

# Contrails

## The Design of Organic Coatings for Use in the Space Environment

by

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It has been established that positive measures of temperature control are essential to the satisfactory operation of all types of instrumented and manned aerospace vehicles. The methods by which such control of temperature might be achieved can be classified as either active or passive. Active techniques are those by which electrical, mechanical, chemical or nuclear mechanisms are utilized within the vehicle to generate and distribute heat energy. Passive techniques are those measures which are static in nature, incorporated at the time of design, and therefore, not readily amenable to change while the vehicle is in operation. Passive methods include selection of the basic materials of construction, insulation, and various types of surface treatments.

Of all these methods for controlling the temperature of spacecraft and satellites, the most important are passive techniques which involve those measures which determine the function of the vehicle's surface in the exchange of heat with its surroundings. In the vacuum of space, all exchange of heat between a body and "cold" space must be by electromagnetic radiation. If excessive heat is generated within a space vehicle by its power sources, this excess must be dissipated radiantly from the body to cold space; or, if on balance the craft radiates energy at a higher rate than it absorbs heat from the sun and planets, then the deficiency must be made up from its own internal sources of power generation. And, of course, if its solar absorptivity is greater than its own emissivity, the vehicle will overheat. The complexity of controlling the heat balance is made more difficult by orbit, space and shape factors, but it has been shown mathematically that all of these problems are surmountable through the application of established scientific principles - if engineers and scientists can design proper materials for the job. The varying degrees of success already attained with scientific space probes, and orbiting vehicles, has pointed up both the existence of the temperature control problem as well as a logical approach to its solution.

A number of different types of surfaces, including organic coatings, have been used successfully in designing for specific heat balances within the various scientific spacecraft which have been launched. Perhaps the two most important questions, as yet unanswered, regarding these coatings are (1) how long will they remain serviceable in the space environment? and (2) what are the capabilities of current technology in providing a variety of practical surface coatings having the required

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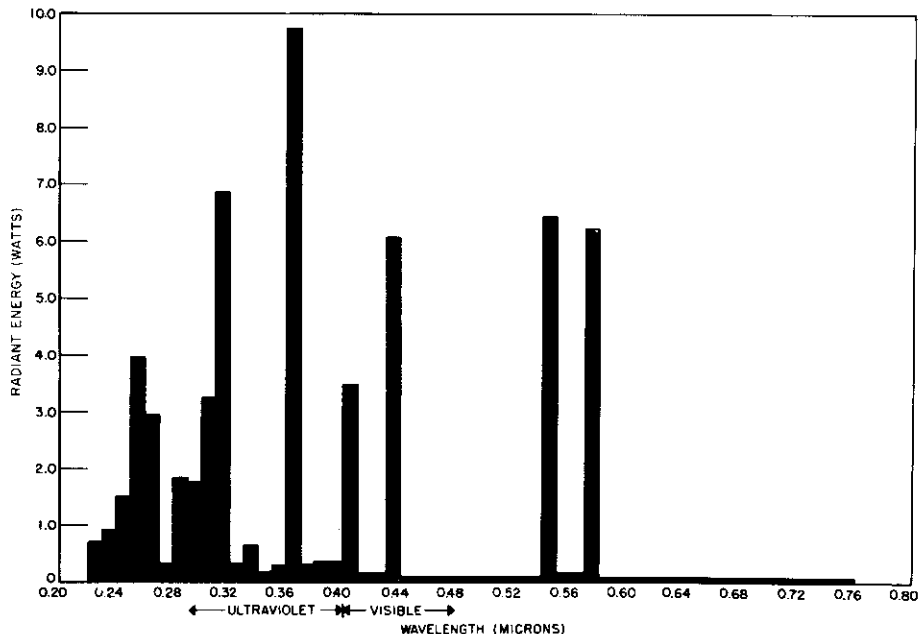
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absorbitivity-to-emissivity ratios to meet any and all design criteria? It is the objective of the U. S. Naval Research Laboratory to provide answers to these two questions insofar as they apply to organic coatings.

Experience has accustomed us to the degradation of surface coatings by their terrestrial environments. However, insufficient knowledge of the environmental factors which will be found in space as yet prevents a reliable prediction of the serviceability of organic coatings, as well as many other materials, in the space environment. Within the earth's atmosphere, organic coatings normally are degraded by oxygen, water vapor and sunlight, in addition to whatever local factors exist (i.e., industrial fumes, salt, abrasives, etc.). Sunlight is the only one of these factors which is believed also to have a marked effect on organic coatings beyond the influence of our atmosphere. In space, sunlight will be very much more intense than at the earth's surface, particularly in the ultraviolet region of the spectrum. In addition, the extreme vacuums of space may promote rapid volatilization of some organic materials, and relatively wide temperature extremes may be encountered. It has been determined, however, that for spacecraft of practical design, in close-in orbits, the maximum temperatures can be held well within the capability of a number of existing coating resins. It is more difficult to ascertain the minimum temperature which may be encountered when the vehicle is in shadow of the earth. For a space research device such as ECHO-1, which consisted of a film of MYLAR bearing an evaporated aluminum coating, it has been estimated that a minimum temperature was reached within five minutes of the time it passed into shadow of the earth (1). The minimum temperature reached is not known, but may have been well below  $-100^{\circ}\text{C}$ . Most organic materials at such low temperatures are very brittle. Hence, it may be that in space, low temperatures will have a relatively greater influence on the serviceability of an organic coating than the maximum temperatures likely to be reached.

