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NASA TECHNICAL NOTE

NASA TN D-7533

JAN 1974
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SLIDING OF POLY(VINYL CHLORIDE) ON METALS STUDIED BY AUGER ELECTRON SPECTROSCOPY

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NATIONAL AERONAUTICS AND SPACE ADMINISTRATION • WASHINGTON, D. C. • JANUARY 1974

1. Report No. NASA TN D-7533	2. Government Accession No.	3. Recipient's Catalog No.
4. Title and Subtitle SLIDING OF POLY(VINYL CHLORIDE) ON METALS STUDIED BY AUGER ELECTRON SPECTROSCOPY		5. Report Date January 1974
		6. Performing Organization Code
7. Author(s) Stephen V. Pepper		8. Performing Organization Report No. E-7469
		10. Work Unit No. 502-01
9. Performing Organization Name and Address Lewis Research Center National Aeronautics and Space Administration Cleveland, Ohio 44135		11. Contract or Grant No.
		13. Type of Report and Period Covered Technical Note
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code

15. Supplementary Notes

16. Abstract

The sliding of poly(vinyl chloride) on nickel, iron, and S-Monel has been studied by Auger Electron Spectroscopy. Polymer was not transferred to the metals, rather, shear appeared to take place at the interface. The metal was progressively chlorinated as the polymer made multiple passes on the surface. The thickness of this chlorine film was the order of one atomic layer. Electron-induced desorption studies indicate that the chlorine is chemisorbed to the metal. These results are interpreted as evidence for mechanically induced and/or thermal degradation of the polymer during sliding. Degradation products of HCl and Cl_2 which chemisorb to the metal are evolved near the interface.

17. Key Words (Suggested by Author(s)) Auger Electron Spectroscopy; Poly(vinyl chloride); Polymer; Transfer film; Sliding contact	18. Distribution Statement Unclassified - unlimited Cat. 18	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 25	22. Price* $2.75

SLIDING OF POLY(VINYL CHLORIDE) ON METALS STUDIED BY

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SUMMARY

The sliding of poly(vinyl chloride) on nickel, iron, and S-Monel in ultrahigh vacuum has been studied with the aid of Auger Electron Spectroscopy. The metal surfaces were cleaned by argon ion bombardment. Both atomically clean and oxidized metal surfaces were used in the sliding experiments. Auger Electron Spectroscopy was used to determine the chemical composition of the metal surface prior to sliding and to determine the changes in the chemical composition of the metal surface during sliding.

The interpretation of the Auger spectra from the sliding experiments was aided by the study of the Auger spectra of (1) vinyl chloride gas chemisorbed on clean metal and (2) poly(vinyl chloride) deposited from solution onto a metal surface. The important aspects of these spectra were the chlorine to carbon Auger peak height ratio and the electron-induced desorption cross section exhibited by chlorine.

The results of the sliding experiments indicated that polymer was not transferred to the metal surface, rather shear appeared to take place at the sliding interface. The metal surface was progressively chlorinated as the polymer made multiple passes on the surface. The thickness of the chlorine film on the surface was in the order of one atomic layer and electron-induced desorption studies showed it to be chemisorbed to the metal. These results are interpreted as evidence for mechanically induced or thermal degradation of the polymer during sliding. The polymer near the sliding interface evolves degradation products of HCl and Cl_2 which are chemisorbed to the clean metal.

INTRODUCTION

The usefulness of plastics in friction and wear applications is well recognized and has given rise to their use in many applications formerly reserved for metals. Accordingly, the study of the fundamental processes associated with the sliding of plastics has

been an active area of research for many years (ref. 1). The investigations have principally been concerned with the measurement of friction and wear as a function of load (ref. 2), sliding velocity and temperature. The technique of electron and optical microscopy (refs. 3 and 4) and autoradiography (ref. 5) have also been used to investigate the transfer of material in polymeric sliding systems.

These standard techniques of examining surfaces have recently been supplemented by Auger Electron Spectroscopy (AES) (ref. 6). This technique uses electron spectroscopy of surfaces in high vacuum to identify the elements heavier than helium present typically in the top three atomic surface layers. The advantages of this technique are (1) oxide films, surface contaminants, and mechanically transferred species of submonolayer concentrations may be identified, (2) the ultrahigh vacuum chamber provides a highly controlled environment for both the generation of atomically clean surfaces and their deliberate contamination with selected gases; and (3) the electron beam that excites the Auger transitions can desorb surface species thus providing additional information on the interaction between the adsorbate and substrate.

Recently, AES was introduced as an analytic tool to the study of the friction and transfer of the polymer polytetrafluoroethylene (PTFE) (ref. 7). It was determined by Auger analysis that a thin film of PTFE was transferred to a metal surface by sliding contact and that the fluorine in the film did not exhibit ionic or covalent bonds with the metallic substrate. The purpose of the present report is to continue the investigation of plastics sliding on metals by using AES to study the sliding of poly(vinyl chloride) (PVC) on nickel, iron and S-Monel surfaces in ultrahigh vacuum. The Auger analysis is used to determine which species were transferred to the metal by sliding contact with the polymer and to determine if the observed transfer was effected by the chemical constitution of the sliding surface. In addition, the coefficient of friction was measured.

APPARATUS

The experimental apparatus has been described in reference 8 and the essential elements are depicted in figure 1. For the sliding experiments the polymer was in the form of a rider with a radius of 0.476 centimeter at the contact end. The metal surfaces were in the form of flat disks 6.35 centimeters in diameter. The riders contacted the disk about 2.5 centimeters from the center. The specimens were mounted in a stainless-steel vacuum chamber which was evacuated from atmospheric pressure by sorption pumps and then by an ion pump to an ultimate pressure of 1×10^{-10} torr. The chamber was bakeable to 250° C. The pressure was measured by a cold cathode discharge gage in the high-vacuum range ($<1\times10^{-5}$ torr) and by a hot-cathode ion gage in the medium-vacuum range ($>1\times10^{-5}$ torr). The cold-cathode gage was positioned about 10 centi-
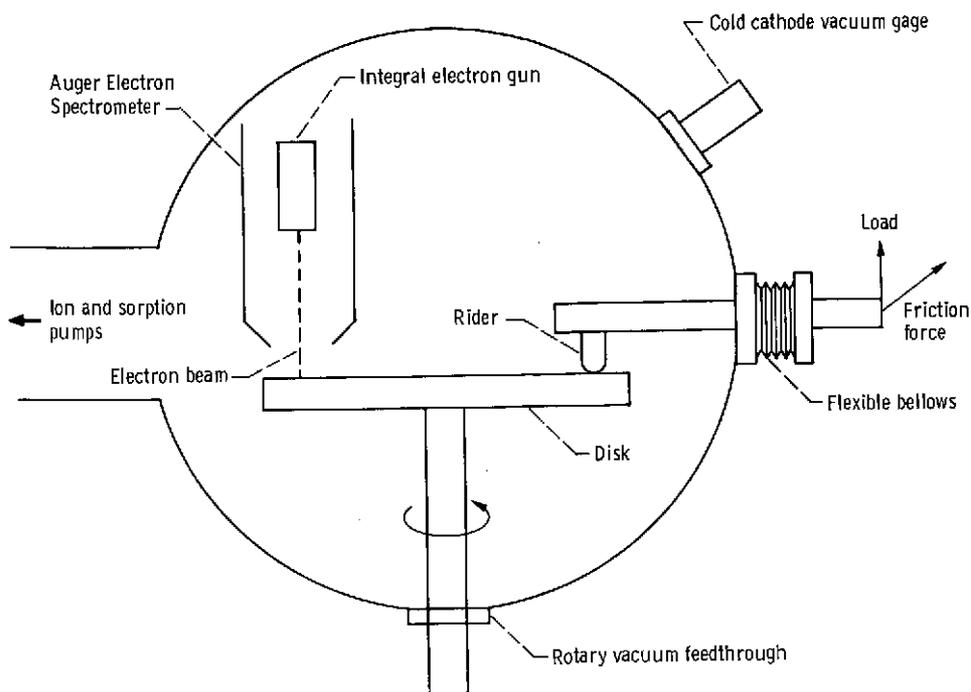
Figure 1. - Experimental apparatus with Auger Electron Spectrometer.

