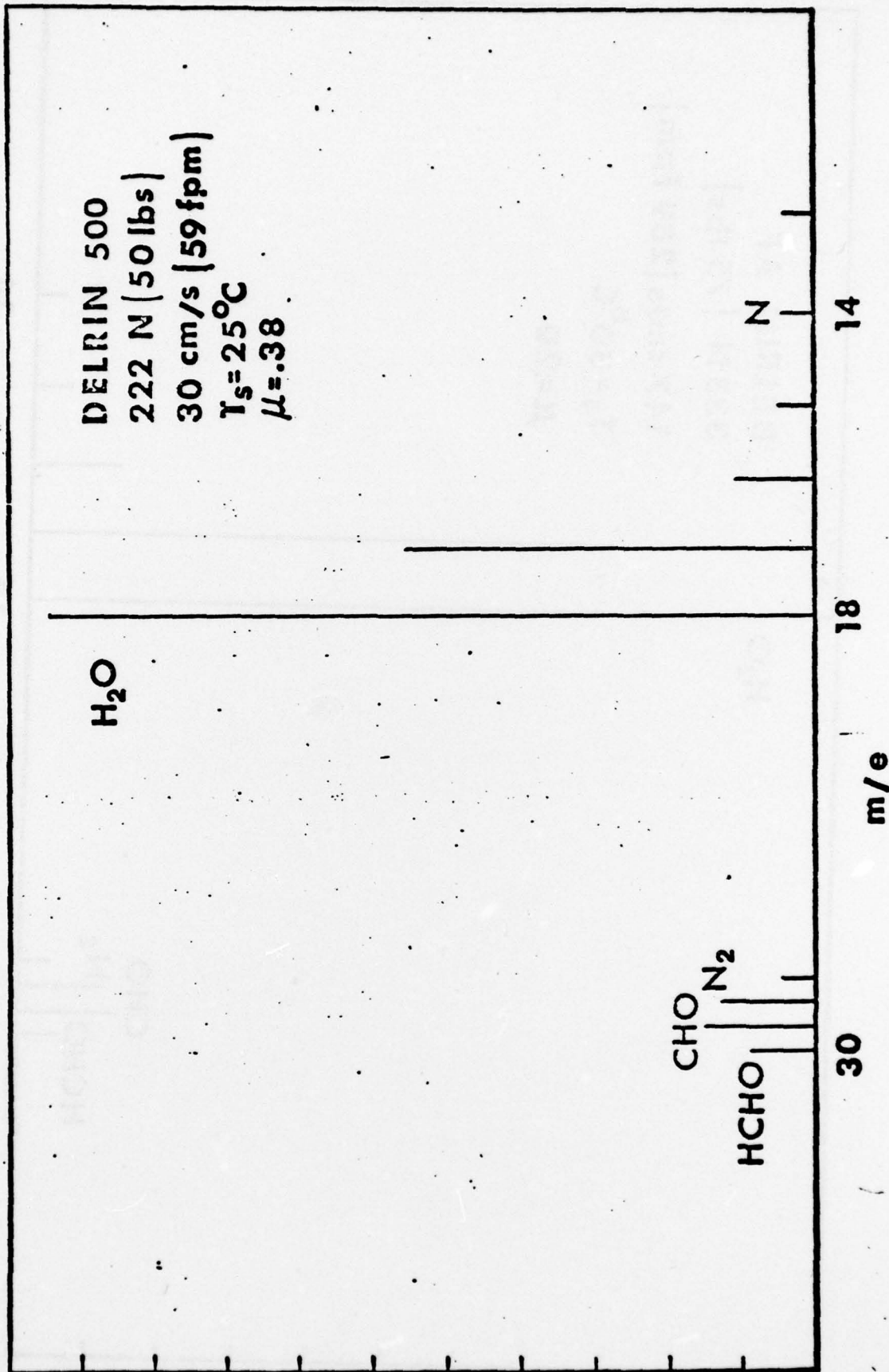


Figure 6. Mass spectrum of gases evolved in the sliding test of Delrin 500 at a speed of 30 cm/sec (59 fpm) and a load of 220 N (50 lbs).