Very little is known of the magnitude of other factors, such as meteoric dust and corpuscular radiation, which certainly will have a deleterious effect on most materials, but which, it is hoped, will have such a low rate of incidence on spacecraft as to be of no consequence insofar as the practical consideration of materials deterioration is concerned.

It appears highly improbable that anyone will accurately simulate a space environment in a terrestrial laboratory in the near future. Therefore, practical experiments must be designed to investigate one or another - perhaps in a few cases - simultaneously two of the parameters which appear likely to affect the serviceability of surface materials in space. The U. S. Naval Research Laboratory currently is particularly interested in determining the effect of intense ultraviolet energy on organic coatings in an atmosphere of air at pressures in the range of  $1 \times 10^{-5}$  mm of mercury or lower. For most experiments, the Laboratory has used a mercury vapor lamp, Type UA-3 manufactured by the General Electric Company. The spectrum of this lamp is indicated in Figure 1.



**Figure 1 - Spectrum of UA-3 Mercury Vapor Lamp  
from 0.22 to 0.76 Microns**

A few experiments have been carried out with a hydrogen discharge lamp which provides significant ultraviolet energy at wavelengths as low as 1150 Angstroms (2).

A large number of organic coatings, both pigmented and unpigmented, have been studied to determine the degree to which their optical and physical properties have been altered by exposure to the stated conditions. The first such experiments were conducted on clear (i.e. unpigmented) resins. For comparative reasons, specimens of each coating were irradiated both in air, at ambient temperature and pressure, as well as under the vacuum conditions. The detailed results of these early studies have been published by the Naval Research Laboratory (3,4,5) and will be only summarized here for purposes of providing background information pertinent to more recent work. The most significant findings based on these early studies were as follows:

(1) The photodegradation of organic polymers in a vacuum is much less rapid than in a normal atmospheric environment for equivalent amounts of ultraviolet radiation. In a normal atmosphere containing oxygen and water vapor, the usual dominant photochemical reaction appears to be scission of the polymer chain, whereas in a vacuum the usual "degradation" reaction is crosslinking. Crosslinking does not deleteriously affect a coating's properties unless it becomes excessive, in which case embrittlement, shrinkage and loss of adhesion may result. Crosslinking is fundamentally much less harmful than scission from the point of view of the coatings technologist.

# Conclusions

(2) As a class, the silicone resins demonstrated the best overall balance of film properties in air and the simulated space environment. This finding was based upon comparative studies which also included alkyds, phenolics, vinyls, styrenated alkyds, melamines, urea formaldehyde and acrylic ester resins.

(3) In general, all of the clear polymer films became very strong absorbers of ultraviolet energy after a few hours of exposure to the experimental conditions. Of course, some resins inherently are strong absorbers of ultraviolet energy under any circumstances, but in these experiments even those resins such as the methacrylates and urea formaldehyde, which ordinarily are not considered to be strong absorbers of UV energy, became strong absorbers after a brief period of irradiation. Obviously, the initially slight absorption of ultraviolet energy by these films rapidly produced compounds which strongly absorb ultraviolet radiation.

(4) Weight loss through volatilization of unpigmented polymers varies widely and appears to be directly related to the opposing reactions of crosslinking and scission. It will be shown subsequently (Table I) that volatilization is much reduced if the polymer films are pigmented. Volatilization of the silicone, melamine, and urea formaldehyde resins was slight to moderate in a normal atmosphere. Under the vacuum conditions, volatilization of the silicone resin was very slight even in the unpigmented film-form. This finding was particularly significant in selecting silicone resins as the principle matrix class for subsequent pigmentation studies. Melamine and urea formaldehyde resins were considered less suitable because of the need, and usual practice of using them in combination with nondrying alkyds.

(5) There was no observable difference, qualitatively speaking, between the reactions induced by the 'near' and 'far' ultraviolet irradiation of unpigmented organic films in a vacuum. Quantitative differences were observed, more or less in proportion to the relative intensities of the two energy sources. As the mercury vapor lamp was the more intense, films irradiated by it were the more rapidly discolored and insolubilized, the latter phenomenon being interpreted as attributable to crosslinking.

Upon completion of the experiments leading to the above findings, the study of pigmented organic coatings under similar conditions was commenced. For simplicity, and to minimize the number of variables, the first formulations consisted of one pigment and one resin. Although these experiments have included formulations at three pigment-volumes (20%, 30%, and 40%), most of the work to date has been conducted on formulations having a pigment-volume (PV) of 30%. Also, most experiments thus far have employed a phenylmethyl silicone matrix, though some have been conducted using other binders such as the acrylic, urea formaldehyde, melamine formaldehyde, epoxy and urethane resins.

The pigmented coatings have been applied to anodized aluminum panels in film thicknesses of 2 mils by means of a draw-down applicator. Follow-



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ing proper curing, the specimens were irradiated in a vacuum apparatus which is illustrated by Figures 2 to 4, inclusive. Pressures were maintained at  $1 \times 10^{-5}$  mm of mercury or lower. The intensity of energy falling on the samples was .75 calories per minute, approximately half of which is below 0.4 microns. The total exposure period was 100 hours, but was interrupted at intervals to make weight loss and reflectance measurements on the samples. The total spectral reflectance of each sample, as referenced to a freshly smoked magnesium oxide standard, was measured between 0.22 and 2.7 microns using a Beckman Model DK-2 Spectrophotometer with reflectance attachment. At the conclusion of the test, the irradiated specimens were compared with identical unirradiated samples for adhesion, flexibility, and general appearance.