meters from the disk. A radiofrequency quadrupole gas analyzer was mounted on the system to analyze the gas species leaked into the system.

The metal disk was mounted on a rotary magnetic vacuum feedthrough that was either driven by a motor when the rider was in sliding contact or else manipulated by hand for precise positioning of the disk. The rider was supported on an arm that was mounted on a gimbal and sealed to the chamber with a bellows. A linkage at the end of the retaining arm farthest from the rider was connected to a strain gage assembly that was used to measure friction force. Load was applied by a deadweight loading system.

For Auger analysis the surface of the disk is bombarded with 2000-volt electrons (1 to 10 μA) from the integral electron gun. The energy of the secondary electrons emitted by the surface is analyzed by the cylindrical mirror electron spectrometer surrounding the electron gun. The Auger electrons found in the secondary electron energy spectrum identify the elements heavier than helium present in the surface region to a depth of about three atomic layers. The spectrometer analyzed a spot (~1 mm diam.) on the disk 180° away from the contact point of the rider. The disk is rotated 180° to bring the point of contact of the rider under the electron beam for Auger analysis. Electrostatic deflection plates in the electron gun permit the electron beam (and thus the spot analyzed) to be moved radially in and out of the circumferential track of the contact. The Auger spectrum was displayed either on an X-Y recorder or a strip-chart recorder as was appropriate.

An atomically clean surface was obtained by subjecting the disk to argon ion bombardment. This was accomplished by applying a 1600-volt negative potential to the disk at a chamber pressure of 40 millitorr of argon. Under these conditions a glow discharge surrounded the disk. The argon ions sputtered the surface of the disk and exposed clean metal. Usually 10 minutes of sputtering was sufficient to obtain an atomically clean surface. Although not shown in figure 1, a retractable metal cup was inserted over the rider radius to prevent deposition of metal sputtered from the disk. This cup also prevented the rider from being subjected to the CASING (crosslinking by activated species of inert gases) treatment (ref. 9). At the termination of sputtering, the argon was pumped out by sorption pumps and the ion pump was turned on to return the system to a pressure $<1\times10^{-9}$ torr within 10 minutes. The system pressure after sputtering was sufficiently low to allow the disk to remain clean for at least 1 hour.

MATERIALS

The disks used in the experiments were nominally high-purity nickel, iron, and S-Monel (a copper-nickel-silicon alloy). The disks were lapped flat and then polished to a mirror finish with 6-micrometer-diameter diamond paste. A profilometer trace at highest sensitivity ($\times$50 000) indicated a peak-to-peak surface roughness of less than 2×10^{-6} centimeters. Microscopic examination of the surface with oblique illumination revealed some widely spaced random scratches.

Two different types of PVC were used in this investigation. The first type was a well-characterized polymer supplied by Louis Cohen and Donald Witenhafer of B. F. Goodrich Company. These polymer specimens were in the form of 0.952-centimeter- (3/8-in.-) diameter translucent yellow spheres that had been hot-pressed from the resin at 218° C (425° F). The PVC resin, Geon 101EP (M_w = 115 000, M_w/M_n = 2.2) had been stabilized with 3 pph of dibutyl tin dioctyl dithioglycolate. For use as a rider, a sphere was joined to an aluminum rod with epoxy.

The second type of polymer used was a commercially available 0.952-centimeter- (3/8-in.-) diameter rod of plastic identified only as poly(vinyl chloride). This material was an opaque gray-green. The color probably resulted from epoxy plasticizers used to improve the handling characteristics of the polymer. For use as a rider, a radius was machined on the rod. Despite the differences in appearance and composition, both forms of PVC gave the same results in the sliding experiments.

4

PRELIMINARY EXPERIMENTS

To date AES has been used to study elementary systems such as the atomically clean surface or those surfaces that have been contaminated with simple gases. However, the sliding of PVC on a metal offers a much more complicated situation. For this reason auxiliary experiments were conducted to study the Auger spectra of simpler, but related systems. First, the monomer of PVC, vinyl chloride gas was adsorbed on a clean metal surface. Quantitative aspects of the peak heights in the Auger spectrum of the adsorbed species are considered together with the stability of the Auger spectrum. Secondly, poly(vinyl chloride) could be studied. The stability of the spectrum was of principle interest here.

Vinyl Chloride

In this section certain aspects of the Auger spectrum of vinyl chloride adsorbed on a metal surface that are relevant to the study of PVC sliding on metals are discussed. Since AES provides only an elemental analysis of a surface, the presence of molecular compounds on a surface can only be inferred from the relative amounts of the molecular constituents present in the Auger spectrum. The situation is further complicated by the fact that Auger electron yields on a per atom basis differ from one element to another.

```
H      Cl
|      |
C  =   C
|      |
H      H
```
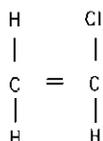
(a) Vinyl chloride molecule.

```
   /  H      Cl   \
  |   |      |     |
  | — C  —   C  —  |
  |   |      |     |
   \  H      H    / n
```
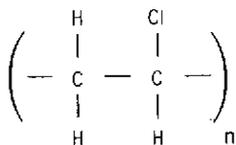
(b) Poly(vinyl chloride)
repeat unit.

Figure 2. - Structure of vinyl
chloride molecule and poly-
(vinyl chloride) repeat unit.

The structure of the vinyl chloride molecule and the PVC repeat unit is depicted in figure 2. Since hydrogen is not detected by AES, the relevant constituents are carbon and chlorine. In both structures there are twice as many carbon atoms as chlorine atoms.

Thus, to determine whether PVC is present on the disk after sliding, it is first necessary to establish the relative intensity of the carbon and chlorine Auger peaks when there are twice as many carbon atoms on the surface as there are chlorine atoms. The chemisorption of vinyl chloride provides such a test surface. The relative carbon-chlorine intensities measured will then establish a necessary criterion to be met by the Auger spectrum of PVC.

It is also necessary to consider the stability of the Auger spectrum of the chemisorbed vinyl chloride. The time dependence of an Auger spectrum is due to the desorption of surface species by the incident 2000-volt electron beam. Such electron-induced desorption has been observed for both chemisorbed species (ref. 10) and for surface polymers such as PTFE (ref. 7). Since the stability of the spectra is quite different in the two cases, it is expected that the study of electron-induced desorption for vinyl chloride and PVC would provide an additional criterion for the identification of PVC on a metal surface following sliding.

