

ENVIRONMENTAL CONSIDERATIONS FOR THERMAL PROTECTIVE COATINGS

R.M. VanVliet

J.J. Mattice

Directorate of Materials and Processes, ASD

Introduction

As pointed out in accompanying papers, coatings and temperature control materials will have to survive and function reliably on and within space probes in a totally new environment when using thin films as coatings, we must consider the optical and physical changes which will result from long exposures to high vacuum, multiple forms of radiations, and elevated temperatures. This summary will point out those elements of space environment which are of chief concern to the proper performance of coatings and will consider the major interactions resulting from such exposure. The progress and challenges concerned with achieving reliable coating systems are reviewed. Some suggested approaches to potentially fruitful areas of study are emphasized.

Elements of the Space Environment

Figure 1 lists the environmental factors which may deteriorate outer surfaces of the space vehicle. Figure 2 illustrates the major problems encountered with all types of coating materials and outer surfaces when exposed to the high vacuum of space. It must be kept in mind that in space and in the transition region between the atmosphere and space, pressure or density factors are vectorial. The ARDC Model Atmosphere defines the upper layers of air with considerable precision for stationary vehicle. But the aerospace vehicle may be moving at orbital or escape velocities which are over 20 times as fast as the average gas molecule. Thus, the pressure on the front of the space vehicle may be quite high even in the rarefied upper atmosphere while the pressure to the rear is very low. When the space vehicle leaves the atmosphere, it must also contend with vectorial plasmas such as the solar wind or plasma (about 600 miles/sec) and high energy Van Allen radiation. In addition, the outgassing of the space vehicle itself may add significantly to the local environment. Thus, it is difficult to describe a precise vacuum condition for a space vehicle. While the definition of the vacuum environment may be difficult, many of the effects of this environment can be anticipated on the basis of terrestrial experiments.

The most obvious effect of vacuum is the evaporation or sublimation of high vapor pressure materials. The rate of vaporization of a homogeneous solid can be obtained from the Clausius-Clapeyron and Langmuir relationships as follows:

$$G = \frac{P}{17.14} \sqrt{\frac{M}{T}}$$



where:

G is the rate of evaporation in grams cm-2 sec-1.

P is the equilibrium vapor pressure in mm of mercury.

M is the molecular weight of the gas.

T is the absolute temperature in K.

This equation can be used to compute the rate of evaporation of pure metals or pure compounds used as exterior coatings. For example, cadmium plating will evaporate at 44 mils per year if held at 260°F.

Dissociation and surface changes are important considerations in the performance of coating materials and will be discussed later as a function of the class of the material.

Intense radiation is the second major element of the space environment. For the purposes of this discussion we might divide these numerous radiation types into two broad classes; electromagnetic and particulate. Figure 3 outlines the various types and approximate fluxes of electromagnetic radiations. The electromagnetic component of cosmic radiation has low intensity and is rather inconsequential as far as coatings are concerned. When nuclear reactors are used in the space vehicle, gamma radiation of high energy may be present in large quantity and thus become an important consideration.

Soft x-rays are emitted in considerable intensity by the solar corona. The intensity is variable with solar activity ranging from 0.1 to 1.0 erg/cm²/sec at one astronomical unit (Earth distance). The solar x-rays vary in wavelength from about 1 to 100 angstroms.

The ultraviolet spectrum of the sun ranges from about 100Å to 4000Å. The vacuum and far ultraviolet radiation (see figure 3) is dominated by band emission and varies considerably with solar activity. There is also an ultraviolet continuum which extends into the vacuum and far ultraviolet but increases in intensity at longer wavelengths. The total intensity of this radiation is not accurately known but probably varies from about 20 to 50 ergs/cm²/sec. No appreciable amount of this radiation penetrates the earth's atmosphere. The near ultraviolet (2000-4000Å) has an intensity of about 10⁵ ergs/cm²/sec or over 9 percent of the sun's energy. Virtually all the energy below 3000Å and most of the energy between 3000 and 4000Å is filtered out by the atmosphere as shown in figure 4. As a result, coatings may absorb 10 to 100 times as much ultraviolet light above the atmosphere as in the surface of the ground on a clear day. Thus the ultraviolet light is definitely the most serious radiation problem particularly in the case of organic coatings.