Figures 5 to 8 inclusive show the total reflectance curves of several pigmented silicone resin formulations. Figures 9 and 10 have been included in order that a comparison may be made of the pigmented coatings with two standard types of uncoated metal surfaces. Minor "peaks" and "valleys" in the exact spectrophotometer traces have been averaged in the curves of the accompanying figures. The reflectance values obtained have, in each instance, been shown over two wavelength spans. This has been done in order to more clearly illustrate the changes in spectral reflectance which occurred in the lower wavelength regions of the spectrum, i.e., below 0.8 microns, which region is included in the top curves of figures 5 to 10, inclusive. The rapid and large decrease

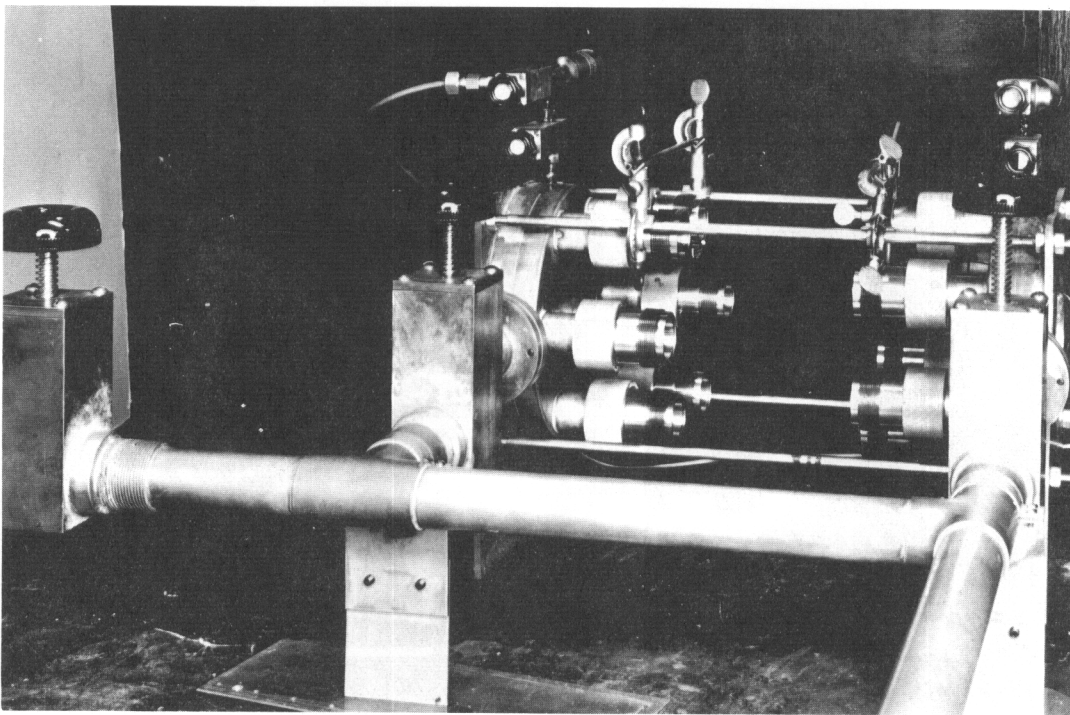


Fig. 2 - Vacuum Manifold for Twelve Sample Compartments  
(Quick-Couplings in Place)

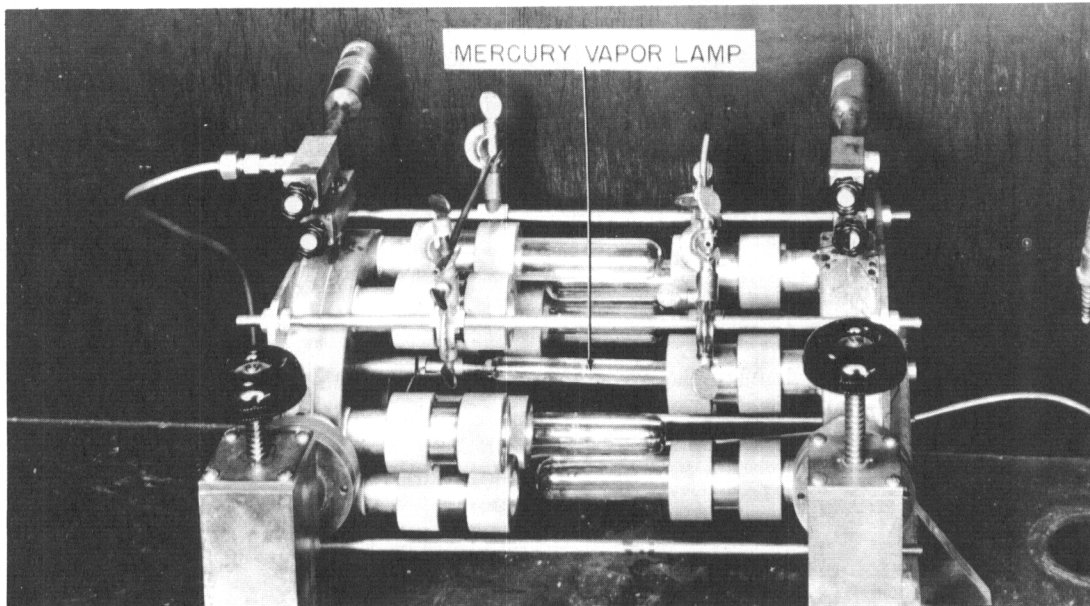


Fig. 3 - Partial Assembly of Vacuum Manifold and Sample Compartments Showing Position of Mercury Vapor Lamp

