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# EFFECT OF VACUUM ON MATERIALS

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ORGANISATION EUROPÉENNE DE RECHERCHES SPATIALES  
EUROPEAN SPACE RESEARCH ORGANISATION

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## EFFECTS OF VACUUM ON MATERIALS

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**ABSTRACT.** The selection of materials for use in space environments requires knowledge of these unusual parameters and of the effects they have on materials. Most of all the parameters of the space environment are the same as those of terrestrial environments, except that the former are generally more severe. However, in space a new condition is imposed — vacuum. The degradative effects of this alien condition on metals, alloys, lubricants, ceramics, coatings, thin films, and polymeric systems are discussed. In some instances, a vacuum environment can be extremely beneficial to systems so that a component can be designed to take advantage of the environment. Methods of prevention of premature failure in a space environment as well as proper testing are also presented.

### 1. BASIC INTRODUCTION TO EVAPORATING PROCESSES

#### 1.1 PRESSURE AND MEAN-FREE-PATH

The principal environments that affect the behavior of materials in a space environment are those of particulate radiation, ultra-violet (UV) radiation, micrometeorites and high vacuum. Although I shall discuss only the singular effects of vacuum on materials, it should be immediately noted that the simultaneous occurrence of additional conditions, *i.e.* synergetic effects, can and indeed do hasten any degradative mechanisms. For example, radiation can accelerate evaporation into vacuum, and the mechanisms and effects of radiation damages to materials in vacuum are often different from the effects in air.

The central parameter in a space environment is a high vacuum of infinite pumping capacity with pressure as low as  $10^{-12}$  to  $10^{-16}$  mm Hg or lower. Figure 1 depicts the manner in which pressure at the earth's surface, about 760 mm Hg, decreases with increasing alti-

tude. To refresh your memory as to what this means - the 760 mm Hg pressure refers to the fact that, at sea level, a column of mercury will be supported by this pressure and that the column of mercury will be 760 mm high. At about 100 miles of altitude, the mercury column is  $10^{-5}$  mm high, at 500 miles the column is  $10^{-9}$  mm in height, and so on.

Now what are the implications of these dramatic decreases in pressure? Well for one thing, a material having a certain volatility on the surface of the earth continually ejects molecules which are driven or rather bounced back to the surface of material from whence it originated. Indeed, unless acted upon by an outside agency, e.g. heat, light, chemical energy, etc., the surface of the material will be in equilibrium such that the number of molecules which leave the surface will equal those that return. Needless to say, as the pressure surrounding the material is decreased, the probability of collisions between the gaseous molecules, constituting the ambient pressure, and the ejected "materials" molecules becomes increasingly improbable. Hence, those molecules that leave the surface will travel farther before colliding and returning. In a very high vacuum, there are so few gaseous molecules that the ejected molecules will not return at all.

The distance traveled by molecules before colliding with another molecule is known as the mean-free-path and its relation to pressure is:

$$\text{Mean-free-path} = \frac{KT}{\pi Pd^2} \dots\dots\dots(1)$$

- K = Boltzmann constant
- T = Absolute temperature, °K
- P = Pressure, mm Hg
- d = Diameter of the molecule

Therefore, for a given material or molecular species, the mean-free-path increases in an inversely proportional manner to the pressure and directly proportional to the temperature. Thus, the mean-free-path of air at sea level is about  $5 \times 10^4$  meters, but at 125 miles of altitude where the pressure is  $10^{-6}$  mm Hg the distance is about 50 meters and at  $10^{-10}$  mm Hg (750 miles altitude) the mean-free-path is  $5 \times 10^5$  meters. Hence, we now have the circumstance that, for all practical purposes, molecules leaving a surface do not return and the material sublimates, i.e. goes from the solid to the vapor phase directly (by omitting or by-passing the liquid stage) at a rate dependent upon its vapor pressure.



Now, to summarize this very brief introduction, it can be stated that the extreme vacuum of space causes subtle changes in material behavior due to the removal of layers of surface gases and a more gross effect due to the loss of material by sublimation or evaporation.

## 1.2 SURFACE PHYSICS

Solid-state physicists have classified three types of surfaces, (1) technical, (2) clean, and (3) pure. In general, it is the technical surface that engineers use, and it is of unknown purity in that it contains oxides, absorbed and adsorbed gases, etc. Electron diffraction patterns even of very highly polished, "clean", specular surfaces will show patterns for oxides, oil films, etc.

In actual practice, many phenomena, although thought of as a bulk or a solid-state property, are really functions of the nature of the surface. Perhaps one of the most common phenomena alluded to is that of metallic fatigue. As is well known, this type of failure most frequently originates at the surface. Wadsworth<sup>1</sup> concluded that the fatigue life of metals is increased as the pressure is reduced – his observations being made at a minimum pressure of  $10^{-5}$  mm Hg. It should be pointed out, however, that pressure, *per se*, is *not* the active parameter, but rather that the increased life is a function of the degree of the exclusion of oxygen and water vapor. For example, work performed by Frankel, Bennett, and Holshouser<sup>2</sup> demonstrated that a polar film also having the additional ability to intertwine its upright molecular branches acts as an effective barrier to the migration of those ever-present, terrestrial, corrosive, gaseous molecules and results in a greatly extended fatigue life.

In essence, therefore, the problem is basically concerned with the nature of the vacuum itself and the rapidity with which oxide layers can re-form. It is readily shown from kinetic-theory considerations that the number of molecules of a pure material leaving a unit area of surface per second,  $q$ , is given by

$$q = P(A/2 \pi MKT)^{1/2} \dots\dots\dots (2)$$

- |                        |                          |
|------------------------|--------------------------|
| P = Vapor pressure     |                          |
| A = Avogadro's number  | M = Molecular weight     |
| K = Boltzmann constant | T = Absolute temperature |

This equation can then be converted to the more practical expression:

$$G = 5.04 \times 10^3 P(M/T)^{1/2} \dots\dots\dots (3)$$

G = Grams of material evaporated per square  
centimeter per day

P = Vapor pressure of the evaporating spe-  
cies in mm Hg

T = Absolute temperature, °K

It is assumed, in this expression, that every molecule leaves the surface without colliding with other gas molecules; in other words, it assumes the surrounding pressure equals zero mm Hg. In actual practice, however, this ambient pressure may be as high as  $10^{-4}$  to  $10^{-5}$  mm Hg because of the heterogeneous or unequal distributions of molecular kinetic energies. It is apparent, then, that the rate of loss, G, at a specific temperature is proportional to the product  $P(M)^{1/2}$ ; in other words, as long as the surrounding pressure is  $10^{-4}$  to  $10^{-5}$  mm Hg, corresponding to a reasonably long mean-free-path, only the vapor pressure and the molecular weight of the specimen control the loss rate at a specific temperature.

Before we consider the behavior of actual materials in vacuum, it is best to make mention of the assumptions used in the derivation and the practical aspects of using Equation 3 indiscriminately:

- (1) Pressure, P, is ordinarily measured under equilibrium conditions with all that this attains to in practical situations, *i.e.* equilibrium conditions are virtually impossible to obtain.
- (2) No account is taken of internal or self-diffusion within the sample.
- (3) Oxide films or similar films present on the surface act as diffusion barriers and effectively limit evaporation rates.
- (4) Most materials of interest, especially metal alloy systems, have characteristics that defy analytic treatment, for example, Henry's and Raoult's laws are found to give but poor agreement in comparison with experimental data.

It should be pointed out that another criterion for vacuum stability is found in Trouton's rule:

$$\Delta H_{\text{vap}} = \frac{C_T}{T_m} \dots\dots\dots (4)$$

- $\Delta H_{\text{vap}}$  = Heat of evaporation, cal/gm-mol
- $T_m$  = Melting point, °K at 760 mm Hg
- $C_T$  = Constant, usually very close to 21 cal/gm-mol-°K

All this empirical equation simply states is that the most stable material is probably the one with highest melting point.

## 2. INORGANICS

### 2.1 HETEROGENEOUS ENERGIES

Let us now turn our attention to the effects of a vacuum environment on inorganics.

Figure 2 relates the vapor pressure of a metal to a specific temperature. What this shows is that, for example, at 2800°C, tungsten or wolfram requires a pressure of 10<sup>-5</sup> mm Hg to vaporize. Any temperature below this will not cause any sublimating effects. Needless to say, we are not generally concerned with these very high melting point metals, except as filaments in incandescent lights, spectrometers, etc., or until we enter the field of power-propulsion elements. However, if we now enlarge and replot the left side of the curves, Figure 3, we see that cadmium and zinc are affected at temperatures only slightly above the ambient on the surface of the earth. It is now apparent as to why corrosion proofing by means of cadmium plating is not a very sound practice for spacecraft components. Magnesium can become troublesome at relatively elevated temperatures of about 200°C. These data assume a completely homogeneous and hence uniform sublimation from the surface and do not take into account the ameliorating effects of coatings, alloying agents, etc.

However, it is well known that, on an atomic scale, surfaces have wide energy distributions, ranging from very high for the disoriented grain boundaries to the very low of completely ordered lattices. Thus, we can have selective sublimation in certain discrete areas of the surface. For instance, sublimation is more rapid along those more closely packed crystal planes (at the solid-vacuum interface), than along the less energetic. This causes a microetching effect on the surface and thus we have a roughening of the surface, causing a degradation of optical quality surfaces and disturbing the thermal equilibrium of control surfaces.

A related effect is the accelerated sublimation taking place at the grain boundaries of alloys. Although this phenomenon may be somewhat superficial as a result of surface tension effects, reaching equilibrium status as depicted in Figure 4, the fact is that small surface notches are introduced, as shown in Figure 5. This obviously has implications on the crack initiation and propagation properties of the material. Indeed, comparative data indicate a remarkably dramatic decrease in static strength properties as follows:

TABLE 1  
EFFECT OF VACUUM AND HEAT ON MAGNESIUM

Finish	Exposure	Area (in <sup>2</sup> )	Ultimate Stress (psi)	0.2% Yield Stress (psi)	% Elongation 1-in Gage
Bare	None	0.0140	37 900	33 600	5.7
Bare	Heat aged	0.0145	38 200	34 400	13.0
Bare	Heat & Vacuum	0.0140	24 300	10 000	3.2

- 1) Heat aged at 232°C for 168 hours.
- 2) Heat and vacuum, held at 232°C and  $1 \times 10^{-7}$  mm Hg for 168 hours.

Needless to say, a dynamic or repeated loading situation would show an even greater decline in load carrying ability.

## 2.2 FRICTION, COLD WELDING AND LUBRICATION

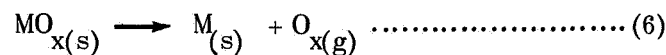
Frictional phenomena must be considered in high vacuum. Adsorbed surface films, such as oxides, are not formed as in the earth's atmosphere. Once these films are removed either by volatilization or as a result of frictional wear, an uncontaminated surface results. The contact then made by these clean surfaces, *i.e.* at localized asperities, result in extremely high stresses and high local temperatures, and thus can result in galling, seizing and/or cold welding. This tendency of clean metal surfaces to stick together is of considerable concern in the selection of materials for bearings, electrical contact relays, slip rings, and the like.

Inorganic compounds such as oxides can degrade by two mechanisms – simple sublimation or by decomposition to its elemental form. In general, the former process is relatively unimportant until appreciable temperatures are reached, but it is the latter mechanism that is of importance in contact problems. Using the basic Arrhenius rate equation:

$$K = S \exp(-\Delta H_a/RT) \dots\dots\dots(5)$$

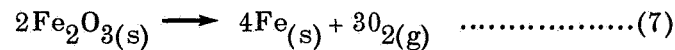
- K = a rate constant, molecules/cm<sup>3</sup>- sec
- S = frequency factor, molecules/cm<sup>3</sup>- sec
- $\Delta H_a$  = heat of activation, ergs/mole
- R = universal gas content, ergs/mole-<sup>o</sup>K
- T = absolute temperature, <sup>o</sup>K

and the basic chemical reduction equation:



- M = Metal
- O<sub>x</sub> = Oxide

or in the case of steel bearings:



we can then derive Figure 6, the amount of time required to re-form a monomolecular oxide layer as a function of pressure. Two conclusions can be obtained from this:

- 1) The re-formation of protective oxide barriers is exceedingly difficult in space.
- 2) The testing of bearings or investigations involving friction and wear are really quite difficult to perform in vacuum chambers to give meaningful scientific results. In addition to oxide removal, or highly energetic surface formation, materials in contact require some degree of miscibility in one another, *i.e.* two metals which obey Hume-Rothery's rules for at least partial solid solution formation, or alloying, are more likely to adhere or cold weld than systems that are totally immiscible. For example:

TABLE 2

<u>Adhesion</u>	<u>No Adhesion</u>
Fe-Al	Cu-Mo
Cu-Ag	Ag-Mo
Ni-Cu	Ag-Fe
Ni-Mo	Ag-Ni

Figure 7 dramatically illustrates the phenomenon of cold welding, wherein portions of the steel race have been literally torn out by the action of the miscible steel bearings. There is a bright side to this picture, however, This is shown in Figure 8, whereby solid-state welding can be made to occur as a result of this phenomenon. Thus, in future manned flights, small repairs can conceivably be made and the propagation of potentially catastrophic fatigue cracks minimized.