About one third of the sum's energy is in the visible and most of the balance is in the near infrared to 30,000Å or 3.0 microns. The absorption of this energy determines the primary heat input to the satellite or space probe. The heat from the earth, satellites, and other low temperature bodies is radiated primarily at wavelengths greater than 3 microns. Microwaves and radiowaves are at longer wavelengths and are radiated at low intensity by all celestial bodies and by the interaction gas and plasmas in space. The sun and other stars radiate radiowaves at high but variable intensity.

The second major type of radiation is particulate in nature and is illustrated in figure 5. The cosmic component of this radiation consists of the highest energy particles or ions. The bulk of the cosmic radiation is protons with small quantities of heavier nuclei.



When this radiation and the accompanying electrons are trapped in the Earth's magnetic field, it is known as Van Allen radiation. The low energy electrons in the Van Allen belt are rated as a potentially serious materials problem with effects similar to ultraviolet, but the absorption of this radiation is believed to be relatively low.

The solar magnetic field continuously ejects a hydrogen plasma known as the solar wind. This plasma is believed to have a temperature of 220,000°K or 26 ev upon reaching the earth. This is about equal in intensity to solar x-rays. Little is known about the effect of this plasma on coatings.

Neutrons are associated with reactors and would pose many problems where reactors are used for power generation. On the other hand, alpha particles are of minor concern since their penetration is slight.

Micrometeorites or space debris forms the third element of the space environment. This was considered a major hazard of space flight until the actual launching of satellites. Now it is tentatively classed only as a long term hazard comparable to some of the milder radiation effects, in altering the properties of coatings.

Organic Thin Films and the Space Environment

The Problem of Vacuum

Many writers have stated that the greatly reduced pressure of the space environment makes the use of organic polymers as plastics and films impractical because of sublimation. It is now reasonably clear that a given polymer will not volatilize as a result of vacuum alone. Residual lower molecular weight species present as a result of incomplete polymerization, are often responsible for observed outgassing of polymer films. Therefore, the vacuum is no real problem when considered by itself provided the polymeric material is reasonably high in molecular weight and free of lightweight components (obviously an idealized situation).

The above points illustrate where a good deal of effort could be directed. Little work has been done on the basic film forming polymers to optimize the properties of flexibility, toughness, and adhesion, where the polymer must be used as is. Specifically, further study should include the development of polymer systems which are internally plasticized and the preparation of low molecular weight plasticizers which have little tendency to volatilize when dispersed in a film. That low molecular weight compounds may be retained in a polymeric substrate may be seen from figure 6. In this case, a class of polyhydroxybenzophenones is shown to diverge from the well known Henry's Law. The low volatility of these compounds is the result of hydrogen-bonding to electronegative centers in the polymer chains. For high vacuum applications where a plasticizer is required, new materials which act in a similar manner if severe outgassing is to be avoided will have to be made available.

In many cases the broad molecular weight distribution of polymers may be a limiting factor. However, figure 7 shows how one polymer, poly- α -methylstyrene, may differ in molecular weight distribution as a function of initiation method. The latter sedimentation pattern shows that nearly mono-disperse material may be obtained when the polymerization technique is directed towards this end. It is highly probable that modification of existing techniques, along with the development of novel ones would lead to the availability of a number of common film forming polymers of very narrow molecular weight distribution. Such materials might then be used to prepare films with a very low concentration of lightweight components.



Vacuum and Temperature Combined

Figure 8 lists a number of general classes of film forming resins and the gross changes usually observed when these materials are exposed to temperature in vacuum. It can be seen that at present no unmodified organic films are available for extended application over 500° F. Performance of even the silicone at this temperature is marginal due to cracking and adhesional failures. Again, however, the polymer chemist has provided a possible answer in the form of several new promising raw polymers with enhanced thermal stability. Some of these are listed in figure 9. Adaptation of these materials to useful, thermally stable films is one of the tasks of the industrial research laboratory. The Air Force needs temperature resistant basic resins with good physical and color stability. Base polymers with these properties and capable of low temperature cure are also in demand.

Additional basic and applied research are required to define and improve properties of the new materials. We should study these materials quantitatively in terms of degradation mechanism and kinetics under oxidative and non-oxidative conditions. Such studies should be carried out both in the finely divided and thin film states.