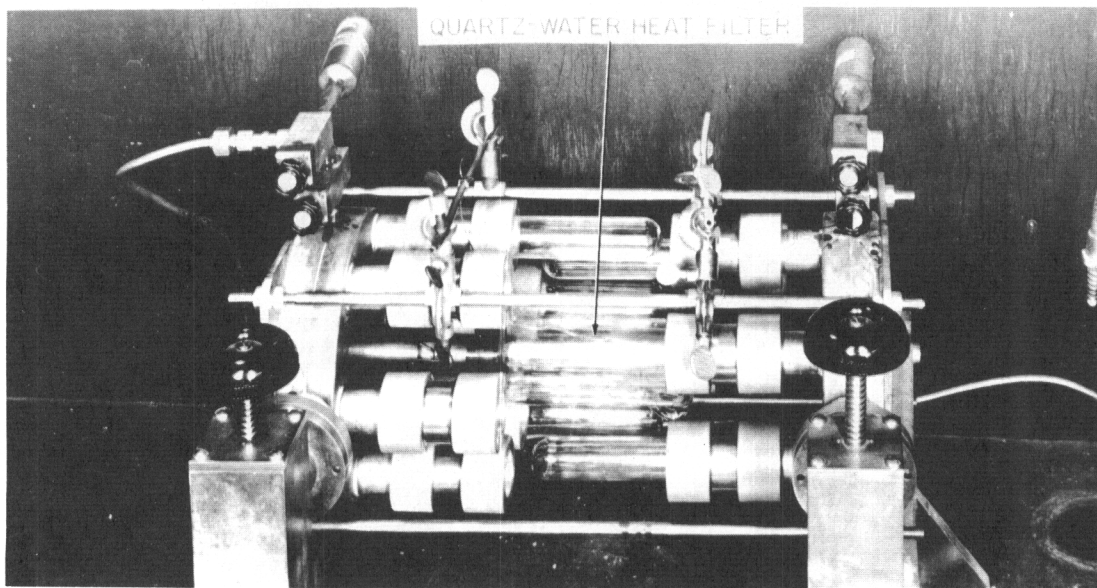


Fig. 4 - Partial Apparatus Assembly Showing Quartz-Water Heat Filter Surrounding Mercury Vapor Lamp

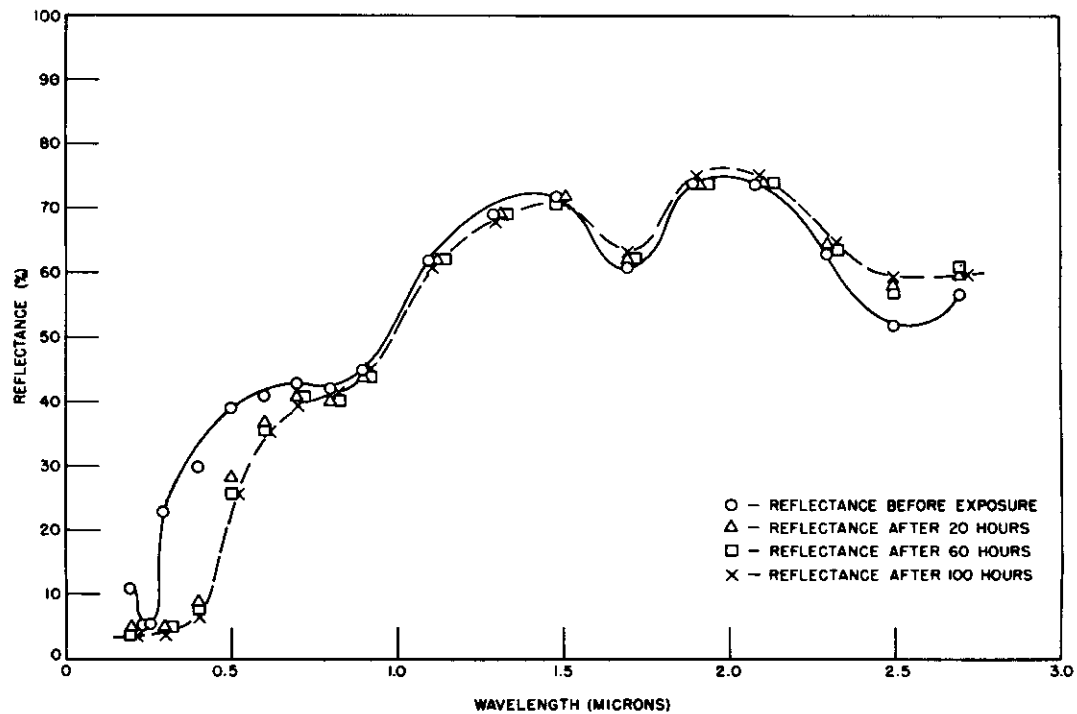
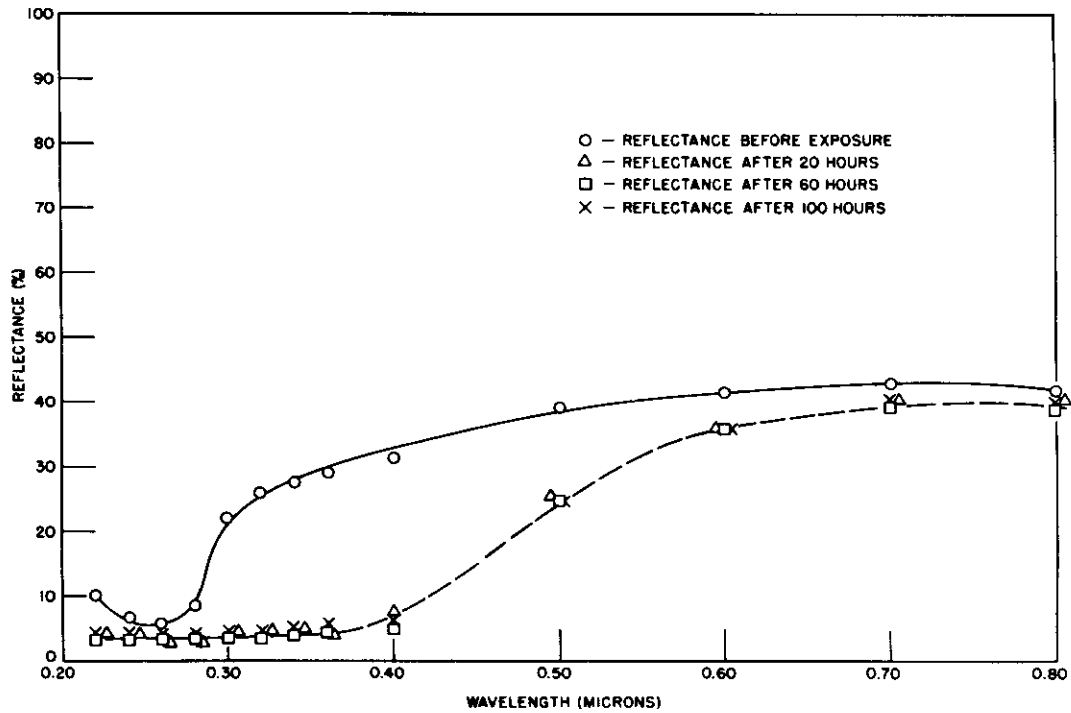