The question of lubrication, as you undoubtedly are aware, is a particularly difficult one in space. Conventional liquid lubricants evaporate, at some finite rate oxide coatings decompose or wear out, and of course, moisture or gases do not exist in significant quantity for lubrication. There has been considerable work done to develop new lubricants having low vapor pressures, such as di-ester oils and silicone oils. Certain solid lubricants, such as Teflon or MoS<sub>2</sub>, have been used quite successfully, in limited applications. In general, how-

ever, and because of the lack of solid, substantiating evidence, invariably almost any system being designed depends on some form of labyrinthic passage, *i.e.* make the mean-free-path very short and, thus, egress so tortuous as to prevent the molecules from escaping readily.

Appendix A lists the types of lubricants currently used in space applications, but it should be emphasized that this listing is general, necessarily so, because of the unknown nature and frequent changes to basic formulations, manufacturing techniques, etc., employed by the producer.

Another effect of vacuum on liquid lubricants is that of enhancing the creep of the of the lubricant along surfaces. This results from the action of the vacuum in stripping the terrestrial contaminants and thus increasing the surface energy of the metal. By imposing a barrier whose surface energy is lower than the oil, this creep phenomenon can be mitigated. This is schematically illustrated in Figure 9, wherein the energy equilibrium balance

$$E_{s1} + E_{1v} \cos \phi = E_{sv} \dots\dots\dots (8)$$

$E_{s1}$  = surface-liquid energy

$E_{1v}$  = liquid-vacuum energy

$E_{sv}$  = surface-vacuum energy

is disturbed by surface oxide removal, causing  $\phi$  to decrease. Thus as  $\phi \longrightarrow 0$ , the liquid lubricant spreads or creeps out along the shaft.

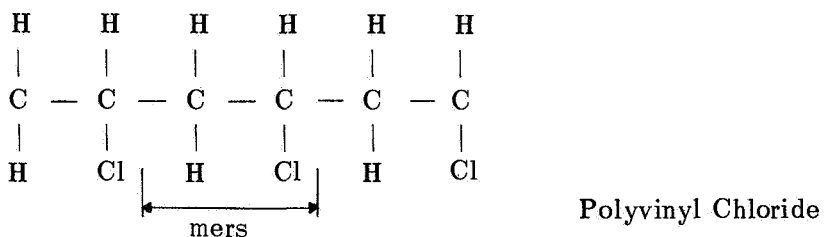
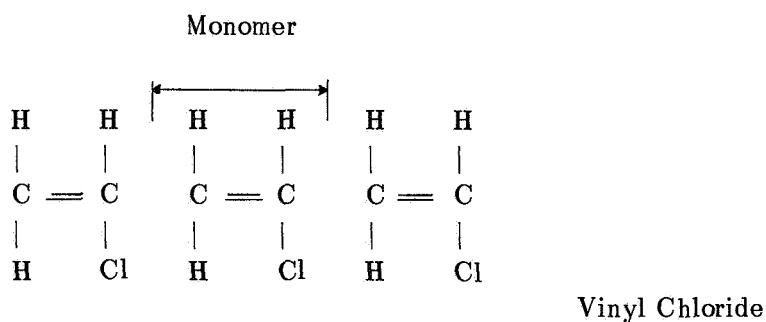
To summarize this portion of the discussion:

- 1) Inorganics are not generally susceptible to the effects of space vacuum, at moderate temperatures.
- 2) Inorganics are affected on a microscopic scale leading to the following conditions:
  - a) Surface roughening
  - b) Initiation of a stress raiser
- 3) Inorganic oxides, upon the application of an outside agency, *e.g.* fretting, vibration, heat, etc., can decompose or fragment exposing freshly formed, highly energetic surfaces. If two surfaces mate or come into intimate contact and there exists a propensity for solid solution alloy formation, the probability is reasonably high for "cold welding" to occur.

### 3. ORGANIC OR POLYMERIC MATERIALS

#### 3.1 OUTGASSING OR DISTILLATION

Plastics and elastomers are formed from the joining together of base monomers or mers thus:



However, during the process of polymerization, the basic monomers do not always stoichiometrically combine. Hence, we have a rather impure material, that is composed primarily of the polymer, but also includes many unreacted fragments. In fact, whenever the molecular weight of a polymer is precisely noted, especially in manufacturer's literature, it should be remembered that what is given represents the mean of a Gaussian distribution, and it is by no means as purported.

Figure 10 shows the actual experimentally determined distribution of molecular weights of a "pure" polymer having a "molecular weight" of 20 250. In addition, to these non-stoichiometric fragments, the material invariably contains mold lubricants, additives for fire retardation, anti-oxidants, plasticizers, etc.



Thus, the behavior of polymeric materials in vacuum cannot be described in any simple manner. However, in general, the manner of outgassing is depicted in Figure 11. As can be seen, the percent weight loss is not only a function of temperature, but also of time. Upon the imposition of a vacuum, the initial and immediate loss is generally attributed to the surface removal of normal atmospheric gases, e.g. water vapor, CO<sub>2</sub>, N<sub>2</sub>, etc., followed by the low molecular constituents normally associated with the totality of the polymer. Raising the temperature obviously increases the mobility of the molecular bonds and the weakest of these now fragment, causing outgassing or distillation. The admittance of a non-vacuum environment results in a weight gain by the addition of adherent molecules, and is not to be associated with the bulk of the material.

### 3.2 EFFECTS OF OUTGASSINGS

Until relatively recently, and very probably still, the majority of polymeric outgassing tests had been of this simple weight-loss relationship. Of greater engineering significance are those sublimates that recondense on cooler surfaces, as shown in Figure 12. Because of the nature of atmospheric gases, except, of course, in copious quantities, a most unlikely probability, these products can be dismissed as potential trouble-makers. It is, however, the unreacted mers, non-stoichiometric polymers, and the additives that can cause failure. This occurs because of the following possibilities:

- 1) Recondense on optical surface and thereby causing a loss of specific wavelength transmission.
- 2) Recondense on thermal control surfaces and thus upset the temperature equilibrium.
- 3) Recondense between contact relays thus causing an electrical open.
- 4) As these types of molecules are readily ionized they are major contributors to corona and arcing phenomena.

Some of these types of behavior are graphically depicted in Figures 13-15. Although the weight loss, *per se*, perhaps could render the material unsuitable for flight, it is really the vacuum condensible material (VCM) that is of concern.

As far as is known, there are only two pieces of apparatus, in the western world, capable of making such measurements, one at the Stanford Research Institute, Menlo Park, California, and the other at the Goddard Space Flight Center, Greenbelt, Maryland. Thus, we obtain not only quantitative measurements of weight loss, but also quantitative analyses of the maximum amount of volatile condensible materials at 25°C and the nature of the sublimate. Figures 16-17 show the internal or working portion of the apparatus.

In view of the preceding, it has been proposed, for a material to be considered for flight use, that the maximum weight loss be < 1% and that the maximum VCM content be < 0.1%. These restrictions can best be illustrated by the example that a pound of a polymer releasing 0.1% at 125°C of condensibles may deposit on a square foot of surface at 25°C a film of about 0.0015 inch in thickness, more than adequate to render optical, thermal or electrical equipment useless. It is true, that many condensed films eventually evaporate, but it is equally true that some will remain in place because of physico-chemical surface reactions or because additional polymerization occurs, as a result of ultraviolet or other radiative energy.

It is natural to conjecture that a polymer's "space vacuum" behavior can be improved by post-curing in vacuum at an elevated temperature. This process frequently does not work because the amount of evaporation of the lower molecular weight constituents is not influenced very much by temperature, although the rate is. However, any post-curing can be deleterious to the prime polymer matrix by causing the more energetic portions (or bonds) to be disrupted and hence, outgas much more rapidly, as shown in Figure 18. Another aspect that must be considered is the possible degradation of mechanical properties. It has been experimentally determined that, although stresses to rupture are increased, in some instances the strains, which are really the ability to prevent catastrophic rupture, are markedly decreased, as shown in Figure 19. This clearly demonstrates the need to spend time and effort to produce and use clean polymeric materials rather than an attempt to "fix" or rectify poor materials.

### 3.3 CORONA AND OTHER IONIZATION PHENOMENA

A problem of major importance is that of corona. Indeed, many spacecraft missions have been compromised or turned out to be magnificent failures as a result of this phenomenon. Occasional corona or spark discharges often do not permanently damage the high-voltage equipment itself, but may result in serious interference with the operation of other equipment

in the spacecraft. Spurious pulses causing random stepping of commutators in encoding circuits, low-power transistors in data-processing circuits being "burned out" by high-voltage "spikes" on low-voltage power distribution lines are examples of the effects of ionization phenomena.

When a gas is not ionized, the individual molecules are electrically neutral. Indeed, the gas is a perfect insulator and no current flows when the gas is subjected to an electric field. However, if the molecules are subjected to a highly energizing field, some electrons will be ejected from the atom and lead a brief independent existence before recombining with another molecule or being removed by encountering a conducting electrode. Thus, what we have, in effect, is a gaseous conduction path. If current carriers are being generated more rapidly than they are absorbed, the gas becomes a fine conductor. It should be noted that ionization is most likely to occur to those weakly bound molecules that outgas first. Figure 20 illustrates the potential necessary to cause ionization as a function of  $pd$ , *i.e.* pressure of gas times distance between electrodes. It should be noted that these curves are only illustrative, because electrode materials and surfaces are also of importance.

If spacecraft equipment involving d.c. voltages of a few hundred volts is to operate in areas which are poorly vented, *i.e.* the mean-free-path is small, it becomes most desirable to encase all conductors that are at high potential by adequate solid insulation. If the applied voltages are alternating, as in the case of a high-voltage converter, there will be at least two discharges per cycle, and the condition is aggravated. It is therefore very important to minimize, if not entirely eliminate, voids in the insulation, and particularly at the interface between conductors and insulation. Vacuum deaeration of potting compounds is necessary to remove air bubbles.

Summarizing the effects of vacuum (thermal) on organics, it can be stated:

- 1) The rate of evaporation of a pure substance in a vacuum is a function of the temperature, its molecular weight, and its vapor pressure. Its rate of removal is nearly entirely controlled by the rate at which the molecules can diffuse through the polymer matrix to the surface.
- 2) All polymers consist of distributions of various molecular weights. Therefore, all polymers tend to lose some of the lower-molecular weight species.
- 3) Most commercial polymers are mixtures of basic polymeric materials and various additives, such as solvents, catalysts, anti-oxidants, manufacturing

aids, etc. These materials usually distill out of the base polymer mixture to form significant portions of the weight loss and the remaining polymer frequently will have properties significantly different than the "advertised product".

- 4) Polymers which are highly cross-linked, in general, have such high molecular weights that they are relatively immune to outgassing.
- 5) Linear polymer distillation can be directly correlated with the molecular bonding energies. Thus, the C-F bond having the strongest bond has become one of the most useful of commercially available plastics, *i.e.* the Teflons.
- 6) Appendix B is a list of the more commonly used polymeric formulations for spacecraft applications.

#### 4. SUMMARIZATION

- 1) When a material is exposed to high vacuum, there are two effects which require primary consideration: (i) the enhancement of sublimation and evaporation processes; and (ii) the removal of physically adsorbed layers of gas from the surface of the material. Although less significant, the subsidiary effects on transport phenomena below the surface must also be considered. The addition of thermal factors (*i.e.* thermal cycling between 0 and 100°C, for example) further increases the effects of space (vacuum) environments on any material, especially organic materials such as the polymers and plastics.
  - a) The release of sorbed gases and vapors can contribute to the degradation of materials in at least two general ways. First, desorption can directly affect the optical properties of material by concentration changes or formation of color centers. Secondly, the movement (diffusion) of gases through the material may produce structural faults, such as cracks and pores, or it may disrupt the bonding between the surface material and the substrate. It also has been observ-

ed that chemical activity is accelerated in vacuum. This is understandable, considering that a protective surface film is not present to inhibit oxidation. In addition, molecular oxygen is readily dissociated by the ultraviolet of space into atomic oxygen and, of course, atomic oxygen is considerably more reactive than the molecular variety.

- b) The actual process of evaporation is fundamentally a true surface phenomenon, even though its rate may be controlled by other factors. As evaporation from localized planes of high surface energy tends to be greater than that from points of lower surface energy, microscopic etching of the surface occurs. This can be most detrimental in the case of thin metallic films, however, because of the self-balancing of surface-tension forces and grain-boundary energies the problem is not particularly severe in bulk materials, but can cause stress concentrator problems and subsequent crack initiation.
- 2) The loss of material in a high vacuum can then be the cause of important mechanical, thermal, and chemical changes in the materials. The full extent of these changes in properties must be related not only to the rate at which material is lost to the surroundings, but also to the nature of the process or processes by which the loss occurs. If losses occur only at the surface and only to the surface material (*i.e.* if the losses do not set-up the long-term migration effects within the bulk material) then the effects may not be severely damaging.
  - 3) In the case of most metals, sublimation losses will be negligible. However, the removal of surface layers of gas, especially oxygen, may prove to be very beneficial to the mechanical properties of the metal in some instances. In some instances where oxide films can move into incipient cracks and thus promote crack growth, it may be expected that the lack of oxygen on the surface may reduce the potential for crack growth and therefore result in greater fatigue life. Other effects such as changes in surface energy and internal diffusion in the vicinity of a stress riser may become significant at extremely low pressures.