A stable and useful 1000°F organic film forming material is a reasonable goal for the relatively near future.

Nuclear Radiation Interactions

The impingement of ionizing radiation in high doses on organic thin films will also result in physical, chemical, and optical changes. However, for exposure to all elements of the space environment, nuclear radiation is not so severe a problem area when compared to the ultraviolet flux. Further, degradative processes operating within solid organic films do not result in a degree of damage comparable to that experienced with fluids, greases, or elastomers. In many cases film properties are enhanced by more complete crosslinking (thus possibly leading to reduced volatilization). Severe failure of films in the laboratory due to ionizing radiation has seldom been observed with the proper choice of polymeric starting materials.

A possible exception to the above statements may be found in the interaction of low energy electrons with organic materials. A considerable flux of this type of radiation, with energies on the order 20 to 200 Kev, as opposed to several Mev has been detected in the earth's magnetic belts. The extent of this potential problem concerning organic films or any other physical class of organic materials has not been defined. Certainly, work should be carried out to define the magnitude of any problem which might exist. Should one become evident, necessary research into degradation mechanism, mode of stabilization, and development of resistant materials should be undertaken.

Considerable effort has been expended in an attempt to understand the mechanism of stabilization of resonant structures to nuclear radiation. One can now predict with some measure of success the resistance of polymeric materials from the structure and aromaticity of the system. These empirical relationships have occasionally been carried over into the ultraviolet radiation problem. It should be kept in mind, however, that the discrete processes of energy absorption, stabilization, and dissipation are quite different for nuclear and ultraviolet radiation. As a result, the presence of highly resonant structures is a very poor measure of the ultraviolet stability of a polymer film.



There are a very few classes of organic compounds exhibiting high absorption and low rate of reaction (a high rate would be expected) to ultraviolet light. These compounds have not been observed to undergo fluorescence or phosphorescence, as do most nuclear radiation stable materials. This very intriguing fact emphasizes the point that one must be very careful in drawing analogies between ultraviolet and nuclear radiation interactions with organic materials.

The Ultraviolet Radiation Problem

The most severe environmental factor we must consider for organic thin films which are to be used as the basis for temperature control systems in space is the ultraviolet radiation which is present above the earth's atmosphere. The reasons for the severity of this problem are many but may be stated generally as follows:

- 1. The ultraviolet radiant flux in space is very intense, especially in the wavelength region 2000-4000Å.
- 2. This same 2000-4000Å region is the primary absorption region for common electron rich bonds such as are found in useful polymeric materials. This may be seen for a typical polyester film in figure 10. Note the decreased intensity and short wavelength cut off for the same polymer in July and December within the atmosphere.
- 3. The energy per photon in this region exceeds the energy of typical bonds, thus making polymer breakdown a distinct possibility.
- 4. Photochemically induced changes or degradations result in the shifting of absorption bands toward or further into the visible region. This condition leads to a shifted temperature balance of the substrate due to higher energy absorption.
- 5. The few film forming polymers which do not inherently absorb ultraviolet light, and therefore should not degrade, are observed to decompose nevertheless due to the photosensitizing (or catalytic) action of impurities which apparently are universally present.

A few basic polymers do exhibit a degree of inherent photochemical stability. One of these is pure melamine formaldehyde, a poor film former. However, even if practical difficulties could be overcome, the finite rate of change, as indicated in figure 11, still prevents use of polymers alone for long term applications which will be required in increasing numbers in the future.

The weight of this evidence would seem to indicate it is inadvisable to consider further polymer films as substrates for temperature control systems. However, as an outgrowth of studies conducted to produce stable polymers in air, a growing volume of data indicates that for many applications certain additives will prevent deterioration of physical and optical properties for an extended time period in the space environment. The technique of incorporating stabilizing additives (U. V. absorbers) does not detract from the fundamental contributions which still need to be made regarding the little known chemistry and mechanism of photosensitization and photodegradation of polymers films. Little, however, can be learned in studying commercially available materials from a fundamental point of view. Specialized polymerizations utilizing high purity reagents are necessary if quantitative mechanistic data are to be obtained.