A nickel disk provided the surface on which the vinyl chloride adsorbed. After argon ion bombardment, the disk exhibited the Auger spectrum in figure 3(a). The disk was stationary during the time (~30 sec) to take the trace. Some argon is present due to im-

(a) Clean surface.

(b) After exposure to 0.75 Langmuir of vinyl chloride.

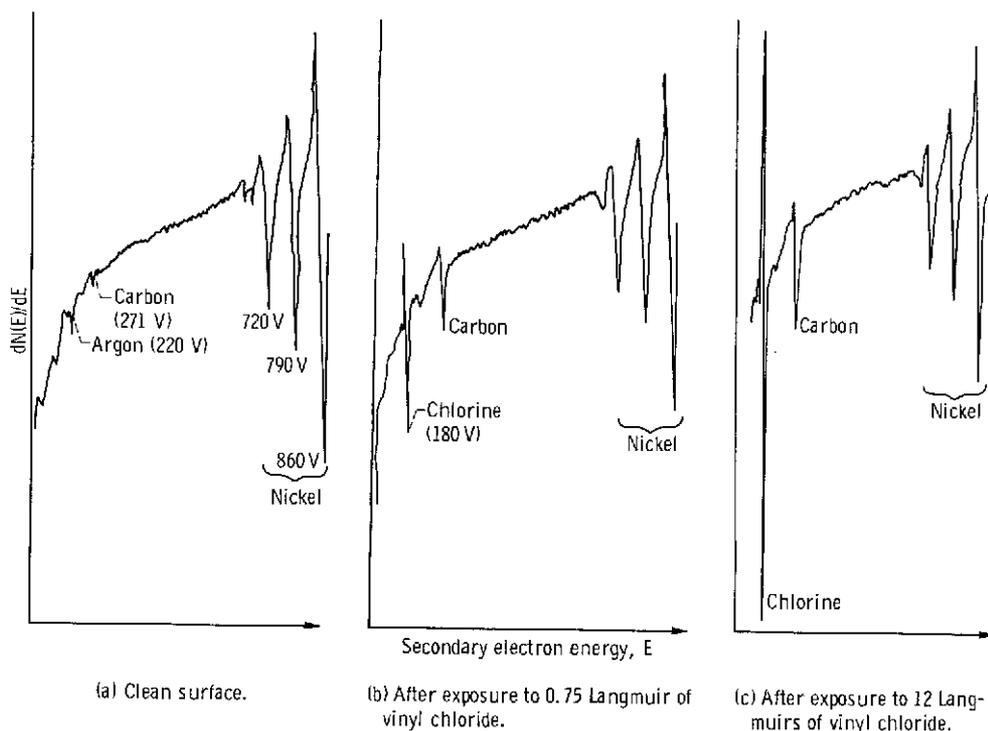(c) After exposure to 12 Langmuirs of vinyl chloride.

Figure 3. - Auger spectra of nickel surface; clean surface, after exposure to 0.75 Langmuir of vinyl chloride, and after exposure to 12 Langmuirs of vinyl chloride. Beam current, 10 microamperes.

bedding of the energetic argon ions in the nickel matrix. The oxygen peak is absent and the carbon is just resolved from the background and much smaller than the high energy nickel peaks, indicating that surface containments were a small fraction of an atomic layer. Vinyl chloride was then admitted to bring the system pressure to 5×10^{-8} torr for a specified time with the ion pump on to provide the different exposures. The residual gas analyzer on the system indicated the mass spectrum of vinyl chloride (ref. 11) with the intensity of other peaks very small, verifying that the clean nickel disk was exposed to high-purity vinyl chloride.
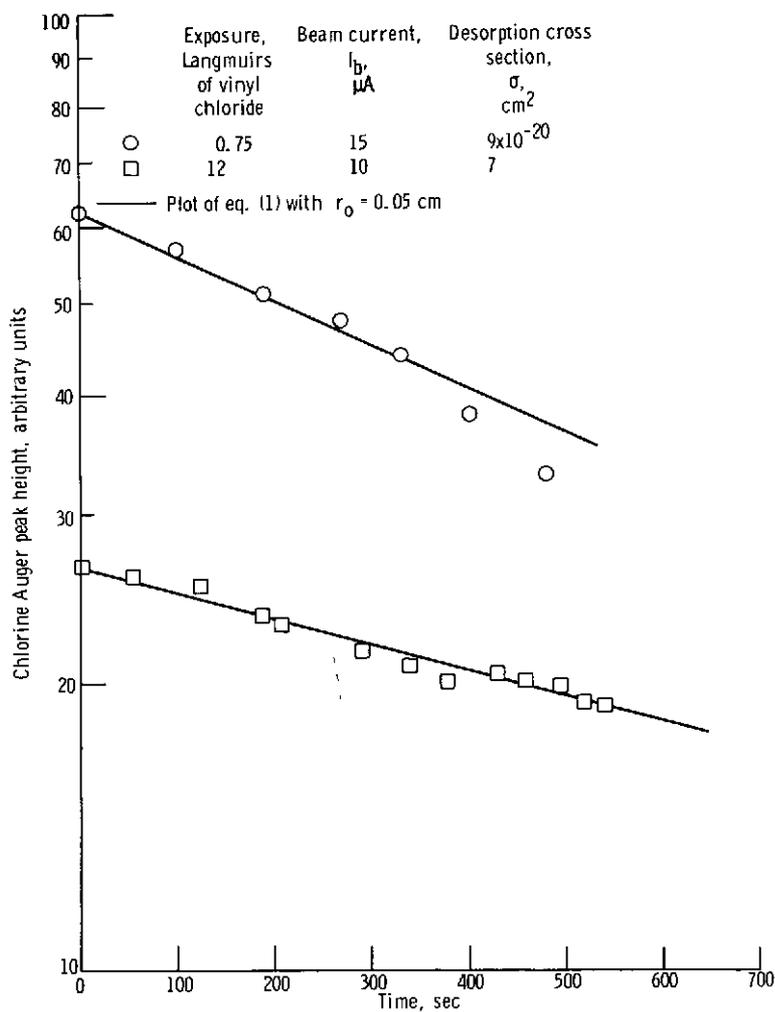

Figure 4. – Time dependence of chlorine Auger peak from nickel disk exposed to 0.75 and 12 Langmuirs of vinyl chloride.

The Auger spectra of the surface after exposures of 0.75 and 12 Langmuirs (1 Lang-muir = 1×10^{-6} torr-sec) are presented in figures 3(b) and (c), respectively. The spectra indicate that the ratio of the magnitude (peak-peak height) of the chlorine peak to that of the carbon peak is 2.23 in the smaller exposure and 4.41 in the larger exposure. The chlorine-carbon Auger peak height ratio saturated at ~5.5 after extended exposure.

The stability of the spectra was studied by observing the time dependence of the chlorine peak. The results are presented in figure 4. The main result here is that the chlorine Auger peak from chemisorbed vinyl chloride is rather insensitive to the incident beam at these beam currents, decreasing only a few percent per minute.