- 4) The possible beneficial effects on strength associated with the removal of the surface-adsorbed gas layer may be offset, however, by the loss of chemical protection provided by the gas layer. This gas layer, for example, may essentially shield the metal from the gases emitted from a propellant during burning or during the volatilization period. Thus any halogen containing propellant may emit halogens which, upon striking the metal surface, may readily combine with the "clean" metal surface, and thus promote corrosion effects. This possible reaction between the clean metal surface and gas released from the propellants justifies the concurrent exposure testing of several components.
- 5) The most significant conclusion that can be deduced from extensive testing of a variety of organic systems is that degradation occurs in an unpredictable manner. Therefore, each candidate formulation and method of preparation must be evaluated, as small changes may drastically affect the stability. As a rule of thumb, however, it should be remembered: (i) that pure polymers are less prone to degradation than impure or mixed formulations; and (ii) that the type of bonding is of prime importance in the determination of stability. This latter point is illustrated in Figure 21, whereby the C-F bond is the strongest and the basic quadriorthogonal C bond the weakest. Thus, polymers whose structure is based on the C-F bond, such as the Teflons, are indeed the most stable of the commercially available plastics.
- 6) In drawing general conclusions based upon experimental observations, the ranking of materials is once again of the same approximate order found in other related areas of investigations. Comparisons of melting points and thermal decomposition temperatures establishes the following order of decreasing stability:
  - a) Ceramic and refractory materials
  - b) Metals
  - c) Non-refractory inorganic materials
  - d) Organic materials.

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## APPENDIX A

### ADVANTAGES AND DISADVANTAGES OF SOME DIFFERENT TYPES OF LUBRICATION AND SELF-LUBRICATING MATERIALS FOR SPACE

#### ADVANTAGES

#### DISADVANTAGES

##### Oils and Greases

Provision of minimum torque and requirement of minimum power

Availability

Evaporation

Creepage through seals

Radiation damage

##### Thin Films of Soft Metals Such as Silver and Gold

Low evaporation ranges

Excellent radiation stability

Renewability by periodic re-evaporation (though this presents other problems)

Electrical conductivity (important for some applications)

Requirement of special processing techniques for applying with good adherence to substrate

##### Bonded Films of Molybdenum Disulfide ( $MoS_2$ )

Low evaporation ranges

Ability to bond with inorganic binders, such as sodium silicate, that have excellent radiation stability

Difficulty of obtaining good adherence for ball bearings

Eventual wear-through

##### Teflon (Polytetrafluoroethylene)

Low coefficient of friction – lowest of any solid

Lack of tendency to cold weld to metal

With fillers, improved wear life and reduced problems of cold flow, heat conduction, and radiation damage

Very poor radiation stability

Release of hydrogen fluoride gas as a decomposition product when irradiated in vacuum



Nylon

Hardness – harder than Teflon

Poor radiation stability

Availability, in crystallized and sintered form, with better dimensional stability than molded nylon

Higher coefficient of friction than Teflon

Lower friction and improved wear life, when filled with molybdenum disulfide

Porous Compacts Impregnated with MoS<sub>2</sub>, Silver or Teflon

Good friction and wear characteristics

Limitation, generally, to sleeve bearings; not available on ball bearings

Provision, by impregnation, of a larger reservoir for lubricants than thin films

Frequent low strength, and non-suitability for gears and other applications other than sleeve bearings

Availability of wide variety of materials

Sapphire, Pyroceram, and Other Hard, Dissimilar Materials

Probability of minimum tendency to cold weld to mating surfaces of metal

Brittleness; may require shock loading to avoid shattering during launching and ascent

Possibility of high wear rates at high speeds

## APPENDIX B

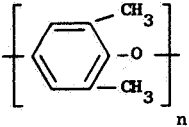
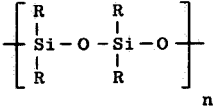
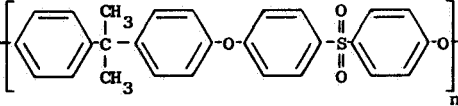
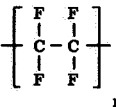
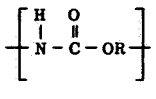
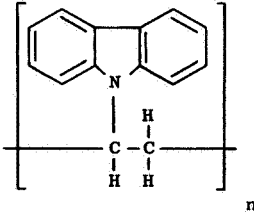
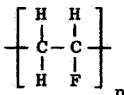
### CANDIDATE POLYMERIC MATERIALS FOR SPACECRAFT APPLICATIONS

Name	Typical Structure	Spacecraft Applications
Acetal	$\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\left[ \begin{array}{c} \text{H} \\   \\ \text{C}-\text{O} \\   \\ \text{H} \end{array} \right]_n-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$	Hardware and Structural Wire enamels
Acrylic	$\left[ \begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array} - \begin{array}{c} \text{R} \\   \\ \text{C} \\   \\ \text{C} \\ / \quad \backslash \\ \text{O} \quad \text{OCH}_3 \end{array} \right]_n$	Seals and gaskets Sleeving
Alkyd	$\left[ \begin{array}{c} \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\ \parallel \quad \parallel \quad   \quad   \quad   \\ \text{C} \quad \text{C} \quad \text{O}-\text{C} \quad \text{C} \quad \text{C} \quad \text{O} \\   \quad   \quad   \quad   \quad   \\ \text{C}_6\text{H}_4 \quad \text{H} \quad \text{OH} \quad \text{H} \end{array} \right]_n$	Protective coatings Thermal coatings
Alkyene glycol	$\text{HO} \left[ \begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array} \right]_x \text{O} \left[ \begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array} \right]_n \text{H}$	Lubricants
Amide	$\left[ \begin{array}{c} \text{H} \\   \\ \text{N} \\   \\ \text{H} \end{array} - \left( \begin{array}{c} \text{H} \\   \\ \text{C} \\   \\ \text{H} \end{array} \right)_5 - \overset{\text{O}}{\parallel}{\text{C}}-\text{O} \right]_n$	Coated fabrics Films and sheets Hardware and structural Tie cord/lacing tape
Butyl	$\left[ \begin{array}{c} \text{CH}_3 \quad \text{H} \quad \text{H} \quad \text{CH}_3 \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad   \quad   \quad   \\ \text{C} \quad \text{C} \quad \text{C} \quad \text{C} = \text{C} \quad \text{C} \\   \quad   \quad   \quad   \quad   \\ \text{CH}_3 \quad \text{H} \quad \text{H} \quad \quad \quad \text{H} \end{array} \right]_n$	Seals and gaskets
Carbonate	$\left[ \text{O}-\text{C}_6\text{H}_4-\overset{\text{CH}_3}{\underset{\text{CH}_3}{\text{C}}}-\text{C}_6\text{H}_4-\text{O}-\overset{\text{O}}{\parallel}{\text{C}} \right]_n$	Hardware and structural
Diallylphthalate	$\left[ \begin{array}{c} \text{H} \quad \text{H} \quad \text{H} \quad \text{O} \quad \text{O} \quad \text{H} \quad \text{H} \quad \text{H} \\   \quad   \quad   \quad \parallel \quad \parallel \quad   \quad   \quad   \\ \text{C} \quad \text{C} \quad \text{C} \quad \text{O}-\text{C} \quad \text{C}_6\text{H}_4 \quad \text{C} \quad \text{O}-\text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\   \quad   \quad   \quad \quad \quad \quad \quad   \quad   \quad   \\ \text{H} \quad \text{H} \quad \text{H} \quad \quad \quad \quad \quad \text{H} \quad \text{H} \quad \text{H} \end{array} \right]_n$	Hardware and structural

APPENDIX B (cont.)

Name	Typical Structure	Spacecraft Applications
Epoxy		<p>Adhesives Circuit boards Foams Hardware and structural Protective coatings Sealants Tapes</p>
Ester		<p>Adhesives Coated fabrics Films and sheets Honeycomb structures Protective coatings Tapes Tie cords/lacing tape</p>
Ethylene		<p>Hardware and structural Sealants</p>
Fluroethylene-propylene co-polymer		<p>Seals and gaskets</p>
Imide		<p>Films and sheets Hardware and structural Protective coatings Wire enamels</p>
Olefin		<p>Shrinkable materials</p>
Phenolic		<p>Hardware and structural Honeycomb structures Lubricant binders</p>

APPENDIX B (cont.)

Name	Typical Structure	Spacecraft Applications
Phenylene oxide		Hardware and structural
Silicone		Adhesives Coated fabrics Foams Hardware and structural Honeycomb structures Lubricants Protective coatings Sealants Seals and gaskets Sleeving Tapes Tie Cord/lacing tape
Sulfone		Hardware and structural
Tetrafluoroethylene		Coated fabrics Hardware and structural Seals and gaskets Shrinkable materials
Urethane		Foams Protective coatings Sealants Thermal coatings
Vinyl carbazole		Hardware and structural Circuit board
Vinyl fluoride		Films and sheets

APPENDIX B (cont.)

Name	Typical Structure	Spacecraft Applications
Vinylidene fluoride	$\left[ \begin{array}{cc} \text{F} & \text{H} \\   &   \\ -\text{C} & -\text{C}- \\   &   \\ \text{F} & \text{H} \end{array} \right]_n$	Films and sheets
Vinylidene fluoride-hexafluoropropylene co-polymer	$\left[ \begin{array}{cccc} \text{H} & \text{F} & \text{CF}_3 & \text{F} \\   &   &   &   \\ -\text{C} & -\text{C} & -\text{C} & -\text{C}- \\   &   &   &   \\ \text{H} & \text{F} & \text{F} & \text{F} \end{array} \right]_n$	Seals and gaskets
p-Xylylene	$\left[ \begin{array}{ccc} \text{H} & \text{C}_6\text{H}_4 & \text{H} \\   & &   \\ -\text{C} & & -\text{C}- \\   & &   \\ \text{H} & & \text{H} \end{array} \right]_n$	Films and sheets

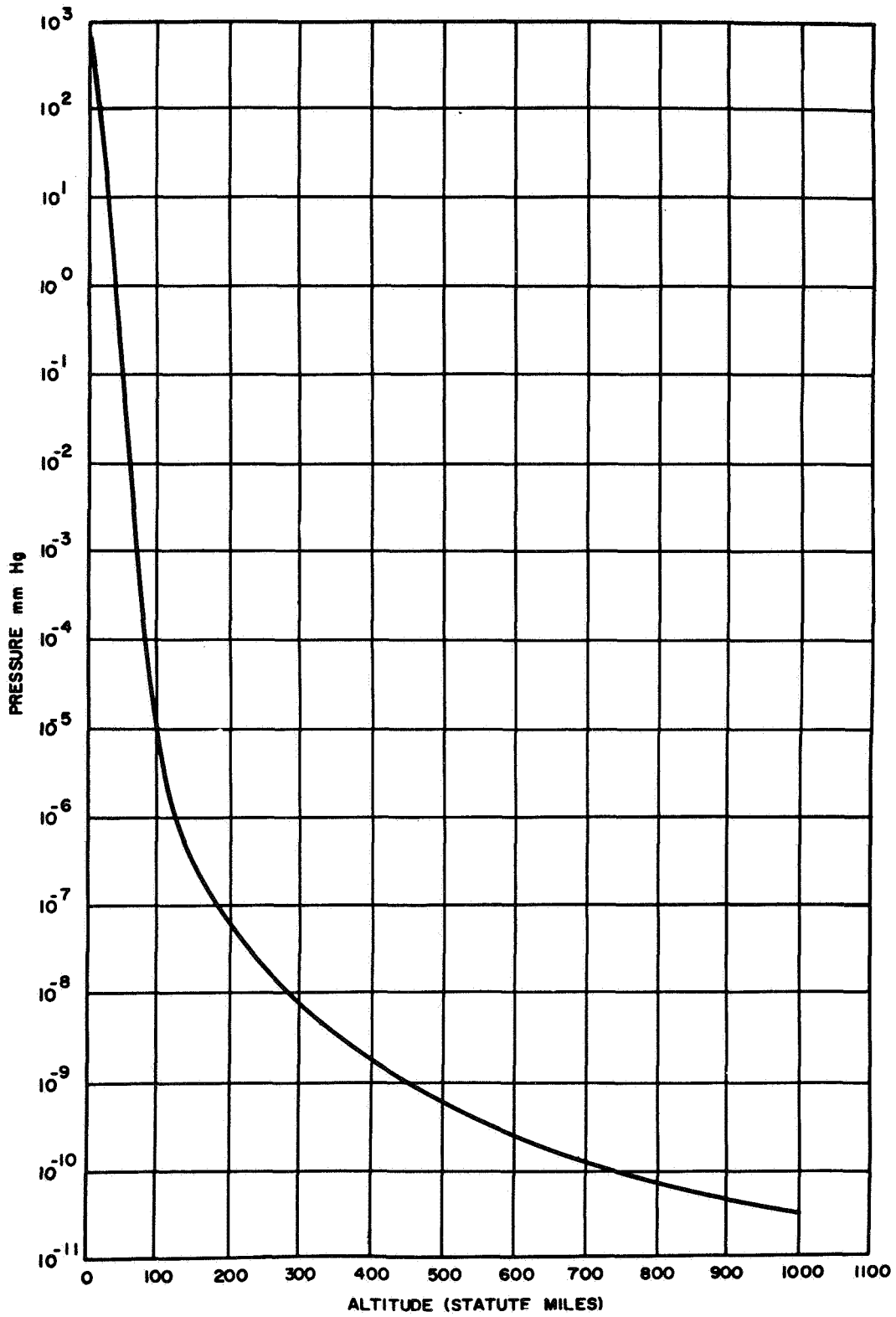


Figure 1. Pressure as a function of altitude.