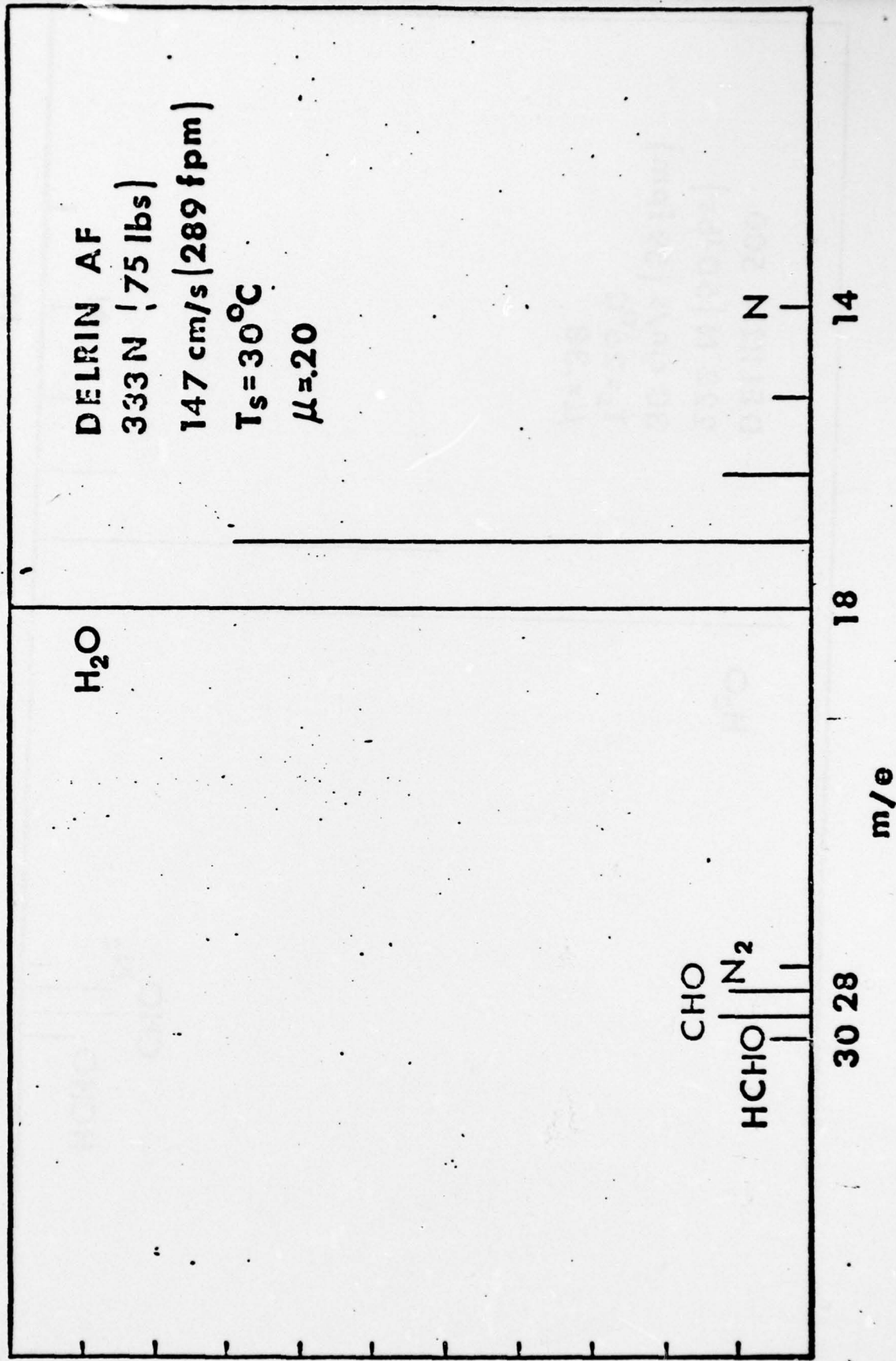


Figure 7. Mass spectrum of gases evolved in the sliding test of Delrin AF at a speed of 147 cm/sec (289 fpm) and a load of 333 N (75 lbs).