Organic Coatings For Use in the Space Environment

Within the last two years the magnitude of the ultraviolet problem concerning organic temperature control coatings, stimulated considerable effort aimed toward a feasible solution. Several important achievements under Air Force sponsored contractual efforts have paved the way to realization of this goal. Some brief highlights include:

- 1. Vapor pressure studies conclusively demonstrating the protective additives are compatible with the high vacuum of space (see the work of Schmitt and Hirt, WADC TR 59-354).
- 2. Successful synthesis of "metallocene" based protective absorbers. Figure 12 points out some structures which have been synthesized and figure 13 shows how one is effective in protecting a silicone alkyd film.
- 3. The feasibility of utilizing unpigmented, wholly organic absorbing systems for a wide range of stable temperature control systems not requiring high temperature stability.

The above areas are presently in various research stages and much work needs to be done. For example, with the availability of new polymer additives, applied effort should be expended to elucidate what specific effects, if any, are manifested by these materials in the formulation and curing of the systems to which they are applied. The thermal stabilities of certain coating systems may be increased or decreased by incorporation of novel materials.

Within the last few years a number of "U. V. radiation effects" studies have been initiated under Government sponsorship and by Industry. For some applications an ultraviolet protective coating system might be applied to prevent physical deterioration of various classes of materials. Structural plastics, which are presently being used and being considered for a host of future space ventures are a case in point. The use of thin covering films would allow the designer to formulate structural members to optimize strength and prevent incorporating large amounts of stabilizing additives into the entire bulk material. Other examples where such protective systems may be employed are textiles and elastomers used in situations where ultraviolet radiation causes damage.

Limitations of Present State of the Art

The temperature limitation of available film forming polymers has been discussed. In addition, when the temperature control application is considered, stable coating formulations with low initial solar absorption are non-existent. More simply, there are presently no thermally and ultraviolet radiation stable usable resins which are visibly colorless. Further, all high stability additives thus far established are colored in the visible (and consequently absorb solar radiation for which the eye is a reasonably good detector).

One must then conclude that presently there are not available temperature control systems which can provide very cold surfaces in space, such as might be achieved by the use of a white-pigmented, colorless, organic resin. Such a system would provide high reflectance to incident energy, low absorption, and very high emittance at long wavelengths for the small amount of energy that is absorbed. Organic coatings are by nature most easily prepared to meet these requirements. Such systems, if available for long term use, would find wide variety of specialized applications.



It should be evident that there is wide latitude for contribution by non-Government research organizations to Air Force materials requirements which are concerned with the adaptability of organic coatings to the space environment.

Inorganic Coatings in the Space Environment

At first glance, the effects of the space environment on inorganic coatings would appear to be a minor consideration. But further consideration places rather severe restrictions on certain inorganic coatings for applications that are routine in a terrestrial environment. However, most of the environmental effects have been only partially explored or merely postulated. Some of these data and postulations are assembled below and in figures 14 and 16.

Ceramic and Anodic Coatings

The evaporation of ceramic and anodic coatings may pose a problem where these coatings are used for high temperature heat radiators. Since this is the most important use of ceramics in direct exposure to space, it deserves further consideration.

Probably the most serious evaporation problem uncovered to date is that associated with the oxides of chromium. Since the prime protective layer on the stainless steels and super alloys is based on chromium oxide, air or chemically oxidized coatings on these alloys will have only limited utility in space. Chromium oxide dissociates at about 780°C and the higher vapor pressure chromium is the primary evaporated specie. At lower temperature the oxides of chromium evaporate at a slower rate. This evaporation apparently takes place slowly even at temperature as low as 600°C. This is unfortunate because oxide films on chromium alloys are one of the best and most easily formed high emittance coatings. A chemical process which would provide a stable emissive coating on the super alloys is seriously needed.

Many oxides are rendered more volatile by their environment. Alumina, in the presence of tantalum will evaporate at a much lower temperature because of the reduction of the alumina. Silica can also be reduced to the more volatile silicon monoxide by the presence of carbon and other materials. As a result of these findings, possible reduction reactions will have to be considered for high temperature vacuum operations where the inorganic compound exists in a more volatile, lower oxidation state.

Dissociation may be promoted by ionizing radiation at high temperature. The ionizing radiation might be the high intensity solar ultraviolet light or nuclear radiation from reactor power systems. Since an effective radiator coating is essential to the operation of nuclear and other power plants in space this vital area urgently needs exploration.