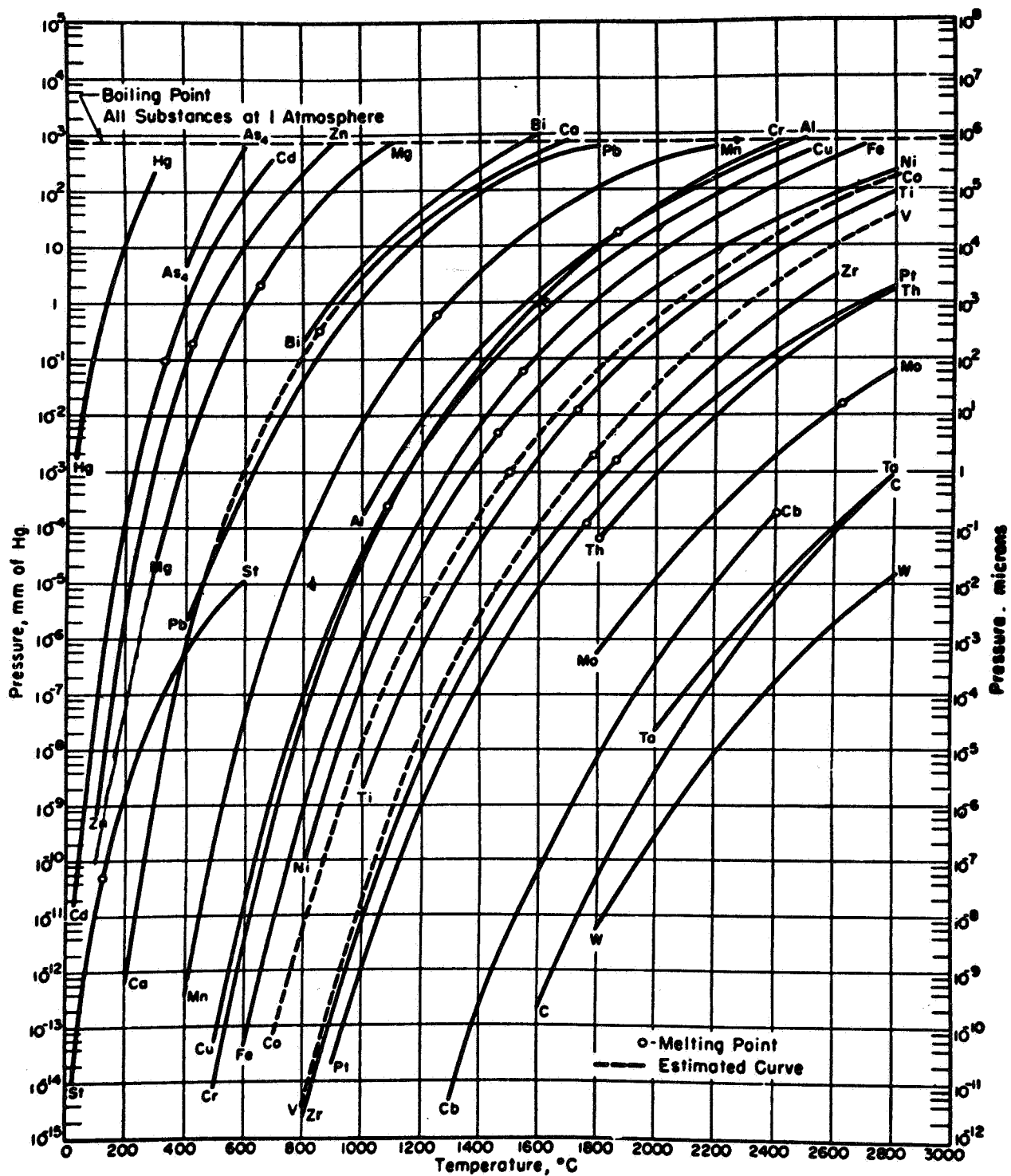


Figure 2. Vapor pressure of a metal as a function of temperature.

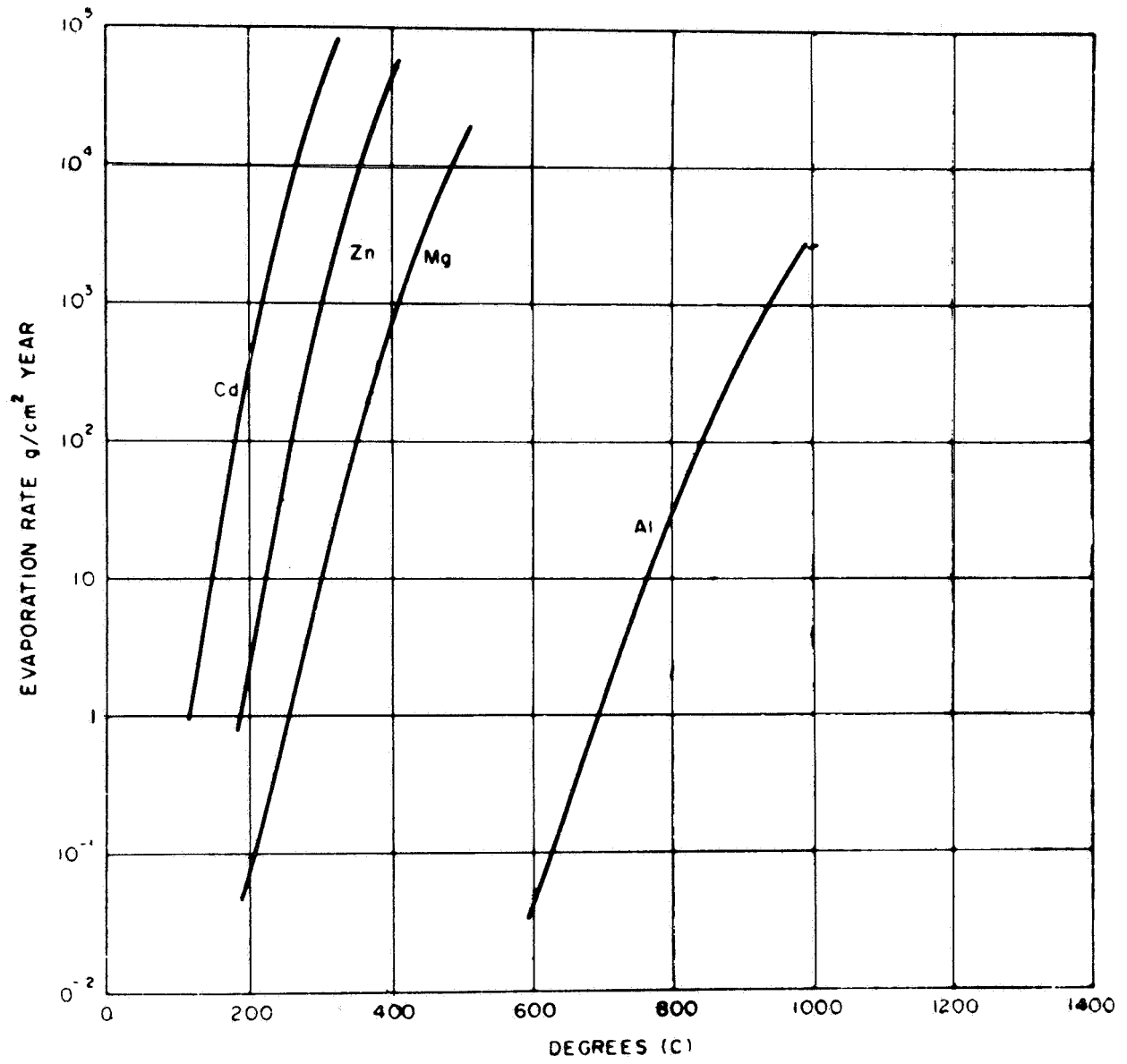


Figure 3. Loss of the metals (Cd, Zn, Mg and Al) as a function of temperature.



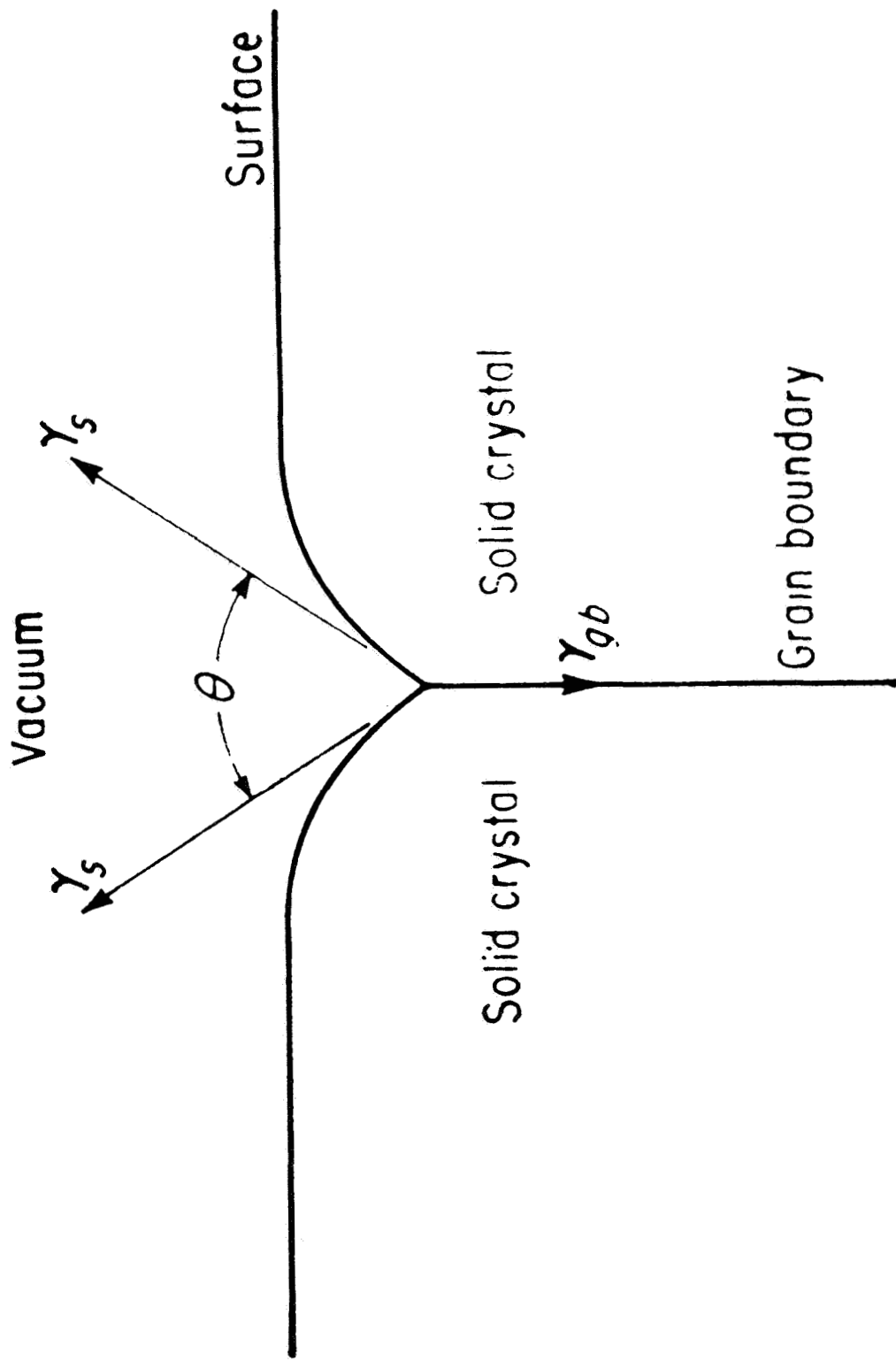
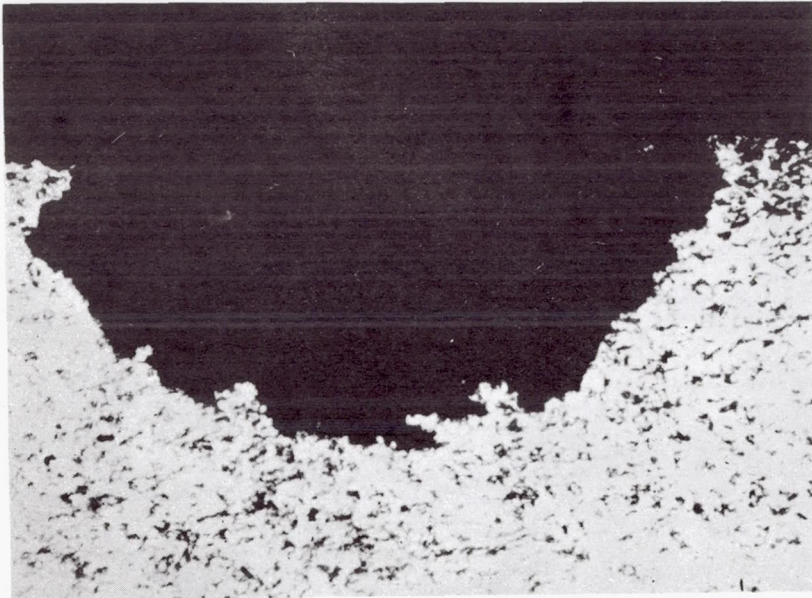
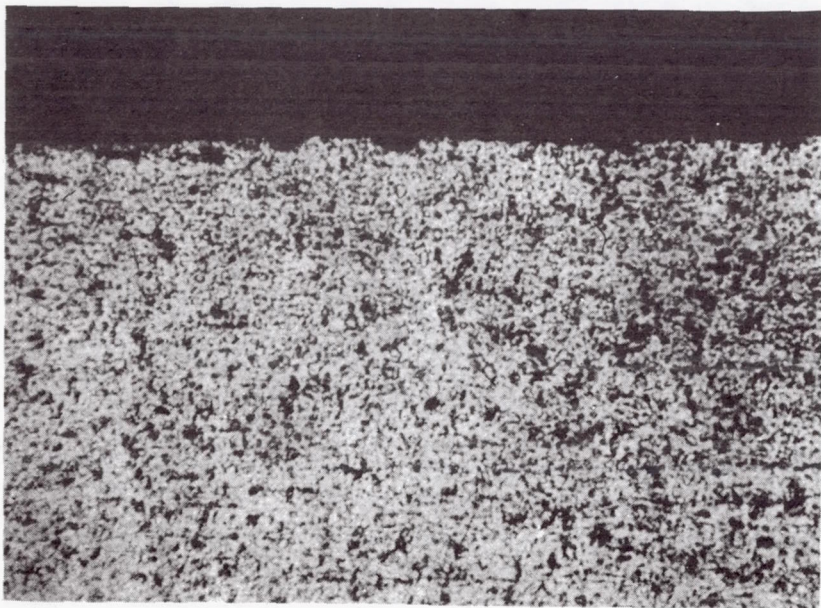