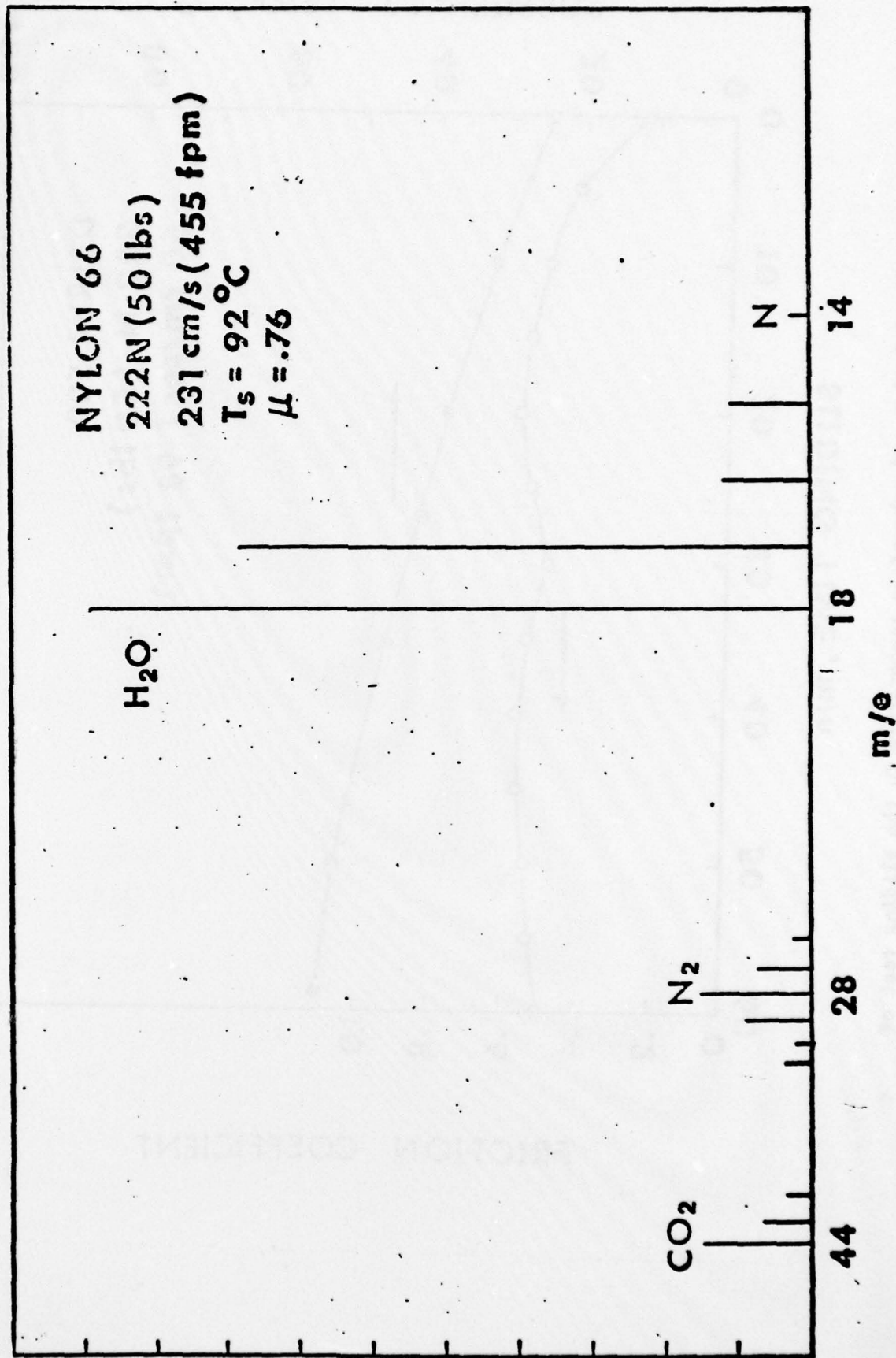


Figure 8. Mass spectrum of gases evolved in the sliding test of Nylon 66 at a speed of 231 cm/sec (455 fpm) and a load of 222 N (50 lbs).