Discussion of Vinyl Chloride

The results obtained here for the chlorine-carbon Auger peak height ratios can be related to the recent work of Meyer and Vrakking (ref. 12). In an investigation of the quantitative aspects of AES they found that the yield of Auger electrons from chlorine was 4.4 to 5.6 times the yield from carbon on a per atom basis. Thus, the chlorine-carbon peak height ratio for vinyl chloride (1 chlorine atom/2 carbon atoms) should be 2.2 to 2.8 The results obtained here for the small exposure are in rather good agreement with the values predicted by the results of Meyer and Vrakking, indicating that in fact, the chlo-rine to carbon peak height ratio for vinyl chloride in either chemisorbed or polymeric form should be ~2.2.

For exposures larger than ~1 Langmuir, the growth of the chlorine peak exceeds the growth of the carbon peak. This result may arise from the following mechanism: as the coverage of the adsorbed species on the surface is increased, there are fewer sites re-maining that can accommodate the entire vinyl chloride molecule. The chlorine part of the molecule may then adsorb with dissociation of the chlorine molecular bond and de-sorption of the part containing the carbon atoms. Other mechanisms by which only the chlorine part of the vinyl chloride molecule adsorbs are no doubt possible. In any case, chlorine to carbon peak height ratios >2.2 are not due to pure vinyl chloride, so that the Auger spectrum of a surface exposed to >1 Langmuir vinyl chloride does not necessarily reflect the Auger spectrum of the vinyl chloride molecule.

The time dependence of the chlorine Auger peak may be related to the theory of electron-induced desorption by the equation

$$S(t) = S(o) \exp\left(\frac{-I_b \sigma t}{\pi r_o^2}\right)$$

(1)

where $S(t)$ is the magnitude of the Auger peak at time t, I_b is the incident beam current, r_o is the radius of the incident electron beam, and σ is the desorption cross section (ref. 10). The desorption cross section is the parameter that characterizes the desorption process and is determined by the electronic environment of the desorbing species. The slope of the lines on the semilog plot in figure 4 yields $\sigma = 9 \times 10^{-20}$ square centimeter for 0.75-Langmuir exposure and $\sigma = 7 \times 10^{-20}$ square centimeter for the 12-Langmuir exposure, indicating that there was little dependence of the desorption rate on the initial amount of chlorine on the surface. The values are the correct order of magnitude for the desorption cross section for species chemisorbed on metals (ref. 10) and indicates that the chlorine in the adsorbed vinyl chloride is in intimate contact with the nickel surface, that is chemisorbed to it.

To summarize the results relevant to the investigation of PVC sliding on metals, it is found that (1) the ratio of chlorine to carbon Auger peak heights is ~2.2 for vinyl chloride and (2) the spectrum is quite stable, the chlorine decreasing only a few percent per minute and is characterized by a desorption cross section of $\sigma = 9 \times 10^{-20}$ square centimeter. This value is consistent with desorption cross sections for chemisorbed species on metals.

Poly(vinyl chloride)

In this section the Auger spectrum of PVC is investigated. The most straightforward method would be to simply use a disk of PVC. However, the normally incident electron beam would cause this insulator surface to charge up, resulting in erratic Auger spectra. Although insulator surfaces may be successfully studied using an obliquely incident electron beam, such an arrangement is not suitable for the present apparatus. Instead, the method used here was to deposit a very thin film of polymer onto a metal disk from a dilute solution of the polymer and then subject this surface to Auger analysis. The film proved thin enough to allow the incident electrons to drain into the metal with no attendant charging of the surface.

The well-characterized polymer spheres were dissolved at room temperature overnight in tetra-hydrofuran to produce a clear, colorless solution 0.135 percent by weight. A steel disk was cleaned until water would wet the surface. It was then dipped into the polymer solution, retracted, and held in a vertical position to dry for a few seconds. This procedure was repeated two more times. The disk was then placed in the vacuum system which was evacuated to $< 5 \times 10^{-9}$ torr overnight. The bakeout was bypassed to prevent degradation of the polymeric surface species.

The carbon and chlorine portion of the Auger spectrum of the surface is presented in figure 5. It should be mentioned here that there was no evidence of the tin stabilizer in the Auger spectrum, indicating that the stabilizer did not adsorb on the surface in appre-
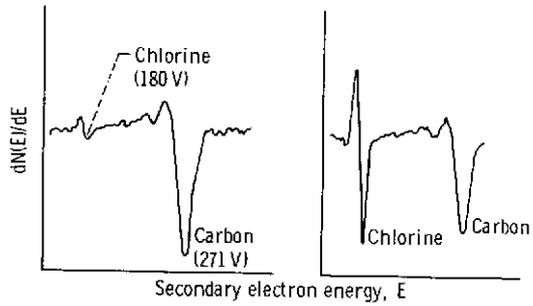
(a) Disk velocity, 0 centi-
meter per second.

(b) Disk velocity, 0.03
centimeter per sec-
ond.

Figure 5. - Chlorine and carbon part of Auger spectrum
of a steel surface on which poly(vinyl chloride) was
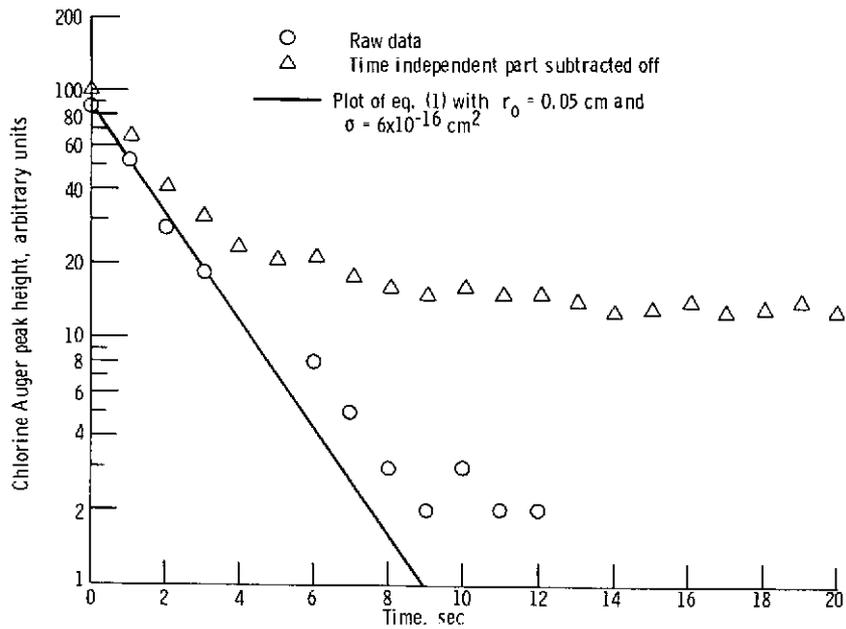deposited from solution in tetrahydrofuran. Beam
current, 1 microampere.

Figure 6. - Time dependence of chlorine peak from poly(vinyl chloride) absorbed from
solution of tetrahydrofuran onto a steel disk. Beam current, 1 microampere.