Another unexplored area is the effect of vacuum on adherence and thermal shock resistance of ceramic coatings. It is well known that non-oxidizing atmospheres during firing can cause the "dewetting" of a porcelain enamel from its metal substrate. It appears probable that this dewetting action might cause loss of bond in high temperature-vacuum exposure unless the ceramic is specifically designed and tested for this application.

Ceramic and anodic coatings are not necessarily free from ultraviolet effects even at room temperature. Figure 15 shows the effect of ultraviolet light on the reflectance of anodized aluminum. Similar effects have been reported for titanium dioxide opacified inorganic coatings. These changes are due to the formation of F and V centers (negative



or positive vacancies, respectively) in the coating and may be caused by ultraviolet light absorbing impurities such as iron oxide. These changes increase the temperature of the space vehicle in a manner similar to that of an organic coating that yellows due to ultraviolet light degradation.

The formation of vacancies has no significant effect on the emittance of coating, i.e., its power to radiate heat. However, the loss of water of hydration can seriously lower the emittance of the coating. Occasionally, crystal change will have similar effects. Thus, a combination of increased absorption of solar energy and decreased emittance at long wavelengths could cause a very large increase in temperature of a space vehicle.

Diffusion can have a dramatic effect on the reflectance, emittance, and other properties of oxide films in a vacuum. Some metals such as titanium permit the diffusion of oxygen at high temperature. Thus the oxide film on titanium could gradually disappear by diffusion into the metal.

Similarly, metals may diffuse through the oxide film to the surface at high temperature. In the atmosphere, this diffusion is not evident because the metal oxidizes as rapidly as it reaches the surface. In a vacuum, oxidation would not take place and considerable reduction in the emittance of the coating might occur. Since diffusion through the high vacancy concentration in iron and chromium oxides has been demonstrated, this phenomena requires further investigation.

The Metallic Film

Figure 16 outlines the effects of the space environment on metal surfaces. The effect of evaporation mentioned before is not necessarily a simple one. The evaporation of chromium from a rough stainless steel surface is reported to have a smoothing or polishing effect leaving a mirror like surface. On the other hand, mirror surfaces of silver undergo thermal etching to give a finely roughened surface after vacuum-thermal exposure.

Computation of the evaporation rate of metal films is frequently complicated by inaccurate or inadequate data. This is particularly true of metals such as aluminum which form tight, adherent, refractory oxide films. Since a very thin layer of metal oxide can virtually stop metal evaporation, data for metals such as aluminum is very difficult to obtain. The rate constants for metal evaporation is generally approximated by extrapolating vapor pressure data from the Clausius-Clapeyron equation. Many references have ignored the fact that data taken in the liquid state cannot be used directly to plot vapor pressures in the solid state. This leads to inaccurate evaporation rates. Cadmium and chromium probably pose the most serious evaporation problem of commonly used metal coatings. For some applications metals may require coatings to prevent evaporation.

Sputtering will be a serious problem for exterior metal coatings subject to long space exposures. Sputtering not only causes loss of material but may also change the metal surface characteristics. Proton sputtering will be a problem on all extended space flights due to the solar wind. Both proton and electron sputtering will be prevalent in the concentrated areas of the Van Allen radiation belt. The yield of metal sputtered, increases with increasing ion energy. Oblique ion impacts generally give higher sputtering yields up to 50 to 60 degrees from the normal. Some metals such as gold and silver develop rough surfaces during sputtering. The yield varies markedly with the filling of the delectron orbitals. Aluminum has the best resistance to sputtering of the reflective



metals. Some of the refractory metal oxides such as alumina and titania have better resistance than the parent metal but this area needs much more study.

Changes in optical properties of metal coatings are important in space vehicle temperature control and mirrors used to concentrate solar energy. These optical surfaces may be destroyed by micrometeorites, sputtering, and evaporation. The degree of damage to the surface will vary with the type of metal, the temperature, and the eroding media. Much more information is needed on these effects. In some cases, a transparent organic or inorganic top coat may ease the problem.