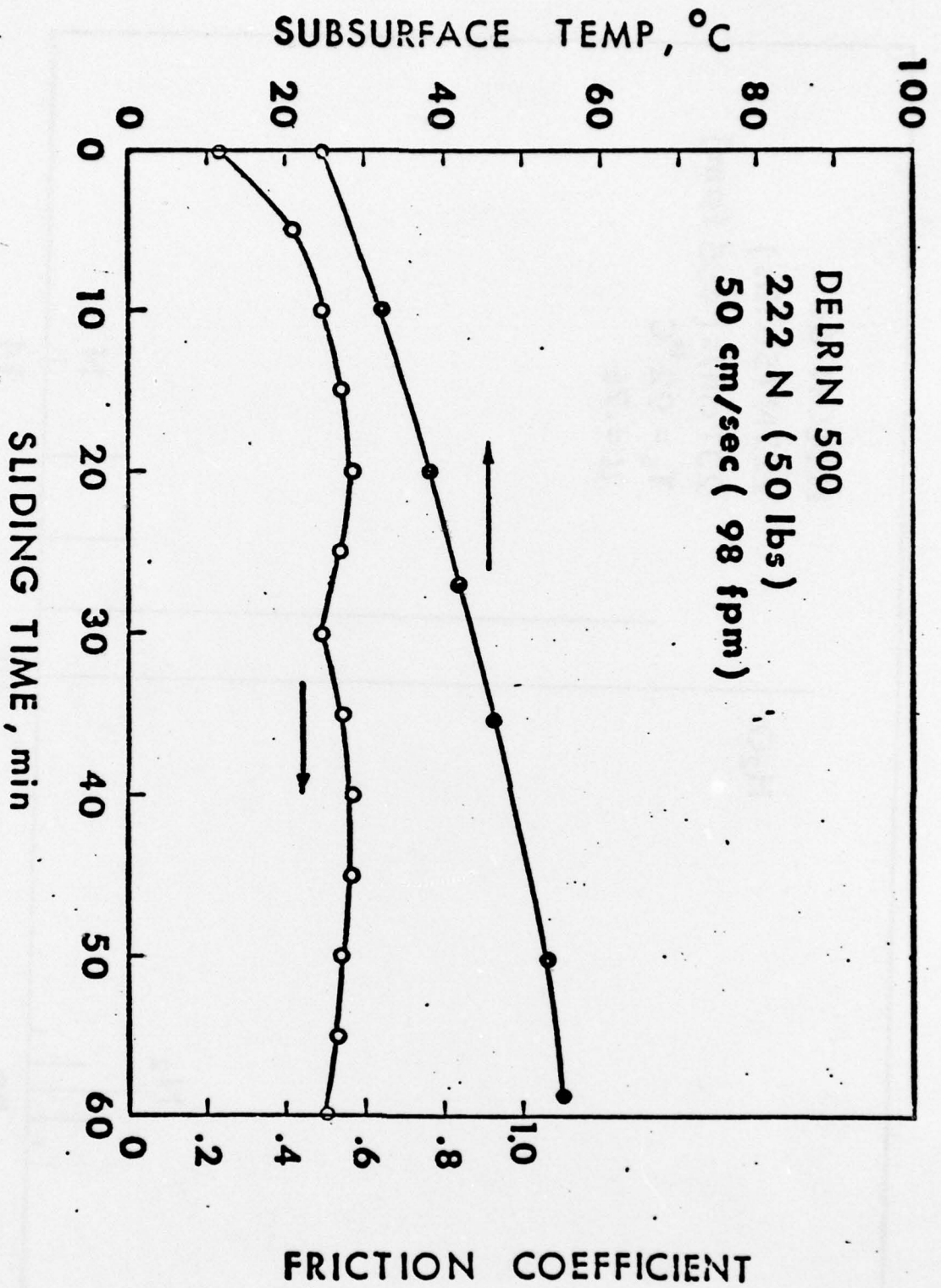


Figure 9. The friction and subsurface temperature in the sliding test of Delrin 500 at a speed of 50 cm/sec (98 fpm) and a load of 222 N (50 lbs).