Fig. 5 - Spectral Reflectance of Unpigmented Silicone Resin on Anodized Aluminum



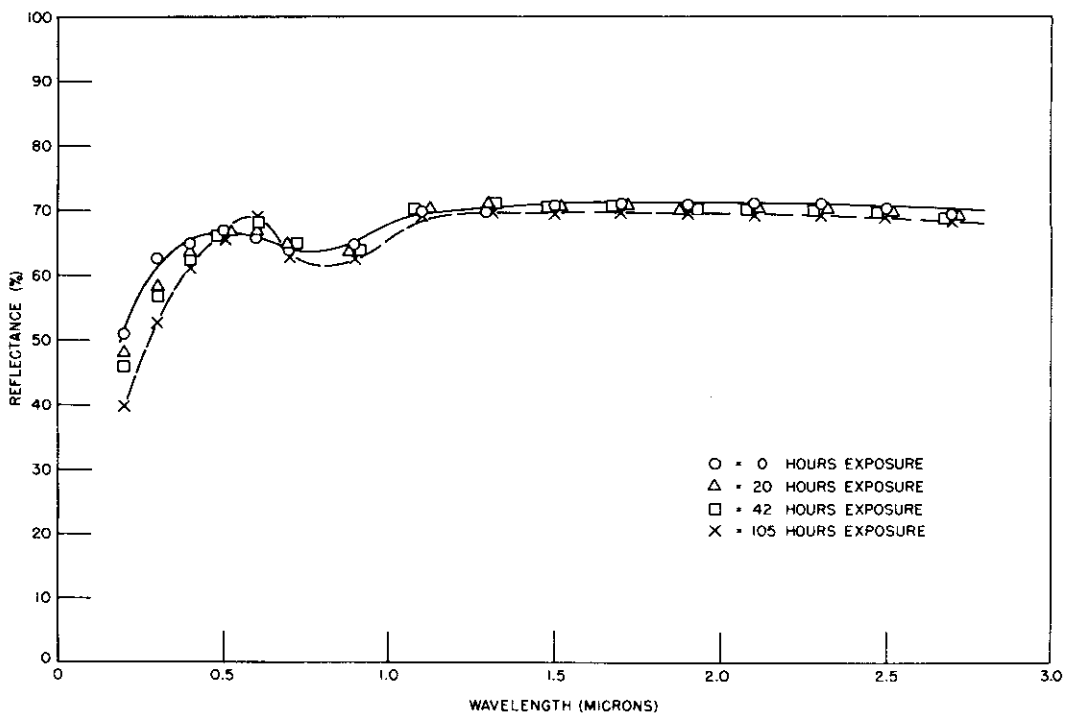
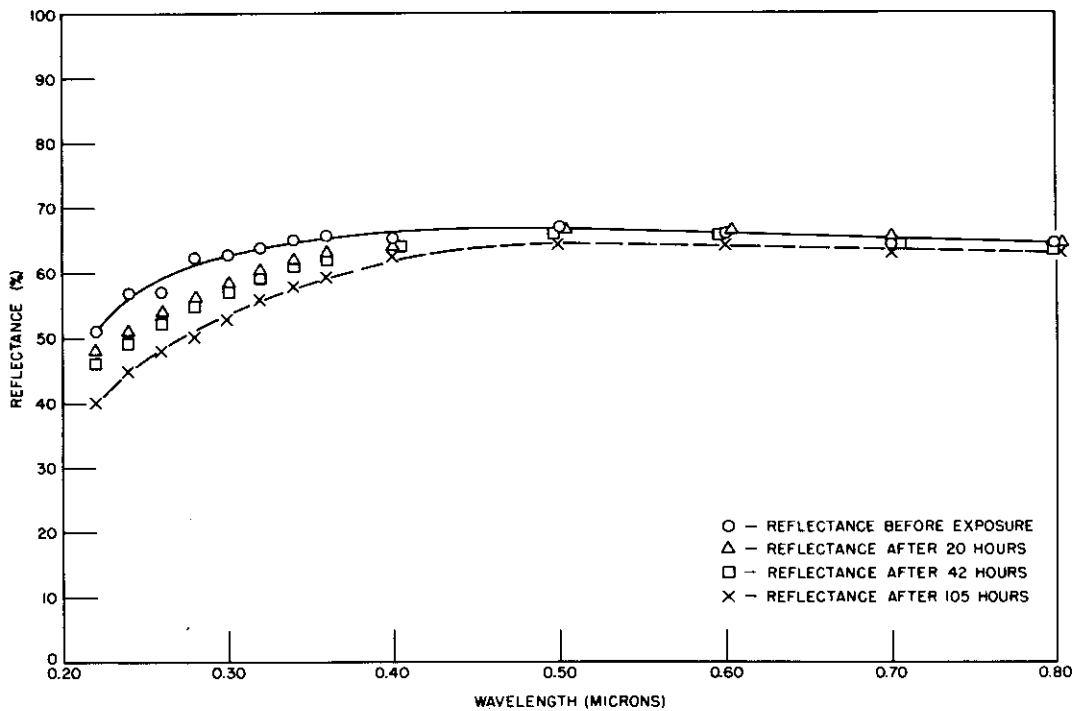