10

ciable amounts. In figure 5(a) the disk is stationary and there is present a very small chlorine peak and a much larger carbon peak. In figure 5(b) the disk is rotating with the surface under the electron beam moving with a velocity of 0.03 centimeter per second. There is a much larger chlorine peak present than for the stationary case. Evidently the chlorine is undergoing electron-induced desorption. The moving surface brings fresh sample under the electron beam, thus continuously providing more chlorine and a higher chlorine signal. This technique of moving the surface at uniform velocity to provide a time-independent Auger signal has been used previously to observe the Auger spectrum of PTFE on metals (ref. 13).

The time-dependence of the chlorine Auger peak height was studied at a beam current of 1 microampere. The results are presented in figure 6. It is seen that the chlorine Auger peak is highly unstable even at beam currents as small as 1 microampere, decaying to about 15 percent of its initial value in a few seconds. Although most of the chlorine on the surface is subject to electron-induced desorption at a high rate, about 15 percent of the initial peak height is fairly stable, at least over the time observed.

Discussion of Poly(vinyl chloride)

The most noteworthy aspect of the Auger spectrum of this surface is the instability of the chlorine peak. If the time-independent portion of this peak is subtracted out, the lower curve in figure 6 results. Fitting equation (1) to this data yields a desorption cross section of $\sigma = 6 \times 10^{-16}$ square centimeter. This is to be contrasted with the value of σ for the chlorine in the chemisorbed vinyl chloride, a value smaller by about four orders of magnitude.

To realize the significance of these results it is necessary to recall some basic ideas on electron-induced desorption of surface species on metals (ref. 10). It has been established that the cross section (desorption probability) for electron-induced desorption of chemisorbed surface species, $\sim 10^{-20}$ square centimeter, is orders of magnitude smaller than the ionization and excitation cross sections for free atoms and molecules, $\sim 10^{-16}$ square centimeter. The ionization of the surface species is the first step in the desorption process, the second being the desorption of the ion. It has been proposed that the small cross section for chemisorbed species is due to the reformation (neutralization) of the bond initially broken by the bombarding electrons by tunneling of electrons from the metal to the excited atom before it can leave the surface. Such tunneling occurs only if the surface species is in intimate electronic contact with the metal, for example, chemically bonded to it.

It was seen that the value of σ obtained here for the chlorine in chemisorbed vinyl chloride is the correct order of magnitude for chemisorbed species. On the other hand, the chlorine in the experiment in which the polymer is adsorbed from solution exhibits a

cross section appropriate for species not in direct contact with the initial surface, that is, in the free state. It is thus concluded that the rapidly desorbing chlorine observed here is in fact a constituent of the polymer and not a species chemically bonded to the metal. The more stable, minor part of the chlorine peak is attributed either to an impurity chemisorbed to the metal or, more likely, to chlorine beneath the topmost polymer strand that is prevented from leaving the surface by a "cage" effect.

In a previous publication (ref. 13) it has been shown that the fluorine atoms in PTFE also undergo high rates of desorption of $\sigma \approx 10^{-16}$ square centimeter. There it was speculated that this behavior should be observed for all atoms having a single valence bond to the polymer chain. Chlorine has only a single bond and so the results presented here support the speculation. One is thus led to the general conclusion that the Auger spectra of halogenated polymers are highly unstable, with the halogen exhibiting electron-induced desorption cross sections of $\sim 10^{-16}$ square centimeter. This is a necessary condition to be met by the Auger spectra of halogenated polymeric species and may be used as an aid to identify such species by AES. It is, however, not a sufficient condition for the identification of polymeric species since all that is required for high desorption rates is that the halogen atom be sufficiently separated from the metal surface to prevent reformation of the broken bond and this may be fulfilled by halogens in low molecular weight species as well as macromolecules.

SLIDING OF POLY(VINYL CHLORIDE) ON METALS

Procedure

The experiments in which solid PVC was slid on metal surfaces were performed in ultrahigh vacuum with the solid polymers described in the section MATERIALS. After insertion of the polymer specimen, the system was evacuated. To avoid degradation of the polymer, the system bakeout was bypassed. Ultimate pressures $<1\times10^{-9}$ torr were achieved overnight indicating that outgassing of the polymer was not important. The metal disk was then sputtered to produce a clean surface. This surface could then be deliberately contaminated or else sliding proceeded on the clean surface.

An important observation was that no pressure bursts ($>5\times10^{-9}$ torr) were observed during sliding. Thus, sliding proceeded without gas species generated in the contact zone diffusing away and chemisorbing on the rest of the clean disk. In fact scanning the electron beam across the track indicated that the species appearing on the disk after sliding were highly localized in the circular track of contact.

After the sliding experiments were completed, the specimens were subjected to microscopic examination. In addition, both surface profilometry (for the disk) and energy-

dispersive X-ray elemental analysis in a scanning electron microscope (for the wear scar of the rider) were employed.

Results

The Auger spectra for the well characterized PVC sliding on a nickel disk are presented in figure 7. Similar results were obtained using the commercial PVC and also for iron and S-Monel disks. After sliding one revolution at 1 millimeter per second at 500-gram load the spectrum of figure 7(a) was obtained. It is seen that sliding PVC on nickel has produced a film on the surface containing chlorine and carbon. The peak height ratio of chlorine to carbon is ~12. With the exception of the region in the immediate beginning of the track, the spectrum is highly stable and uniform around the track. At the beginning of the track there is a lower chlorine to carbon peak height ratio and the chlorine peak exhibits some time dependence. This initial region was difficult to locate and reproducible spectra could not be obtained. In contrast, the great majority of the track exhibited the spectrum of figure 7(a) in all experimental trials.

(a) After one revolution of disk.　　(b) After 15 revolutions of disk.　　(c) Disk out of track.
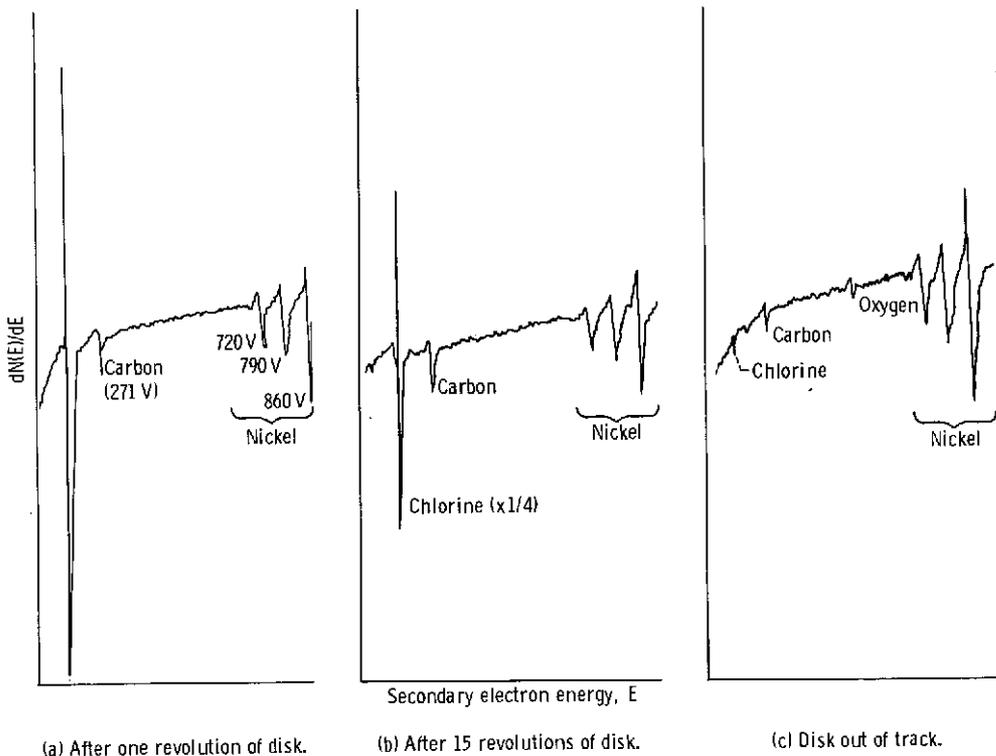
Figure 7. - Auger spectra of nickel disk after sliding poly(vinyl chloride) at 500-gram load after one revolution of disk, after 15 revolutions of disk, and where disk is out of track.