Some metals undergo severe creep at high temperature upon extended exposure to vacuum. This phenomenon has been only partially explored. One approach is to coat the metal with another coating that is more ductile at high temperature. This would insulate the metal from the vacuum environment.

The short circuiting of insulators by the vacuum evaporation of metals has already been noted. The vacuum deposition of volatile metals can also effect heat transfer and other surface properties such as friction.

Summary

Although a knowledge of the properties of materials allows one to compound temperature control systems on paper to prescribed requirements, long term use of many such formulations will lead to deterioration of physical and optical properties, and thus, to altered temperature balances. Conducting effective research to overcome these problems has been hampered by insufficient information about some factors of the space environment. Further, many of the environmental "effects" under study are still only postulated and little is known of the resultant optical and physical changes which will occur should they be proven valid.

Therefore, a large number of research areas are open to further study and clarification. Full Government-Industry cooperation is necessary, successfully to resolve the many problems that confront us.



BIBLIOGRAPHY

1. ASD TN 61-72	"Organic Coatings for Control of Spacecraft Temperatures," R.M. Van Vliet, 1961.
2. ASD TR 61-5	"Development of Heat Barrier Coatings," American Machine and Foundry Co., 1961.
3. ASD TR 61-151	"Reflective Inorganic Coatings," Georgia Institute of Technology, 1961.
4. WADD TR 61-108	"Synthesis of Metal-Cyclopentadienyl Derivatives for Use as Ultraviolet Absorbers," Wyandotte Chemical Corp., 1961.
5. WADD TR 60-704	"Studies on the Protective Ultraviolet Absorbers in High Vacuum Environment," Part II, American Cynamid Co., Feb. 1960.
6. WADD TR 60-773	"Proceedings of Symposium Coatings for the Aerospace Environment," 1960.
7. WADD TR 60-386	"Spectrally Selective Coatings for Temperature Control of Space Probes," R.M. Van Vliet, Oct. 1960.
8. WADD TR 60-703	"The Ultraviolet Degradation of Organic Coatings," Part I "Degradation in Air," Part II "Degradation in Vacuum," U. S. Naval Research Laboratory, Oct. 1960.
9. WADD TR 60-317	"Development of Ceramic Coatings with Controlled Reflective and Emissive Control Properties," A.D. Little, July 1960.
10. WADD TR 60-126	"The Vacuum-Thermal Stability of Organic Coating Materials," Part I. "The Polyurethanes," Lt. Mattice, 28 Oct. 1960.
11. WADC TR 59-268	"Vacuum Volatility of Organic Resins," Lt. G.F. Matacek, 23 Sep. 1959.
12. WADC TR 57-334	"Evaluation of the Mechanisms Which Affect the Performance of Thermal Radiation Resistance Coatings," Armour Research Foundation of Ill. Inst. of Tech. 18 April 1958.