Figure 4. Equilibrium shape and surface tensions developed at the grain boundary of a metal (after Jaffe et al<sup>3</sup>).



Typical pit in cross section in bare magnesium alloy HK31-H24. The general hemispherical shape is typical. Pit depths up to 0.0125 of an inch were measured. Magnification: 100 X, Etchant: Glycol.

Figure 5. Introduction of small surface notches as a result of distillation in vacuum:  
a. Bare magnesium alloy.



Typical pits in cross section  
in Dow 17 coated magnesium  
alloy HK31-H24. Pit depths  
up to 0.001 of an inch were  
measured. Magnification:  
100 X, Etchant: Glycol.

Figure 5. Introduction of small surface notches as a result of distillation in vacuum:  
b. Magnesium alloy imperfectly coated with Dow 17.

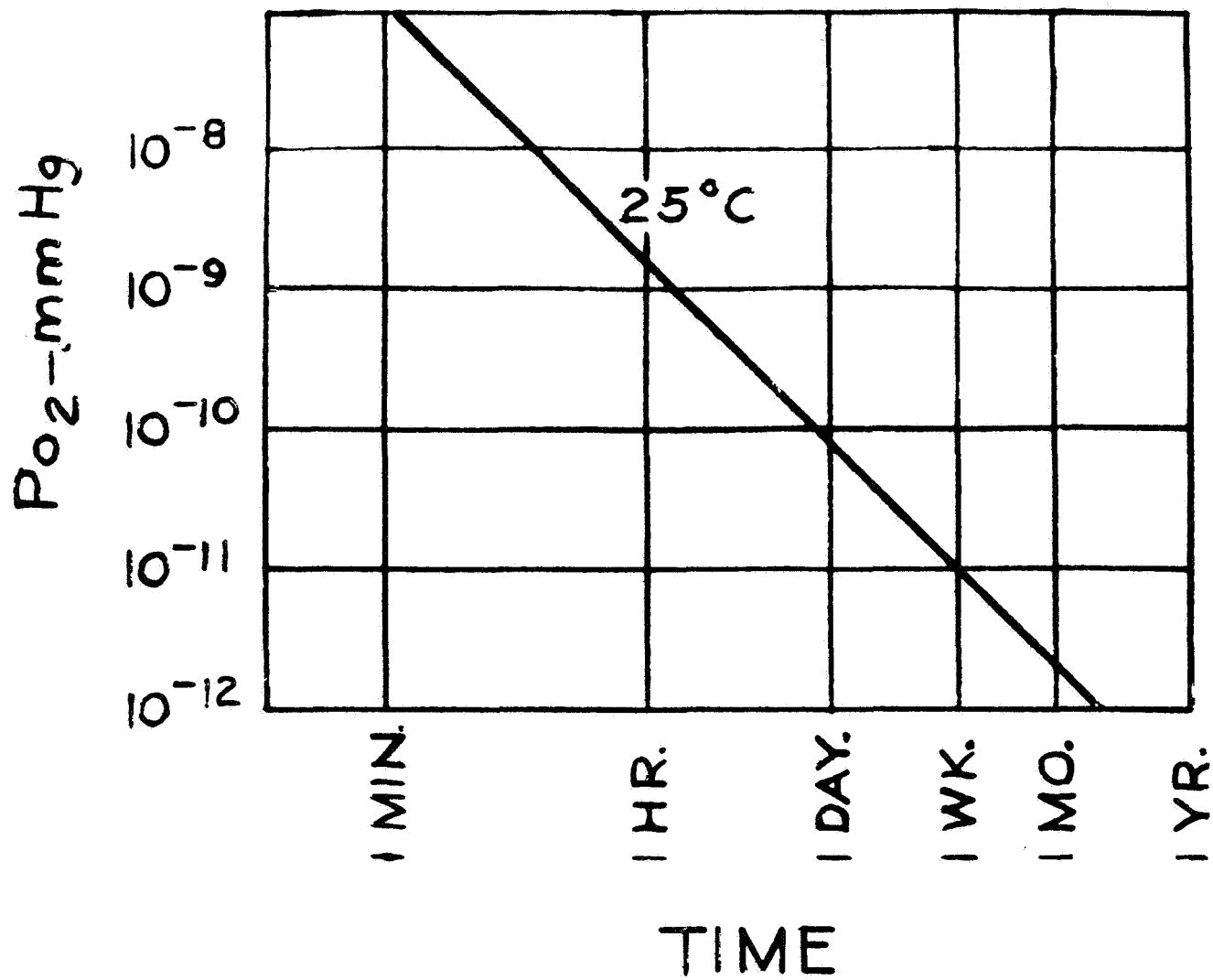


Figure 6. The amount of time necessary to form a monomolecular layer of metal oxide as a function of pressure.

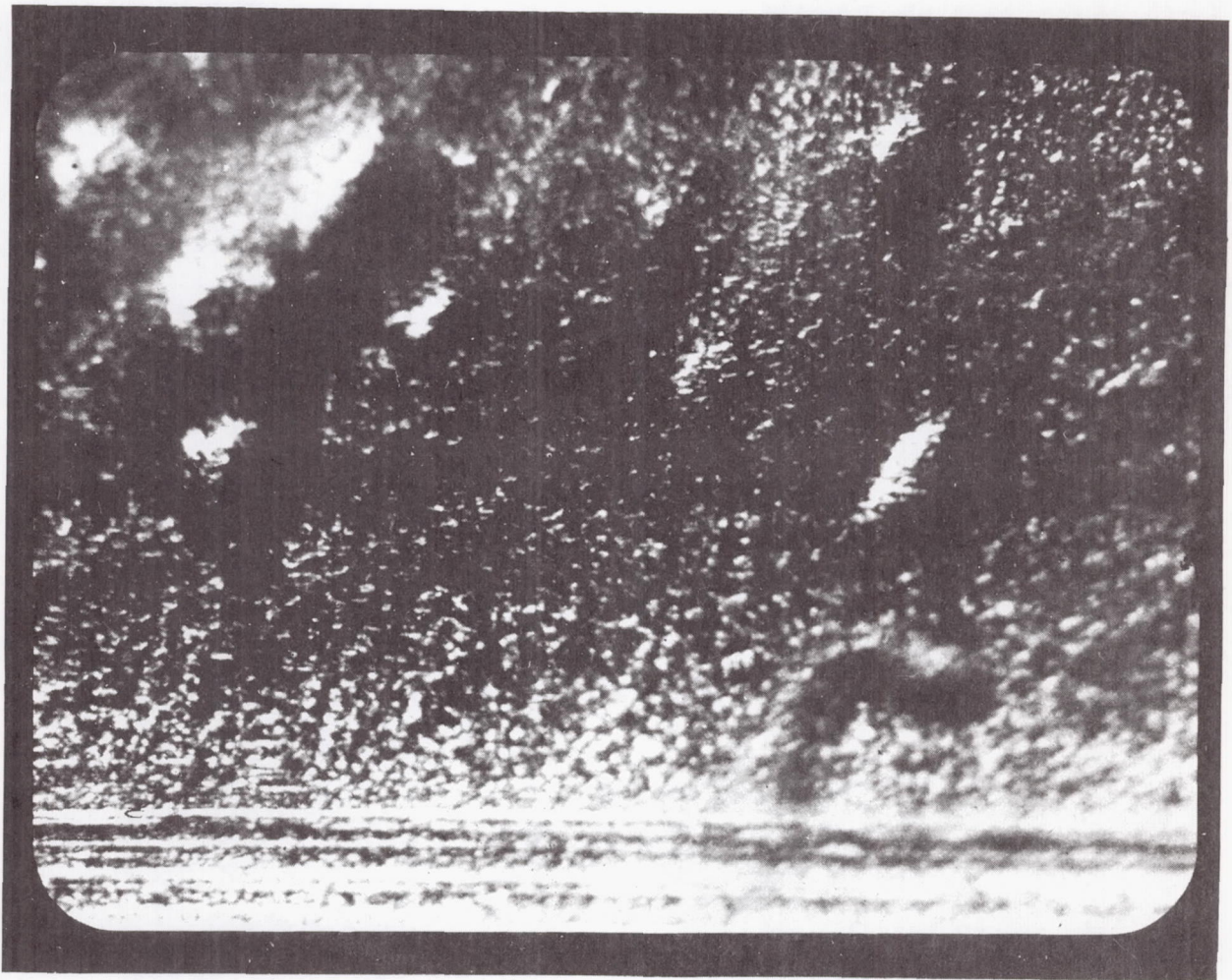
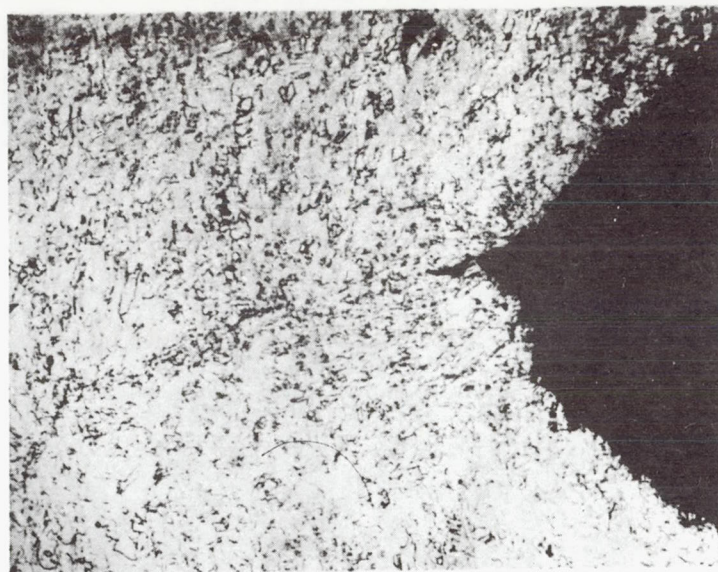


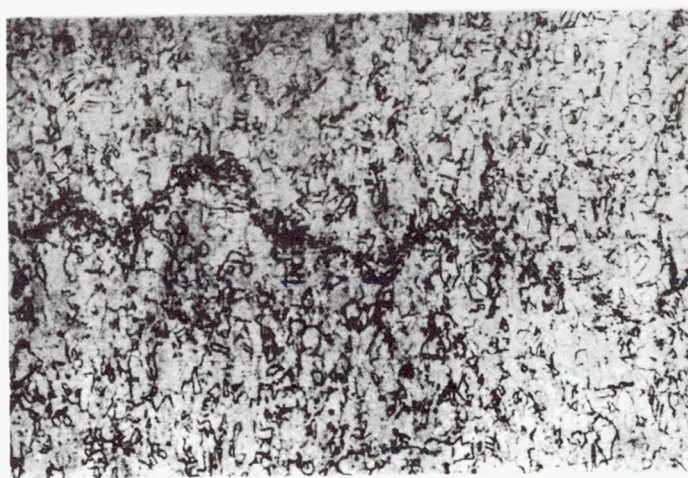
Figure 7. The phenomenon of cold welding, wherein portions of a steel race have been torn out by the actions of miscible steel bearings.