Further sliding at the same load produced a surface with the Auger spectrum of fig-
ure 7(b). Note that the sensitivity of the spectrometer has been reduced by a factor of
four while tracing over the chlorine peak. The chlorine to carbon peak height ratio has
increased to 23 and the spectrum is highly stable around the track. No difference was
noticed between the Auger spectra for the beginning and the rest of the track; it appears
that continued sliding has wiped out the nonuniformity noted previously. The growth of
the chlorine to carbon peak height ratio was a general characteristic of continued sliding
and depended only on the total number of revolutions and not on the sliding velocity. The
highest velocity used here was 46 centimeters per second. Loads of 500 grams and 1000
grams were used with similar results. After extensive sliding, the chlorine to carbon
Auger peak height ratio saturated between 25 and 30.

The stability of the Auger spectrum of figure 7(b) was studied by observing the time-
dependence of the chlorine peak for a 10.6-microampere beam current on the stationary
disk. The results are presented in figure 8. The peak height decreased only a few per-
cent per minute. The use of equation (1) yielded a desorption cross section $\sigma = 5 \times 10^{-20}$
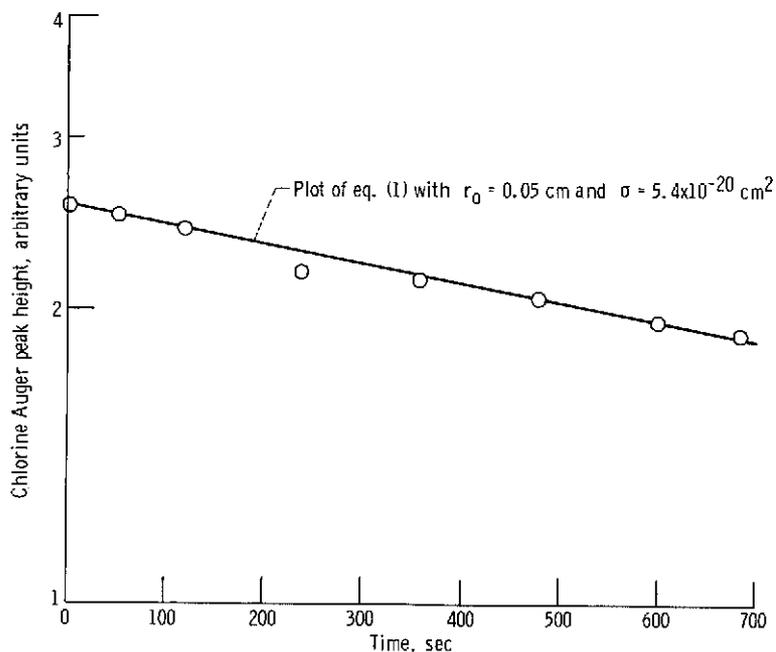square centimeter.

Figure 8. - Time dependence of chlorine Auger peak from nickel disk after sliding
poly(vinyl chloride) 15 revolutions at 500-gram load. Beam current, 10.6
microamperes.

14

An estimate of the thickness of the chlorine and carbon film may be obtained by using the deflection plates to obtain Auger spectra in and out of the track. Figure 7(c) presents the Auger spectrum of the disk outside the track whose Auger spectrum is given in figure 7(b). Although the high energy nickel peaks in the track are somewhat attenuated, they are certainly quite prominant. Since AES is sensitive to ~3 outermost atomic layers, films thicker than ~3 atomic layers would have attenuated the nickel to the point of extinction. If it is assumed that the film is uniform, then the film thickness is certainly less than 3 atomic layers and probably in the monolayer range.

At this point it is possible to draw some conclusions concerning the surface film generated by sliding PVC on these metals. In the first place, consider the chlorine to carbon peak height ratio of 10 to 30. Since it has been shown previously that the chlorine to carbon peak height ratio for stoichiometric vinyl chloride or poly(vinyl chloride) should be ~2.2, the surface film generated by sliding has up to 10 times more chlorine than appropriate to vinyl chloride. In addition, it has been shown that halogenated polymers in general and PVC in particular were characterized by high rates of electron-induced desorption of the halogen. In contrast, the desorption cross section (5×10^{-20} cm^2) obtained here for the mechanically generated film is appropriate to chlorine chemisorbed to the metal surface. It is concluded here that little or no polymer is transferred to the metal by sliding, but instead the surface is progressively chlorinated, with a small amount of carbon also appearing on the surface. The thickness of the chemisorbed film is in the monolayer range.

The friction force of the disk on the rider was measured during the sliding experiments. At the start of sliding a fresh rider, the coefficient of friction was 0.45 and this was independent of the particular metal surface. This value is somewhat larger than that reported for PVC sliding on glass in air (ref. 4). As the multiple pass sliding continued, the coefficient of friction decreased to about 0.25. No dependence of the friction for sliding on both clean metal and metal with a chemisorbed monolayer of oxygen was found.

Although a chemisorbed monolayer of oxygen does not seem to effect the friction, two phenomena associated with chemisorbed oxygen films have been observed. A track was established on a clean disk and then the disk was exposed to oxygen. Although the Auger spectrum of the disk indicated chemisorption of oxygen outside the track, no oxygen appeared in the spectrum of the track. Such a result is understandable in terms of the nature of the film. The chlorination of the track surface by the rider saturates the sites of the surface that are active in chemisorption, thus preventing further adsorption by active gases such as oxygen. The surface has been passivated in the track.

The second phenomena had to do with sliding PVC on a metal with oxygen already chemisorbed on it. The Auger spectrum of a sputter-cleaned iron disk which had been exposed to oxygen is shown in figure 9. The oxygen peak is larger than the high energy iron. The Auger spectrum of the track generated by sliding 200 revolutions is presented in figure 9(b). The oxygen peak has almost disappeared, while the chlorine-carbon com-
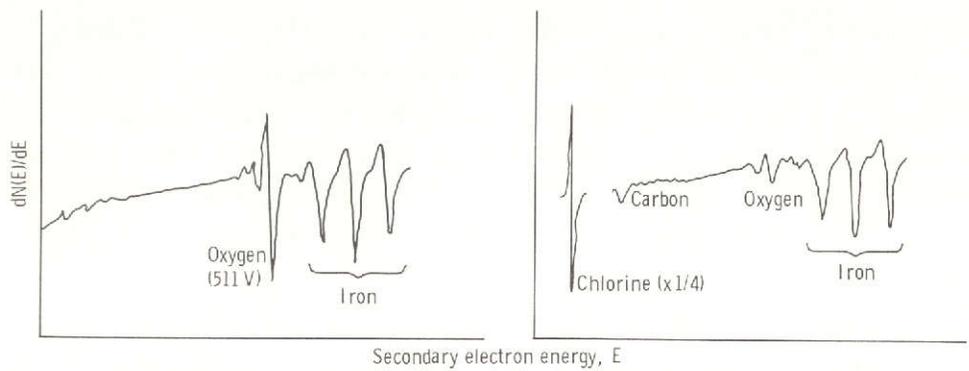
(a) With chemisorbed oxygen.