Contrails

1. Vacuum

Vectorial Effects

- 2. Radiation
- 3. Micrometeorites

Figure 1. Space Environmental Agents

1. Evaporation

Surface Controlled

Diffusion Controlled

- 2. Dissociation
- 3. Complex Changes Affecting Surface Temperature

Figure 2. Gross Vacuum Interactions

1. High Energy

Cosmic-low total energy

Gamma-reactors

2. Soft X-rays

0.1 ergs/cm², variable

3. Ultraviolet

Far U.V. 100-1200A

10 ergs/cm²

Vacuum U.V. 1200-2000A

20-30 ergs/cm²

Near U.V. 2000-4000A

10⁶ ergs/cm³

4. Visible

One Third of the Sun's Energy

- 5. Infrared
- 6. Radiowaves

Figure 3. Electromagnetic Radiation

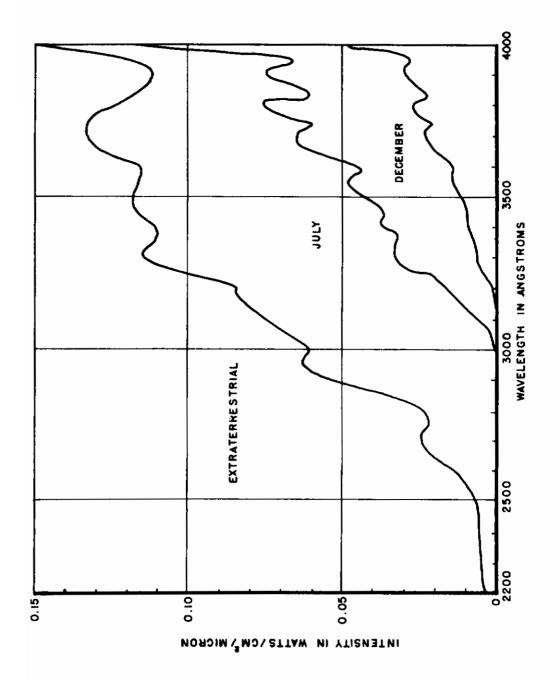


Figure 4. Spectral Distribution of Ultraviolet Light in Space and on Earth



- 1. Cosmic-low total energy
- Van Allen Radiation
 Protons-low total energy
 Electrons-maximum about 3000 ergs/cm²/sec
- 3. Solar Wind-Proton component about 0.4 ergs/cm²/sec
- 4. Neutrons, alpha particles

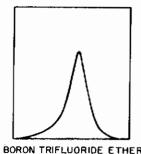
Figure 5. Particulate Radiation

Rate in g/cm ² /day	T,°C	Condition
5.4 × 10 ⁻⁵	25	Pure Compound
1.6 × 10 ⁻¹⁰	25	3.4% dispersed in cellulose acetate film

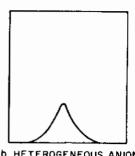
After Schmitt and Hirt, WADD TR 60-704, July 1960

Figure 6. Volatility of 2,2' - Dihydroxy - 4-Methoxybenzophenone in Vacuum

Contrails



a BORON TRIFLUORIDE ETHERATE INITIATION



b HETEROGENEOUS ANIONIC INITIATION

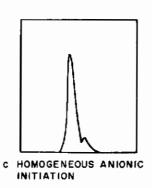


Figure 7. Sedimentation Patterns for Poly-α-Methylstyrene; after Fox & Isaacs, U. S. Naval Research Laboratory, Report 5518, August 1960



Class	Approximate Temp. Limit, F	Physical Changes
Ероху	400	Severe wt. loss
Silicone	500	Cracking, lost adhesion
Polyurethane	350	Severe wt. loss, yellowing
Polyester	350	Severe wt. loss, yellowing
Phenolic	450	Blackening
Vinyls	400	Severe wt. loss, flaking

After Matacek, WADC TR 59-268 and Mattice, WADC TR 60-126

Figure 8. Limitations of Common Film Forming Resins in Vacuum

Class	Basic Chemical Structure	Potential Useful Temperature Range
Borazoles		1500°F
Silazines	$ \begin{array}{c c} R & R & R \\ \hline & Si & N & Si & N \\ \hline & N & Si & N \\ \hline & N & Si & R \end{array} $	800 ° F
Benzimidazoles	$\left\{c \leqslant N \right\}$	1000°F
Polyethers		700°F

Figure 9. Promising New Classes of High Temperature Polymers for use as Coating Resins

Contrails

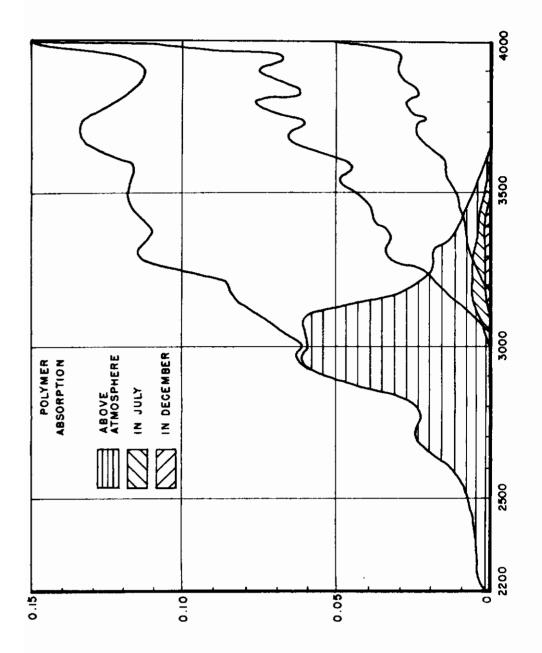


Figure 10. The Ultraviolet Energy Absorbed by a 0.0025 cm Film of Polyethylene Terphthalate when Exposed to Sunlight under Terrestrial and Space Conditions