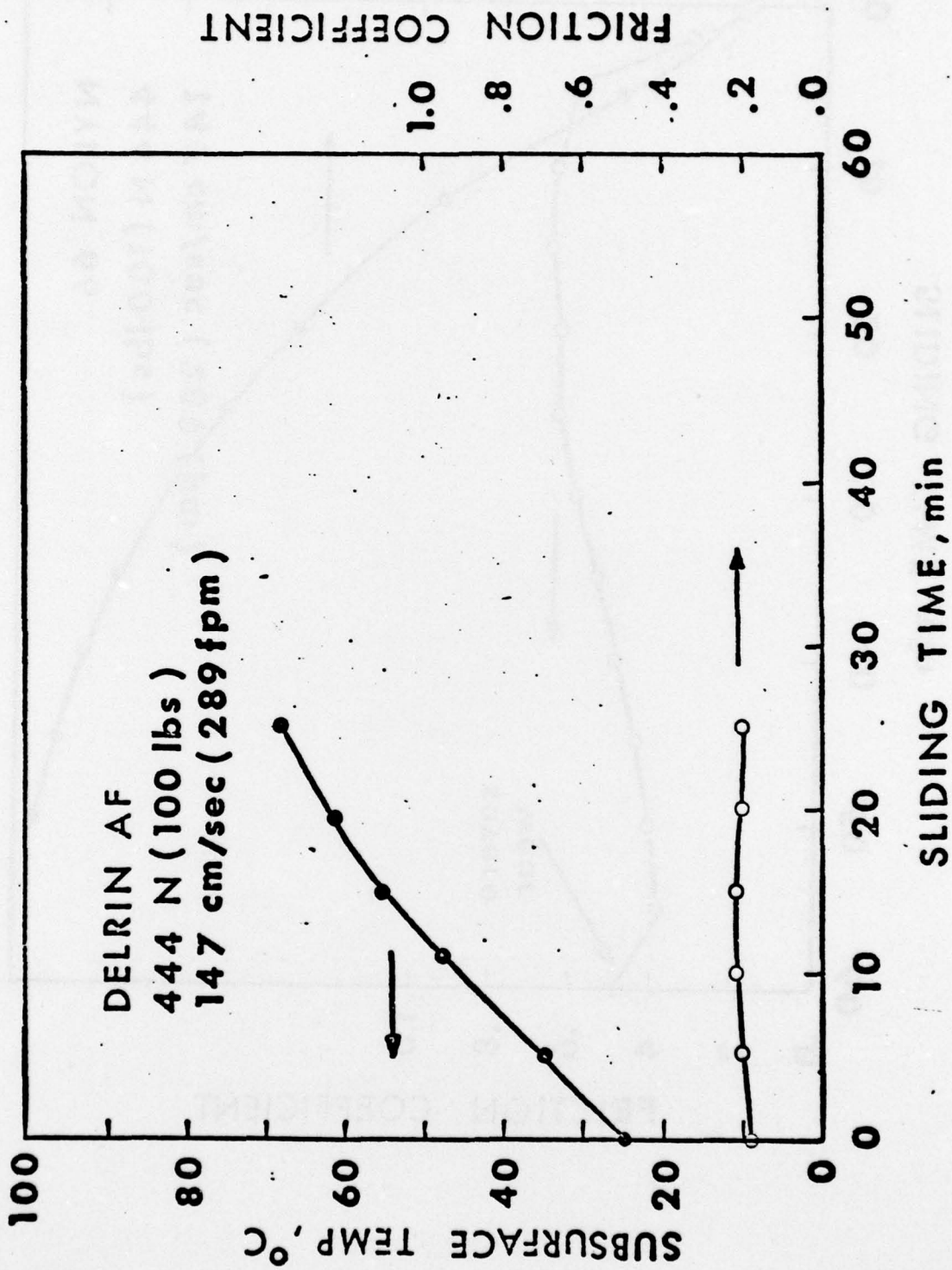


Figure 10. The friction and subsurface temperature in the sliding test of Delrin AF at a speed of 147 cm/sec (289 fpm) and a load of 444 N (100 lbs).