(b) After sliding poly(vinyl chloride) 200 revolutions on oxidized surface.

Figure 9. – Auger spectra of iron disk with chemisorbed oxygen and after sliding poly(vinyl chloride) 200 revolutions on oxidized surface.

plex has appeared. Since the high energy nickel peaks are still strong, it is evident that oxygen has been removed from the surface rather than simply buried in the transfer film.

The mechanism by which the oxygen is removed is suggested by a postmortem examination of the wear scar on the rider. Figure 10 is a photomicrograph of the rider that had been slid on an iron disk. Note the dark areas of the compacted polymer debris. Analysis of the wear scar in a scanning electron microscope with an energy-dispersive X-ray analyzer revealed that the dark areas contained iron, whereas the lighter areas
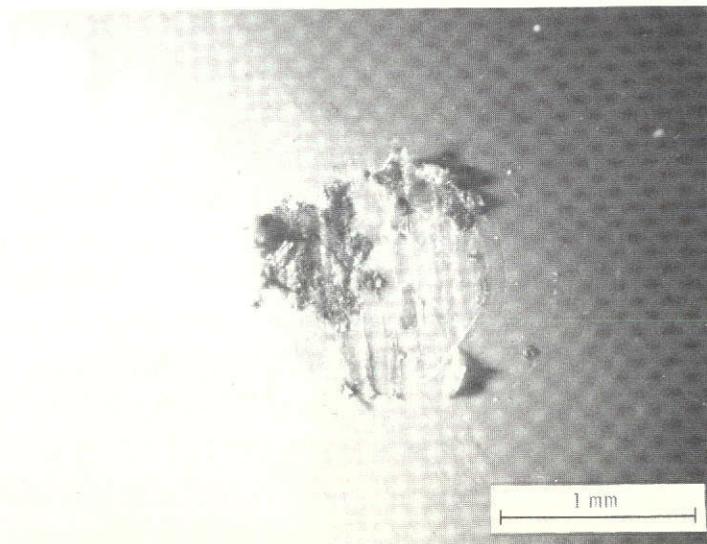

Figure 10. - Photomicrograph of wear scar of poly(vinyl chloride) rider after sliding on iron disk.

contained no iron. Apparently the rider removes a surface layer of metal from the disk and deposits it, along with polymer debris generated during sliding, toward the exit of the contact zone. The clean surface thus generated is simultaneously chlorinated by the rider.

After sliding, the disk also showed signs of damage due to sliding. A circular track was clearly visible in reflected light. Thus, plastic deformation of the metal by the plastic has occurred. However, the damage incurred by the disk is too slight to show up clearly on profilometer traces taken at a maximum sensitivity of 50 000 times.

DISCUSSION

Previous work on the sliding of polymers has taken place within the framework of the adhesion theory of friction (ref. 14). According to this point of view, solid bodies in contact adhere to each other through a variety of atomic forces. The forces responsible for adhesion of polymers to other solids are generally considered to be due to the van der Waals interaction. The points of contact of the solids are referred to as adhesive junctions. The force required to maintain tangential motion is then the force required to shear these adhesive junctions. Identification of the locus of shear has been one of the principle points of interest in the previous work. Shear may take place either at the interface or in one of the two sliding solids, depending on the relative shear strengths involved. Thus, Shooter and Tabor (ref. 2) have stated that a polymer sliding on a harder material will shear in the bulk of the polymer with fragments of the polymer deposited on the harder material. Later work by Pooley and Tabor (ref. 4) on PVC takes a different position and stated that shear occurs at the interface, with no deposition of polymer fragments on the counterface.
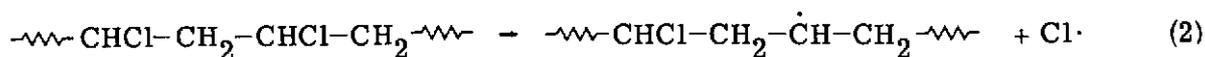
These earlier observations used optical and electron microscopy for determining whether the polymer was transferred. The observation reported here with the much more sensitive tool of AES are in firm agreement with Pooley and Tabor in that little or no polymer is transferred to the metal and shear appears to occur at the interface.

There is, however, certainly more to the situation than just a simple matter of shearing at the interface. Sliding effects both the rider and the disk. It was observed in early work with autoradiographic techniques (ref. 5) that fragments of metal were transferred to the polymer by sliding and static contact. Thus, in addition to the plastic deformation in the track there is some shearing taking place in the metal. This is in accord with the present observation of metal on the PVC wear scar in figure 10. This photomicrograph also shows evidence of wear of the polymer slider. Polymer wear fragments are not observed by AES and have either been compacted at the exit area of the wear scar or else have pushed out of the track altogether at the time of detachment.
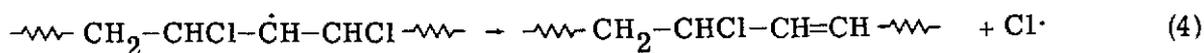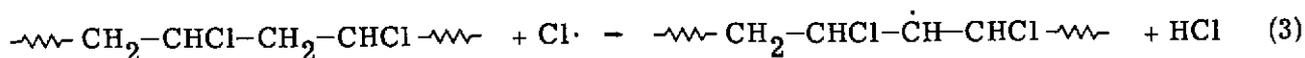
17

What appear to have been polymer fragments on the disk have occasionally been observed, but no positive identification was made. The source of this wear is not clear especially since sliding appears to occur at the interface. It may either arise by abrasion on the scratches remaining in the metal or else may be related to structural chemical changes in the polymer as it looses chlorine to the metal. Although these mechanical effects are interesting and warrant further study, the important effect observed here is the chlorination of the disk and this is now considered in some detail.

It is first necessary to review some relevant aspects of the behavior of PVC. This polymer, as are other polymers, is vulnerable to attack by various forms of energy. In fact, PVC is widely regarded as the least stable of all common polymers (ref. 15, p. 650) and requires stabilizers and plasticizers to improve its handling characteristics. Upon exposure to heat, light, or high energy radiation, PVC evolves hydrogen chloride and chlorine gas. Accompanying the evolution of gas is a change in the physical and chemical constitution of the polymer (ref. 15, p. 673 and ref. 16). A proposed mechanism for the thermal degradation reaction is found in equations (2) to (5) (ref. 15, p. 673).