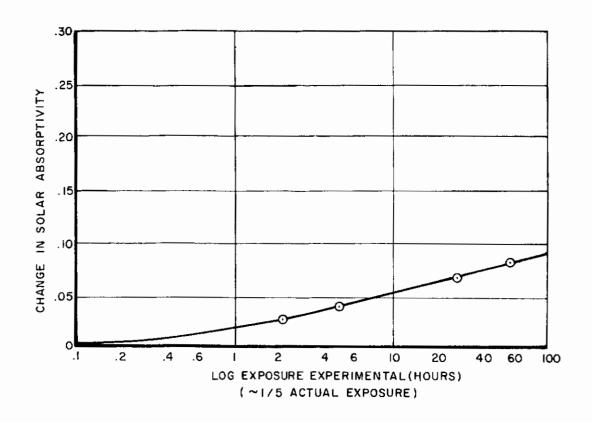
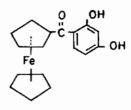


Figure 11. Increased Absorption of Melamine Formaldehyde, a "Stable" Polymer After Schmitt and Hirt, 7th Quarterly Progress Report, Contract AF 33(616) 5945, October 1960

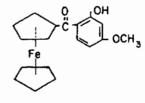
STRUCTURE

NAME

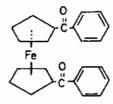
2-hydroxybenzoyl ferrocene (HBF)



2,4-dihydroxybenzoyl ferrocene



2-hydroxy-4-methoxy benzoylferrocene



1,1'-dibenzoylferrocene

Figure 12. Metallocene U. V. Absorbers After Schaaf, WADD TR 61-108, April 1961.



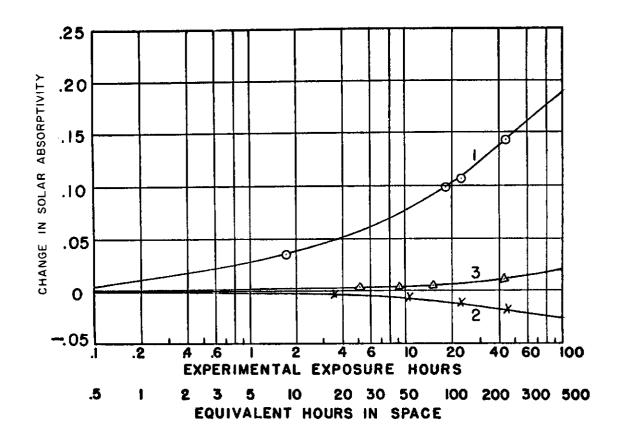


Figure 13. Photodegradation of a Silicone Alkyd.

- 1. Unprotected
- 2. Protected with 1% HBF
- 3. Protected with 5% HBF

After Schmitt and Hirt, Eighth Quarterly Progress Report, Contract AF 33(616)5945, January 1961



- 1. Dissociation and evaporation
- 2. Loss of adherence and shock resistance
- 3. Change in optical or temperature control properties
- 4. Diffusion

Figure 14. Effects of Space on Ceramic and Anodic Coatings

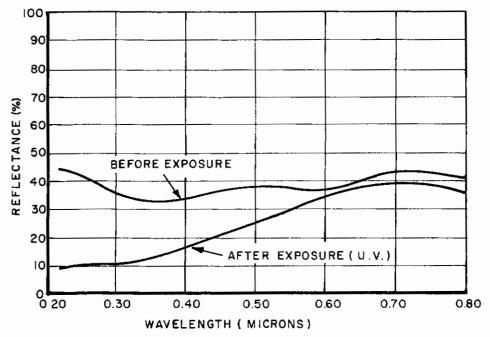


Figure 15. Change in Reflectance of Anodized Aluminum After 100 Hours of Ultraviolet Light Exposure (After Cowling, et al, WADD TR 60-773, 1960)

- 1. Evaporation
- 2. Sputtering
- Optical Properties
 Roughening or Smoothing
 Vacuum Deposition
- Physical Properties
 Creep
 Friction

Figure 16. The Effects of the Space Environment on Metals and Metallic Coatings