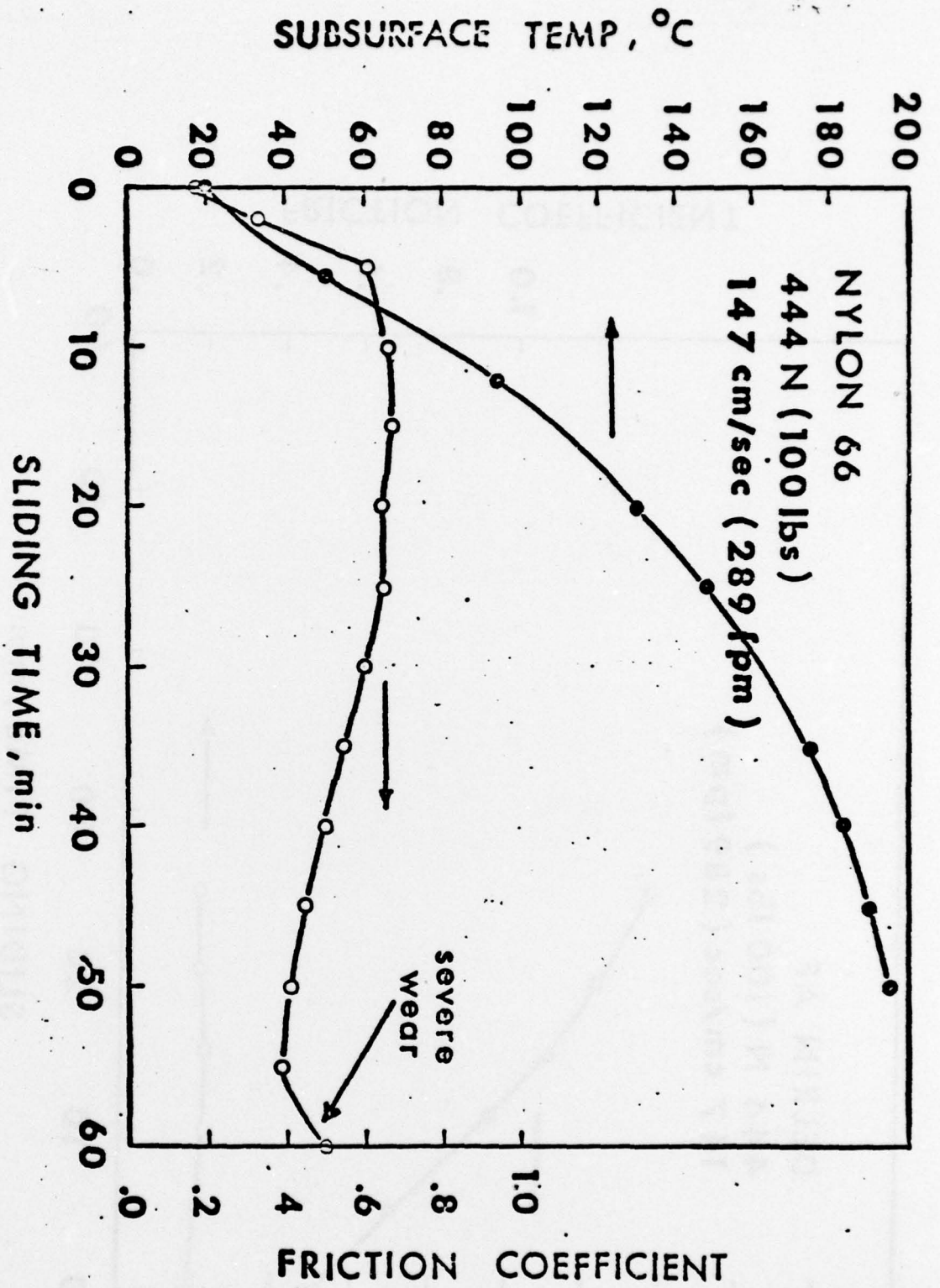


Figure 11. The friction and subsurface temperature in the sliding test of Nylon 66 at a speed of 147 cm/sec (289 fpm) and a load of 444 N (100 lbs).