Fig. 6 - Spectral Reflectance of Aluminum Pigment (leafing type) in Silicone Resin



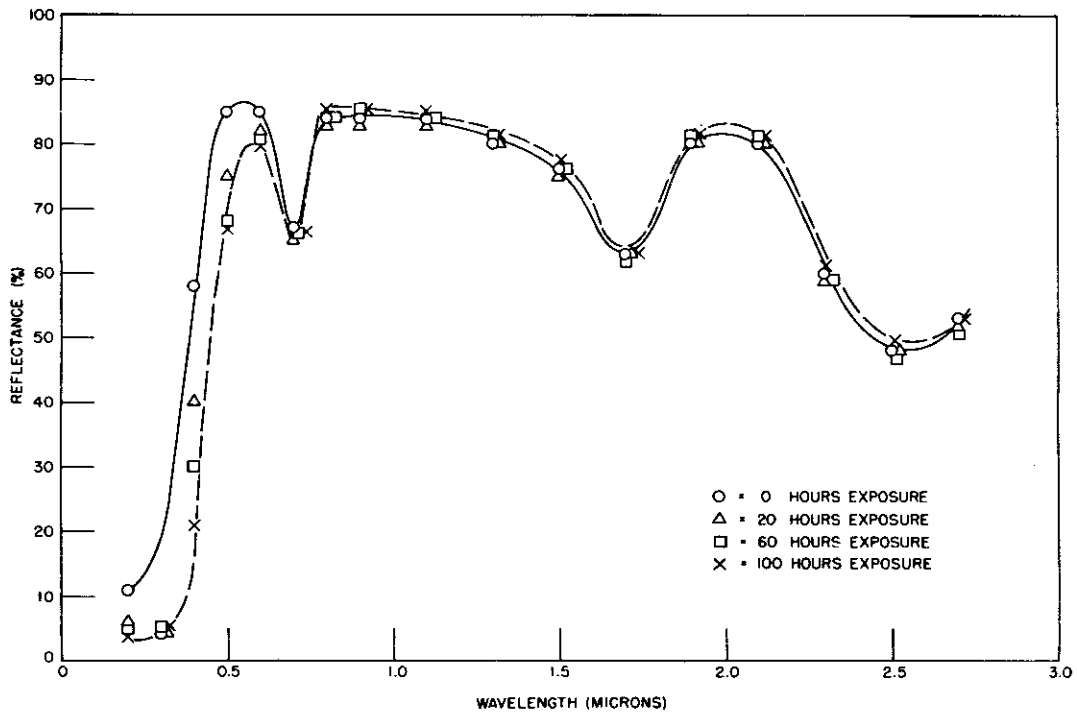
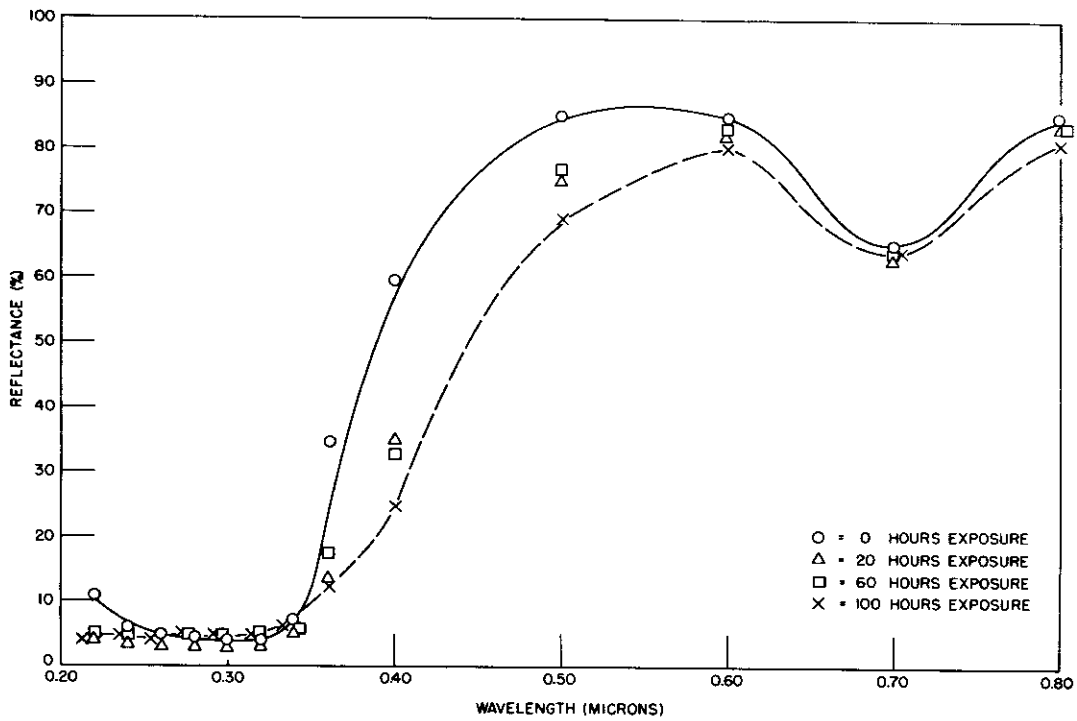