Notch Base

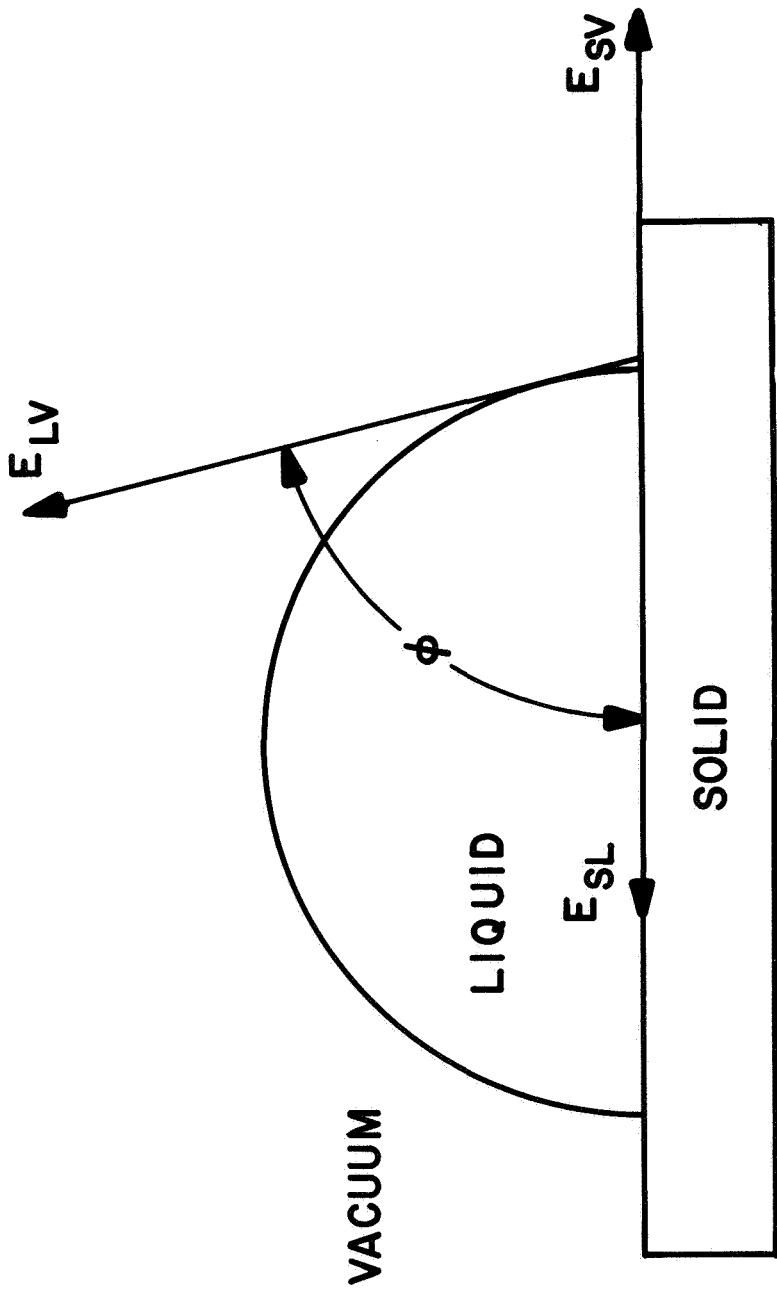


Notch Base



Center

Figure 8. Freshly formed copper surfaces welded together without the application of heat.



**WHEN  $\phi \rightarrow 0$ , LIQUID SPREADS**

Figure 9. Equilibrium energy balance of liquid-solid-vacuum (vapor) interface.

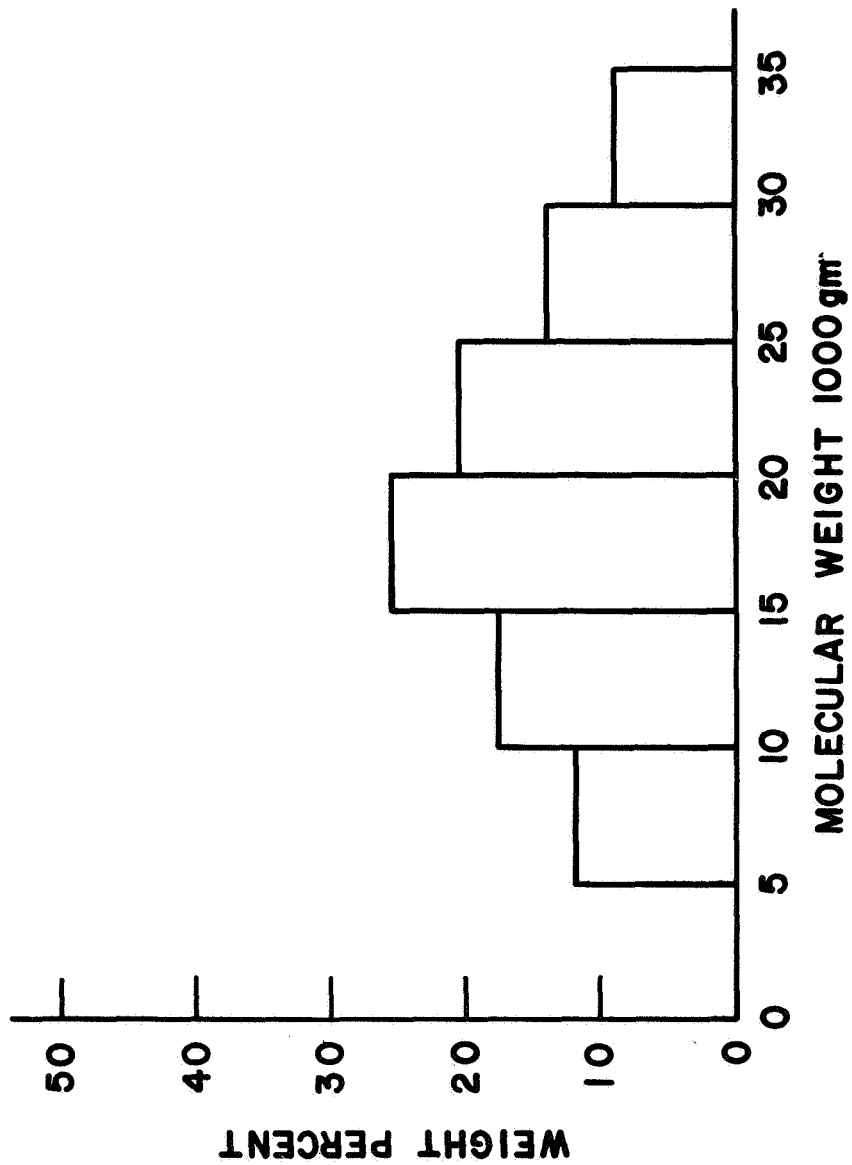
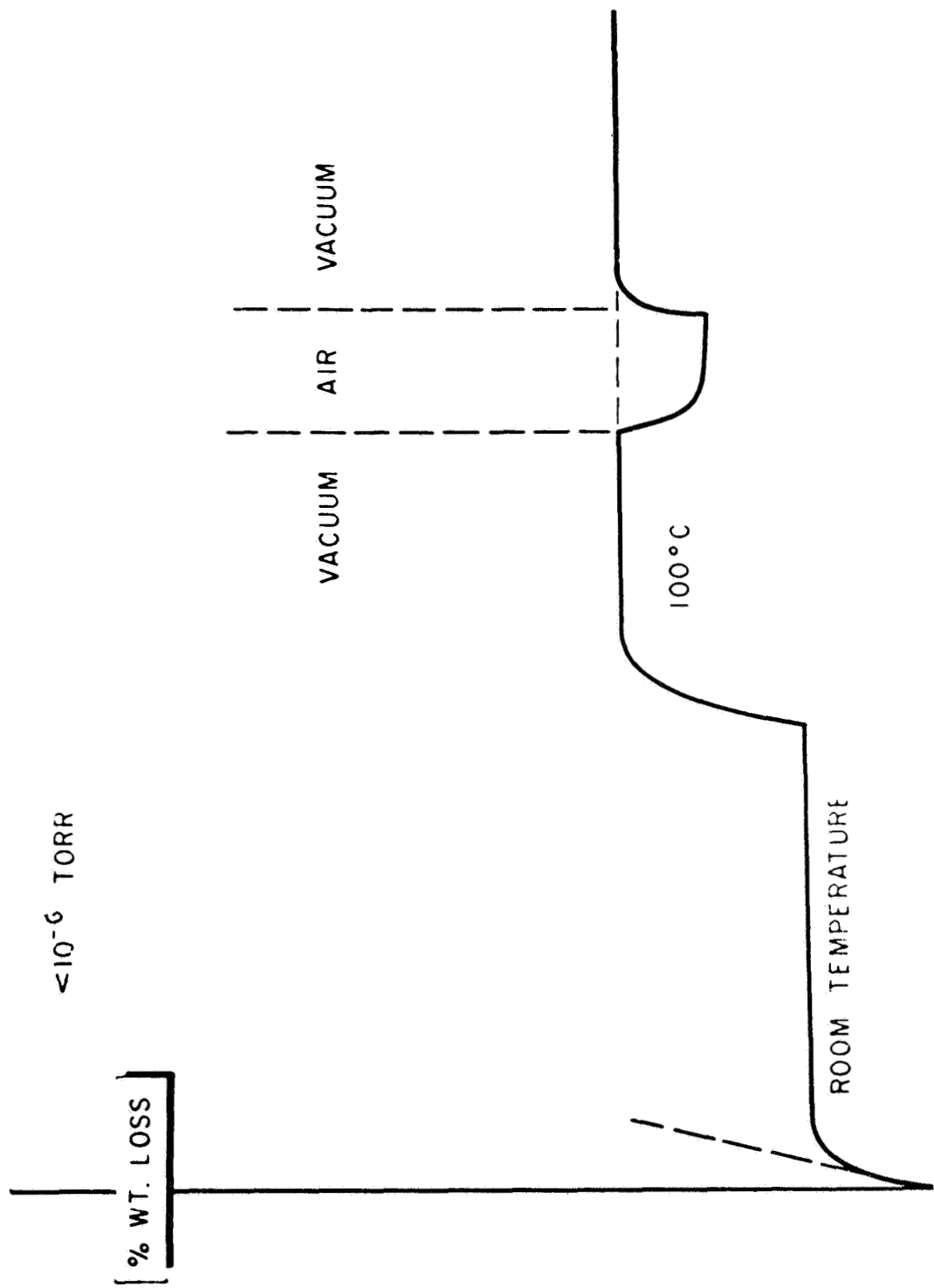


Figure 10. Molecular weight distribution of a 'pure polymer purported to be a material having a molecular weight of 20 250.



THERMAL VACUUM PERFORMANCE



TIME

Figure 11. Generalized manner of polymer outgassing.



Figure 12. Re-condensation of sublimates on cooler surface.

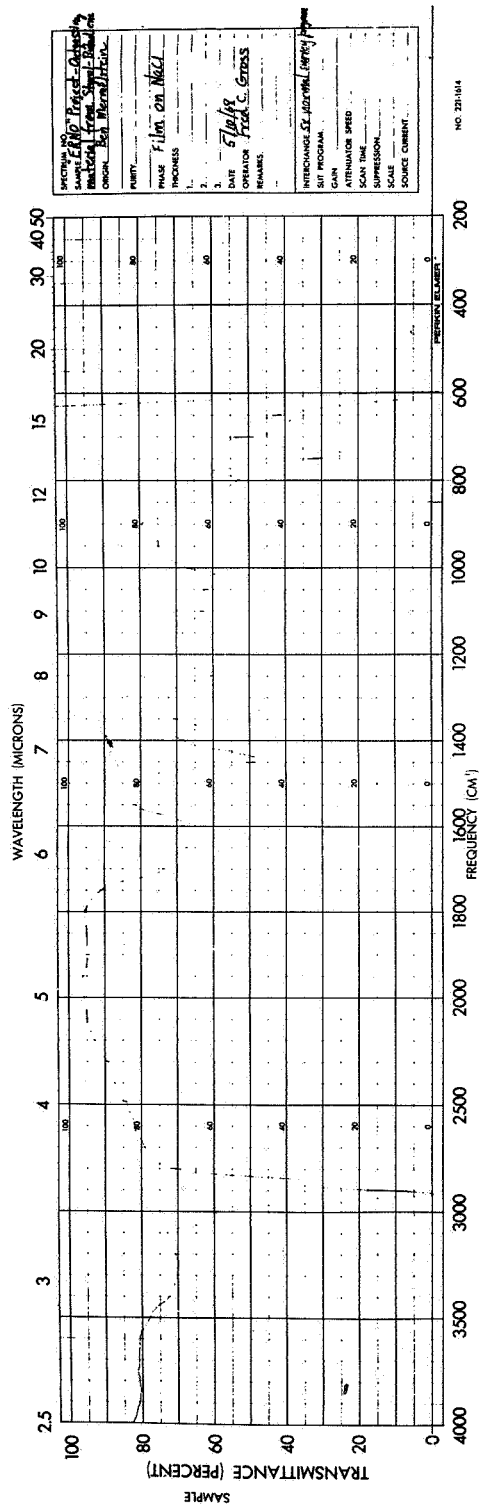


Figure 13. Loss of infra-red transmission as a result of sublimate re-condensation.