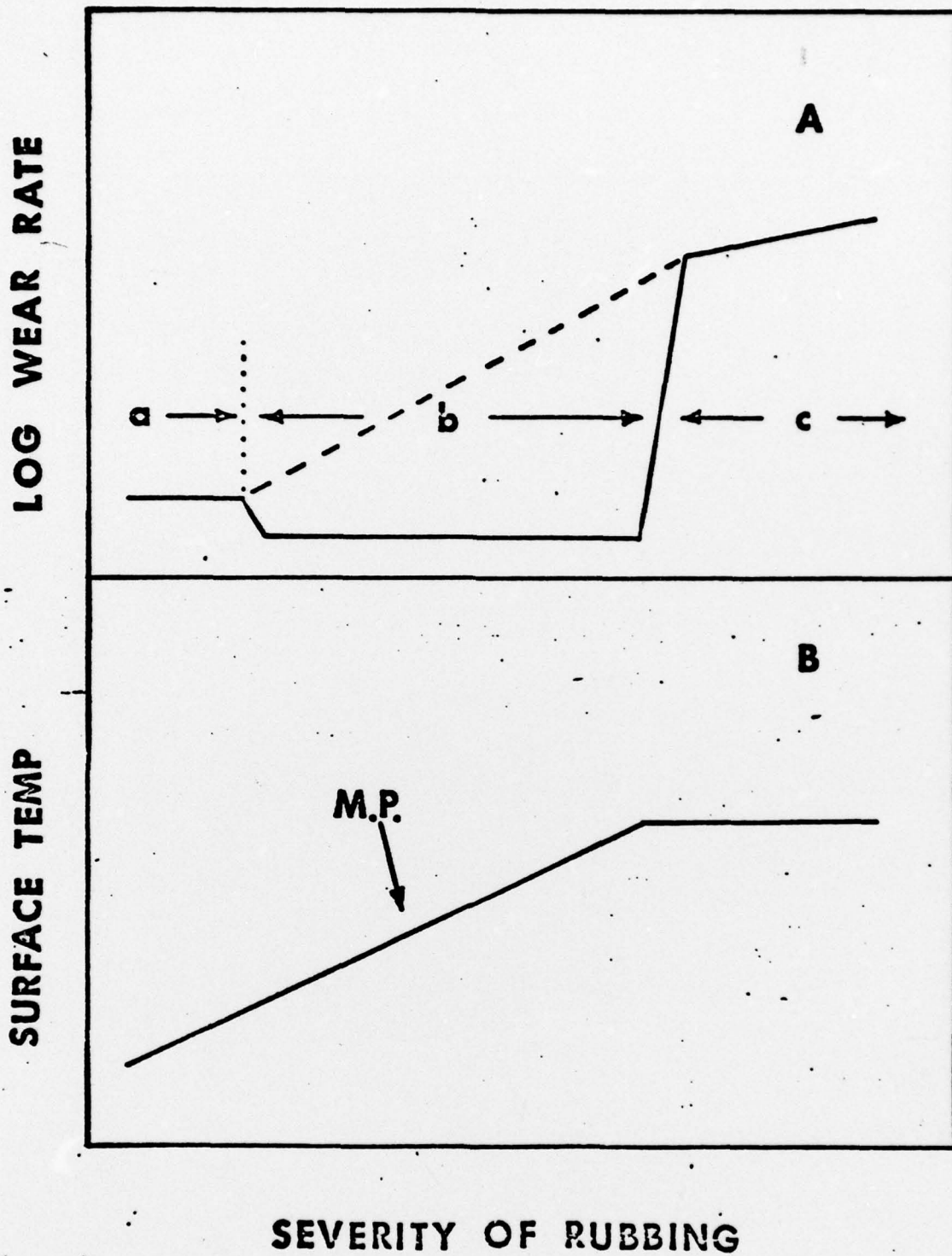


Figure 12. A schematic representation of wear rate and subsurface temperature with severity of sliding.