Fig. 7 - Spectral Reflectance of Zinc Sulfide (30% PV) in Silicone Resin

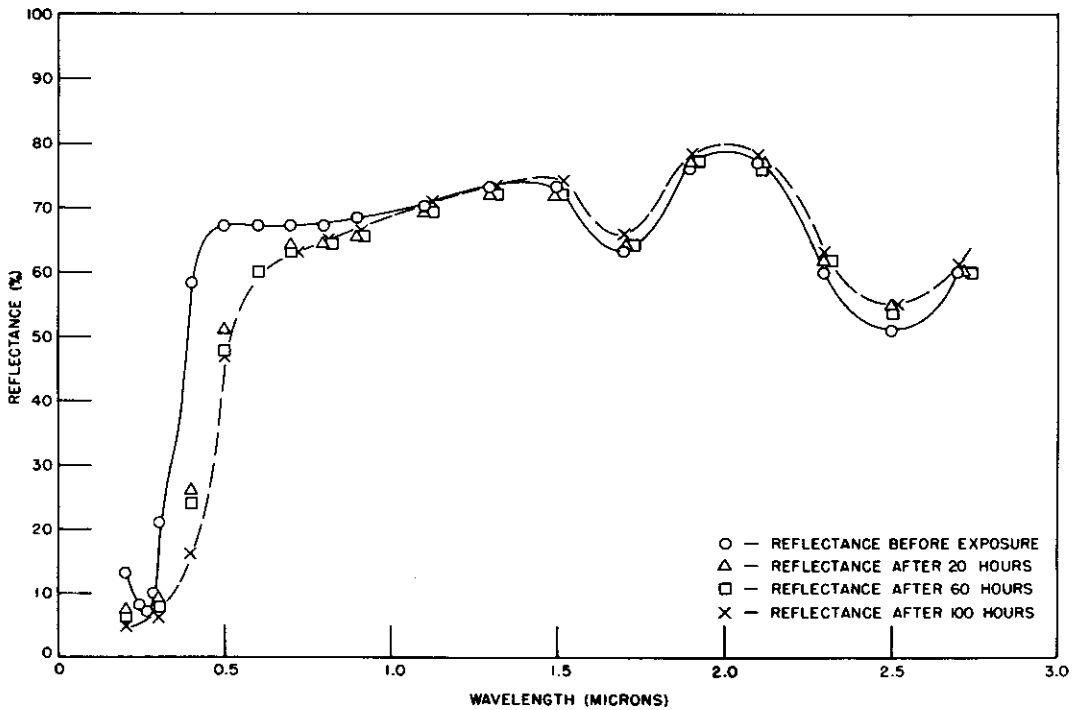
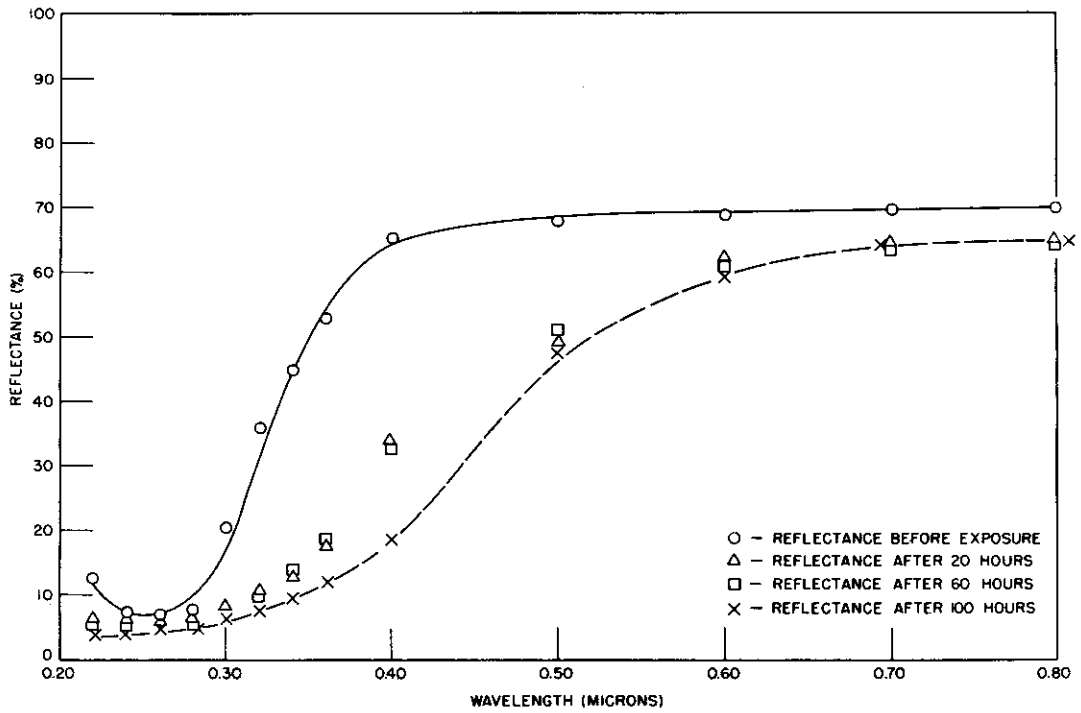