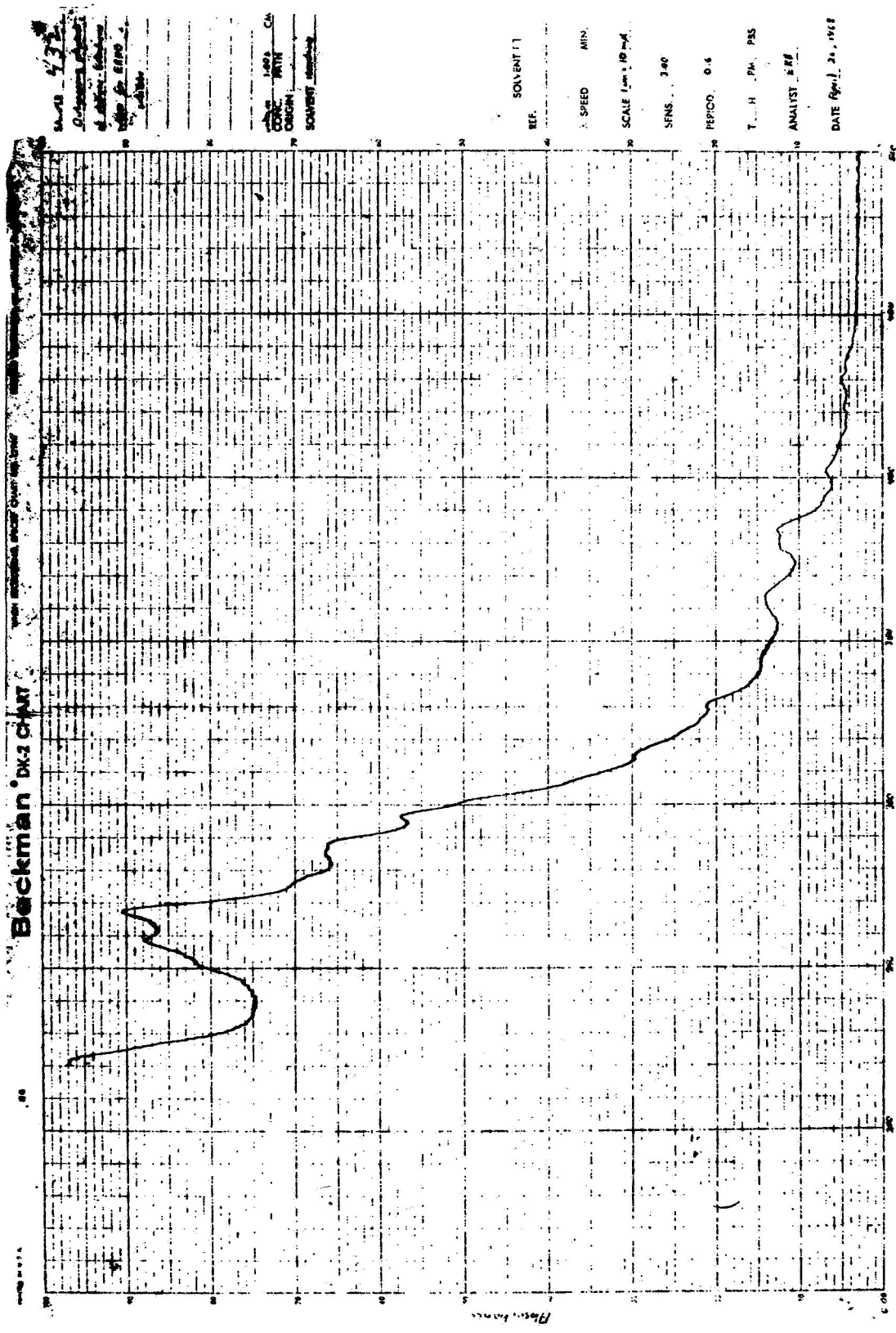


Figure 14. Loss of ultra-violet transmission as a result of sublimate re-condensation.

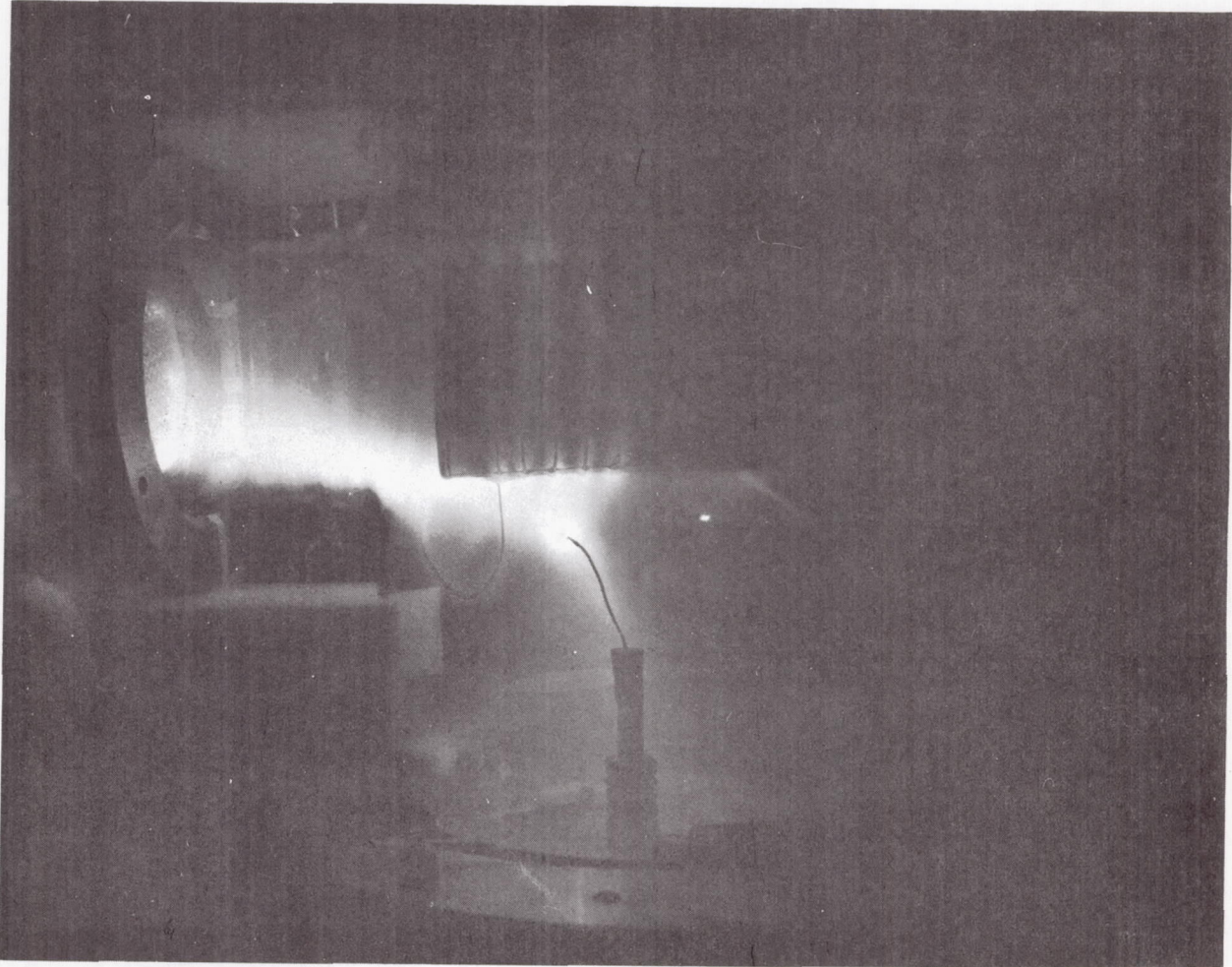


Figure 15. Picture of corona as a result of wire insulation breakdown, releasing easily ionized gases.

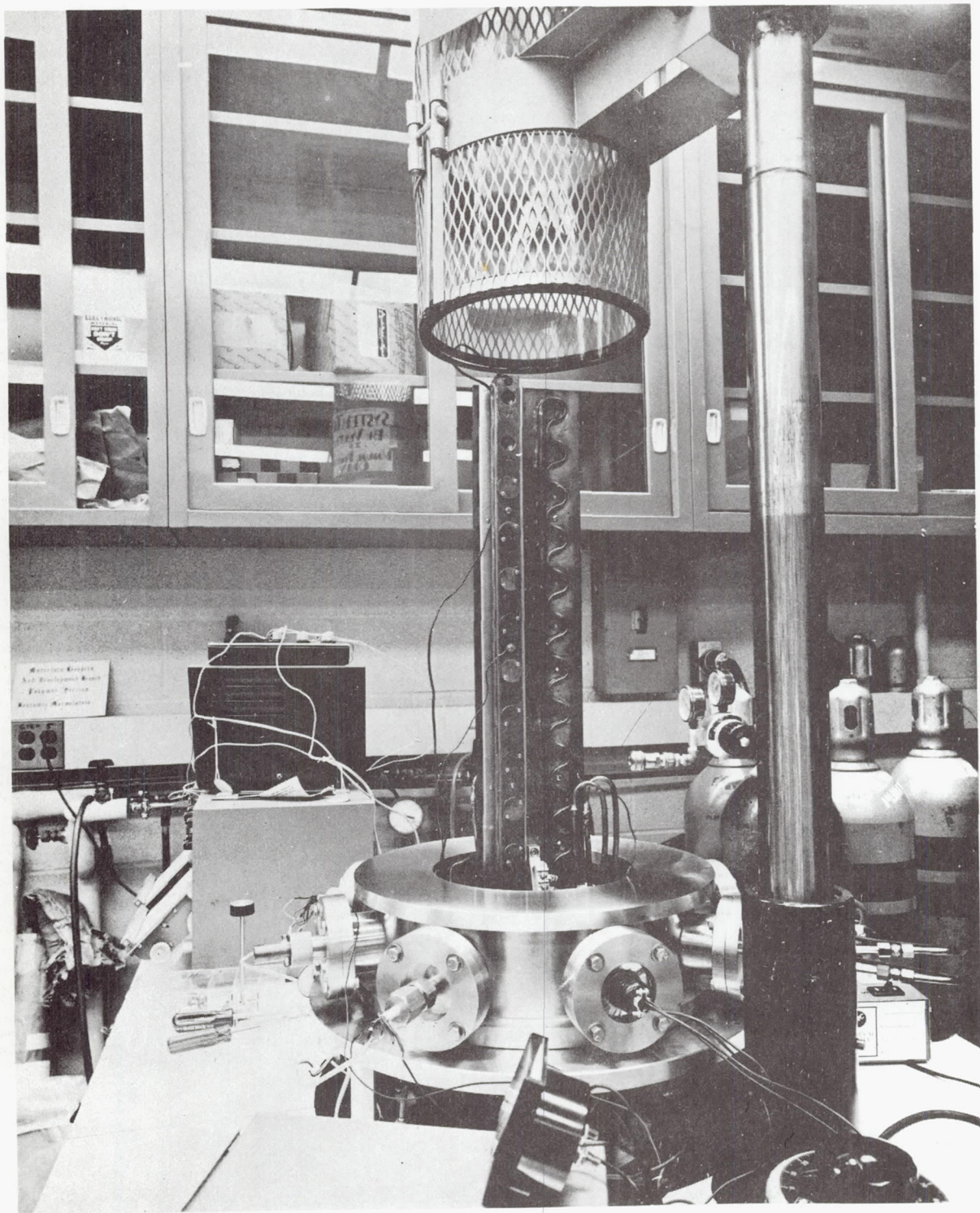


Figure 16. Specimen insert end of VCM apparatus. Temperature held at  $125^{\circ}\text{C}$ .

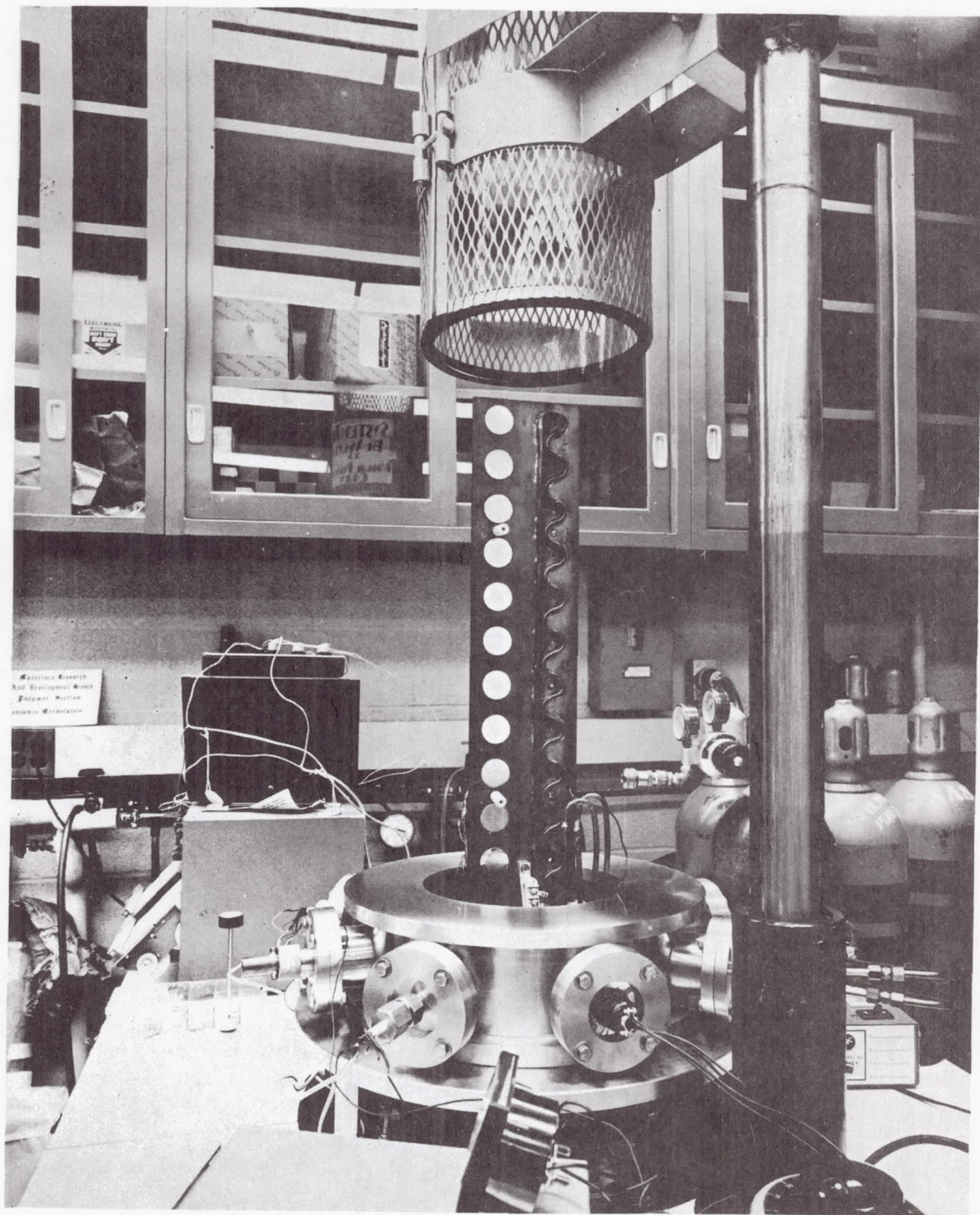


Figure 17. Sublimate end of VCM. Salt discs held at 25°C.