Initiation:

$$-\text{\small ww-} CHCl-CH_2-CHCl-CH_2-\text{\small ww-} \rightarrow -\text{\small ww-} CHCl-CH_2-\overset{\cdot}{C}H-CH_2-\text{\small ww-} + Cl\cdot \tag{2}$$

Propagation:

$$-\text{\small ww-} CH_2-CHCl-CH_2-CHCl-\text{\small ww-} + Cl\cdot \rightarrow -\text{\small ww-} CH_2-CHCl-\overset{\cdot}{C}H-CHCl-\text{\small ww-} + HCl \tag{3}$$

$$-\text{\small ww-} CH_2-CHCl-\overset{\cdot}{C}H-CHCl-\text{\small ww-} \rightarrow -\text{\small ww-} CH_2-CHCl-CH=CH-\text{\small ww-} + Cl\cdot \tag{4}$$

Termination:

$$Cl\cdot + Cl\cdot \rightarrow Cl_2 \tag{5}$$

The reaction proceeds by a free radical mechanism. Thermal or radiation initiation involves loss of a chlorine atom adjacent to some structural abnormality which reduces the stability of the C-Cl bond. The chlorine radical so formed abstracts a hydrogen to form HCl; the resulting chain radical then reacts to form chain unsaturation with regeneration of a chlorine radical. Termination involves the recombination of two chlorine radicals to form Cl_2. Thus, the products of the degradation reactions are HCl, Cl_2, and $\overset{\cdot}{C}l$.

Interesting enough, degradation of the chemical and physical constitution of polymers can also be initiated by mechanical action (ref. 15, p. 676 and ref. 17). The process involves shaking, beating, high-speed stirring, or turbulent flow. For example, shear in-

18

duced degradation of polymeric additives reduces the viscosity of lubricant oils (ref. 17).
Mechanical methods are also used to affect a reduction in the molecular weight of scrap
rubber in order to reduce its viscosity and make it more amenable to further processing.

The reactions of polymers to mechanical action have not been as widely studied as the
reactions to other forms of energy and no specific information has been found for PVC.
It is generally accepted, however, that the primary process in all polymers is chain
scission into radicals (ref. 15, p. 676).

These considerations provide the framework within which the present experimental
results are interpreted. The mechanical stresses generated in the polymer at the sliding
interface either produce chain scission or activate a labile structural abnormality and
initiates the radical mechanism of degradation indicated by equations (2) to (5). The deg-
radation products of HCl, Cl_2, or $\dot{C}l$ evolved at the interface chemisorb directly onto
the clean metal surface, thus accounting for the observed chlorination of the disk in the
track. Since hydrogen is not detectable by AES, it is not possible at present to tell
whether HCl or one of the other forms of chlorine has chemisorbed. Note that the chlo-
rination can proceed on a surface that is not initially clean since it has been demonstrated
previously that clean metal can be generated by sliding contact with the polymer.

The surfaces were chlorinated by the polymers used here in spite of the fact that they
were stabilized against evolution of HCl. However, the stabilizers only inhibit the bulk
evolution of HCl. At the sliding interface the polymer is in intimate contact with the
metal so that the stabilizer does not have an opportunity to absorb or react with the rad-
ical or other forms of chlorine before they reach the metal.

Although a stress-induced mechanism has been cited here as the initiator of the deg-
radation process, the possibility of thermally induced initiation must be considered. It
is true that the current theory of flash temperatures at a sliding interface give a neg-
ligible temperature rise at low speeds (0.1 cm/sec) at which the chlorination occurs.
However, the theory is also generally regarded as rather tentative since little exper-
imental information is available as to the actual flash temperatures generated. In addi-
tion, the theory is macroscopic in nature in that only bulk material properties are con-
sidered, whereas we are confronted here with an atomic phenomenon. It may be that on
the molecular level there is sufficient temperature rise at low velocities to give rise to
thermal initiation. At this point it is not possible to distinguish between a purely mech-
anical process and a thermomechanical process.

The effect of using metals other than those used here can now be considered. In the
first place, since the surface contaminants can be removed by sliding contact with the
polymer, complete surface cleanliness is not important. In addition, the degradation
products of PVC are all active gases that chemisorb on all clean metals so that the chlo-
rination should be independent of the particular metal used. The hardness of the metals,
however, is expected to be an important parameter. Harder metals should act like those
used here except for a greater resistance to abrasion by the rider. Softer metals such

19

as gold or aluminum, however, are more susceptible to plowing and machining by the abraded metal fragments that lodge in the rider. Such behavior has been observed when PTFE slides on aluminum (ref. 7). The gross disruption of both polymer and metal resulted in erratic transfer and removal of PTFE. This erratic behavior would also be expected for PVC sliding on soft metals. Such systems are even less well defined than those considered here and not well suited to study the basic polymer-metal interaction.

The observations presented here, together with those made on PTFE (ref. 7), form the basis of some generalizations regarding the analysis of the polymer-metal sliding interface by AES. Consider the case in which shear or chain slippage takes place primarily in the polymer and polymer is transferred to the metal surface. Such a case is PTFE. The Auger analysis of the surface will produce a spectrum characteristic of the polymer. Whatever degradation products that may be generated by the shearing or slippage will probably not chemisorb to the surface since it will have been passivated by the transferred polymer. If they are present on the surface, their Auger spectrum will be masked by the spectrum of the polymer. On the other hand, if shear occurs primarily at the interface, such as with PVC, then one can expect the typical degradation products to chemisorb on the metal and be present in the Auger spectrum of the surface.

SUMMARY OF RESULTS

Poly(vinyl chloride) was slid on atomically clean and oxidized iron, nickel, and S-Monel in ultrahigh vacuum. Auger Electron Spectroscopy was used to monitor the elemental composition of the metal surface during sliding. The Auger spectrum of both chemisorbed vinyl chloride gas and poly(vinyl chloride) deposited from solution were used to aid in the identification of the species generated by sliding contact of the polymer on the metal. Based on the experimental results, the following conclusions are drawn:

1. Vinyl chloride adsorbed on a clean metal surface exhibits a chlorine to carbon Auger peak height ratio ~2.2. The chlorine undergoes electron-induced desorption with a desorption cross section $\sigma = 9 \times 10^{-20}$ square centimeter. Poly(vinyl chloride) on a metal surface exhibits high rates of electron-induced desorption with $\sigma = 6 \times 10^{-16}$ square centimeter.

2. Poly(vinyl chloride) sliding on metals appears to shear at the interface. Little or no polymer is transferred to the metal surface.

3. Chemisorbed chlorine is the major chemical species that appears within the wear track on the surface. The surface appears to be progressively chlorinated with continued sliding. The thickness of the chlorine film is the order of an atomic layer. Electron-induced desorption studies of the chlorine indicate that $\sigma = 5 \times 10^{-20}$ square centimeter so that the chlorine appears to be chemically bonded to the metal surface.

4. The chlorinated surface is passivated against chemisorption of oxygen.

5. There is some removal of metal by the poly(vinyl chloride). A contaminated surface can be worn by the sliding polymer to expose clean metal, which is then chlorinated.

6. The chlorination of the surface is taken as evidence of thermally or mechanically induced degradation of the poly(vinyl chloride) at the interface, with evolution of HCl and Cl_2.

Lewis Research Center,
    National Aeronautics and Space Administration,
        Cleveland, Ohio, August 31, 1973,
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