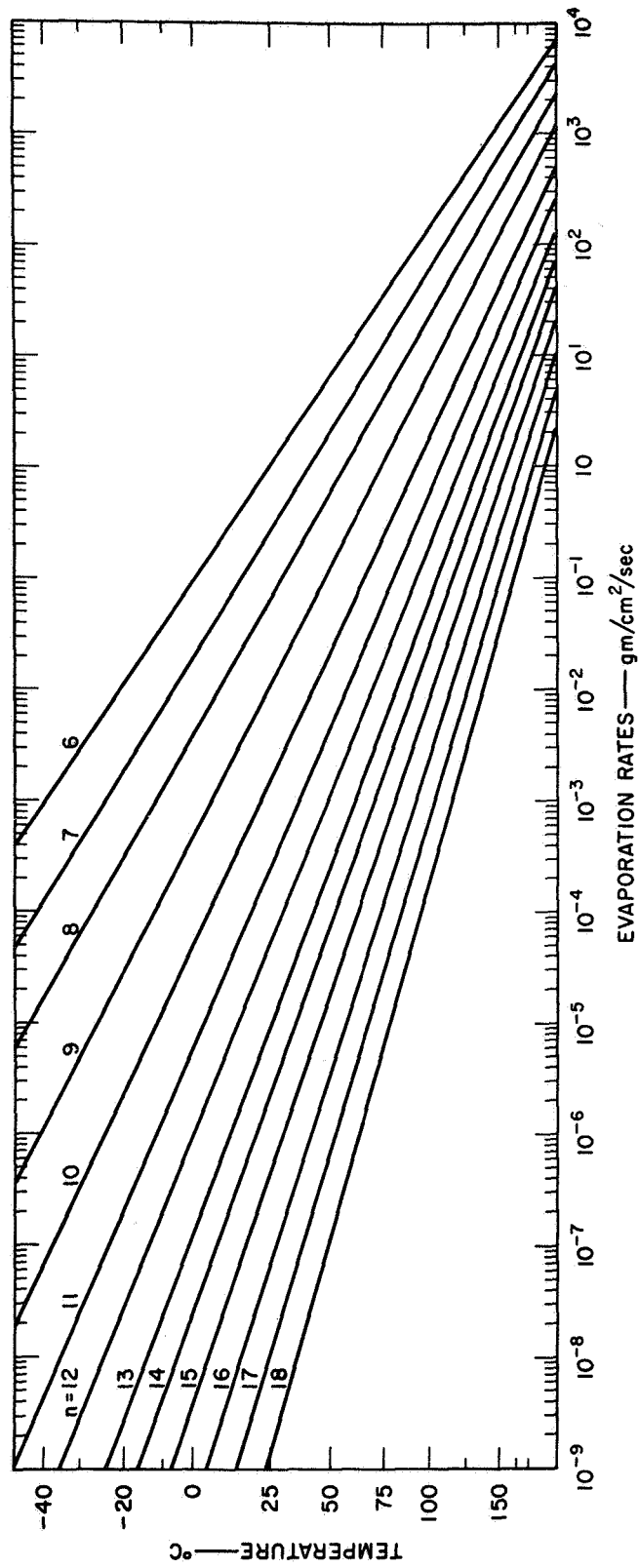


Figure 18. Evaporation rates of silicones as a function of temperature (after Muraca<sup>4</sup>).



EFFECTS OF THERMAL-VACUUM ENVIRONMENT ON SEAL AND GASKET MATERIALS  
(500 hours at 135°C and 10<sup>-6</sup> torr)

MATERIAL*	DIMENSIONAL CHANGE, %	WEIGHT CHANGE, %	DURE HARDNESS		TENSILE, psi		ELONGATION AT BREAK, %	
			Control	Test	Control	Test	Control	Test
<b>Acrylic</b>								
Hycar 520-67-108-1	L, n.c.	-1.06	86.3	89.1	1860	2140	128	88
<b>Butyl</b>								
805-70	L, -1.00	-2.42	77.2	79.9	1120	1100	295	208
EX-1090	L, -0.39	-1.57	70.7	86.6	2240	1710	550	129
EX-1091	L, -0.50	-1.49	71.0	79.8	1800	1840	380	200
EX-1092	L, -0.96	-2.11	76.2	85.7	1880	1380	210	78
FR 60-26	L, -1.60	-4.30	62.5	78.8	2292	1520	554	228
SR 613-75	L, -0.81	-2.15	82.1	81.6	1108	1011	150	216
SR 634-70	L, n.c.	-1.78	71.1	93.1	2058	996	400	97
<b>Ethylene-Propylene</b>								
SR 722-70 (A)	L, -0.95	-1.68	77.0	80.5	2488	2294	269	245
SR 722-70 (B)	L, -0.76	-1.44	77.5	82.5	1571	1990	195	182
<b>Fluorocarbon</b>								
Viton A4411A-990	L, n.c.	-0.54	85.4	86.7	2030	2220	358	273
<b>Silicone</b>								
Hadbar 28-80	L, -0.43	-0.67	85.6	88.6	971	866	116	100
Hadbar 4000-80	L, -0.26	-0.56	77.0	80.8	1108	910	331	282
SE-555 (red)	L, -0.08	-0.76	70.6	69.6	1080	1440	500	512
SE-555 (gray)	L, -0.26	-0.95	60.1	66.8	1115	1380	442	347
SE-555 (white)	L, +0.21	-0.85	60.8	69.0	1640	1461	480	425
SE-556	L, -0.31	-1.04	54.6	65.3	1390	1390	515	458
SE-3604 (24/480)	L, n.c.	-0.18	77.4	78.4	849	917	142	105
SE-3613 (24/480)	L, n.c.	-0.13	70.6	70.7	1020	977	212	122
SE-3713 (24/480)	L, n.c.	-0.25	77.9	77.9	1090	1176	126	117
SE-3813 (24/480)	L, n.c.	-0.33	87.4	88.2	1074	1230	79	80
SE-4511 (24/480)	L, -0.03	-0.21	52.1	57.4	733	753	312	253

Figure 19. The degradation of polymers as a result of excessive curing cycles.

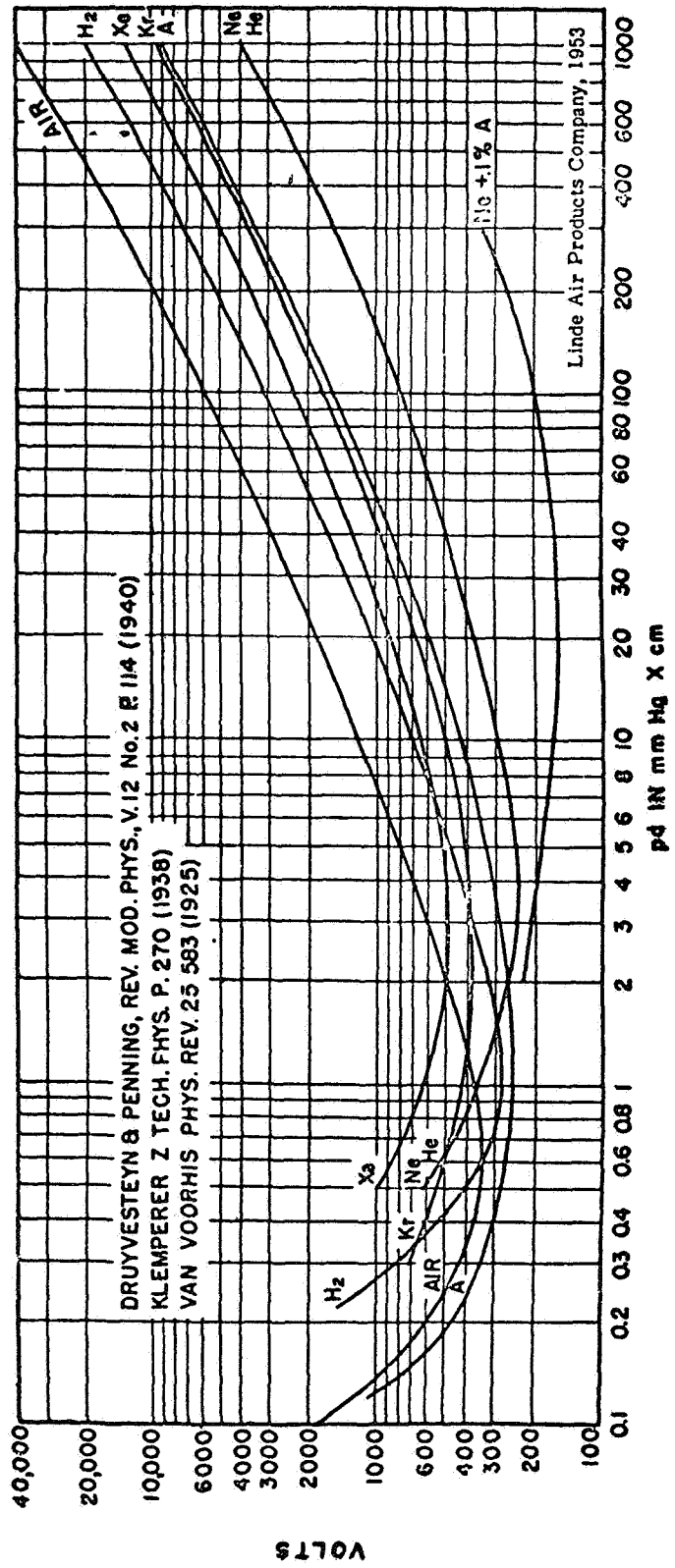


Figure 20. The potential necessary to cause ionization as a function of the pressure of the gas times the distance between the electrodes.

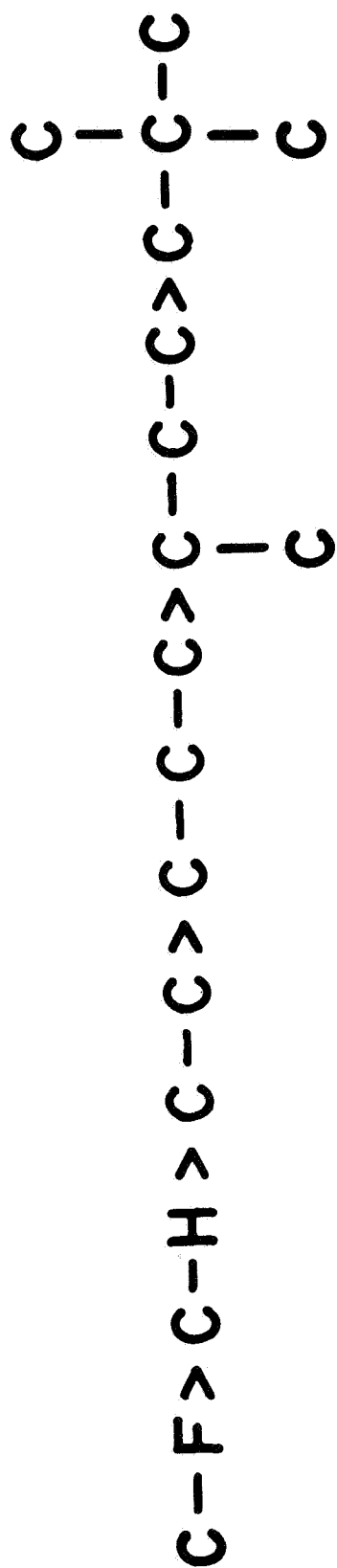


Figure 21. Relative bonding energies of linear carbon combinations.