Fig. 8 - Spectral Reflectance of Basic White Lead Carbonate (30% PV) in Silicone Resin

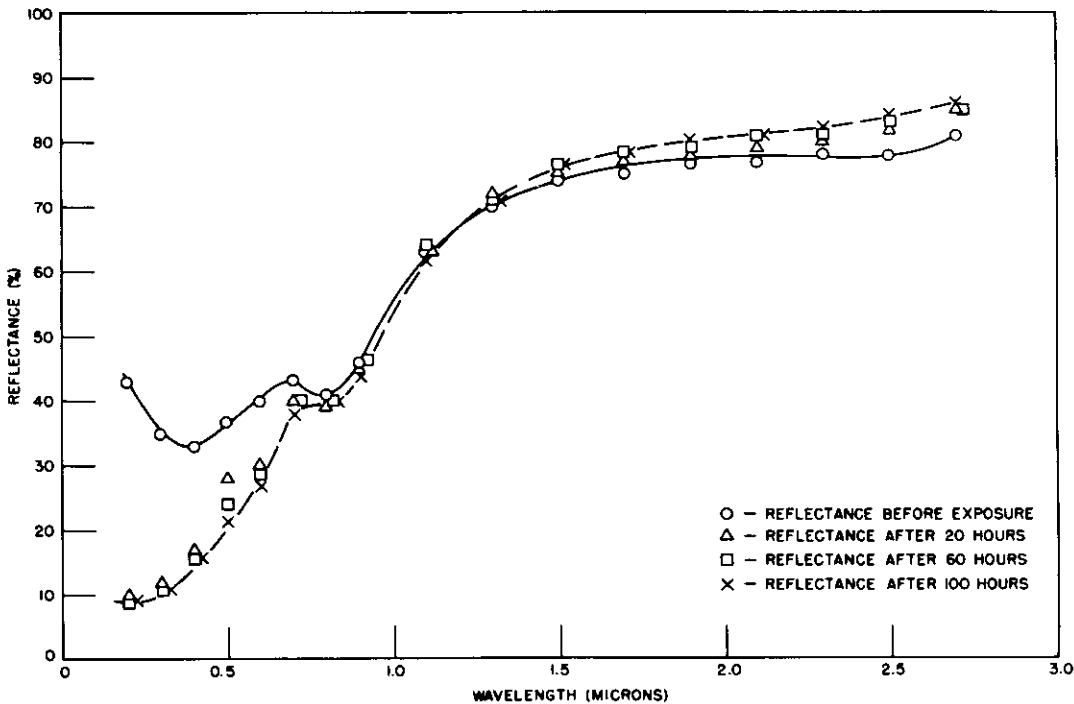
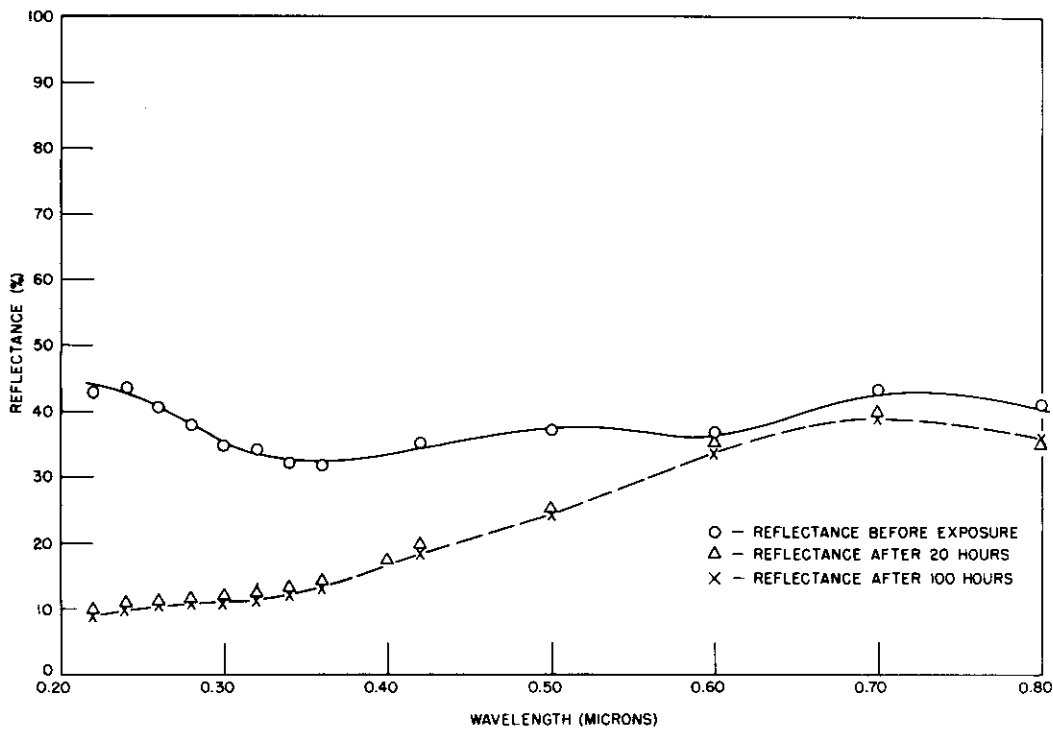


Fig. 9 - Spectral Reflectance of Anodized Aluminum Alloy 24S-T

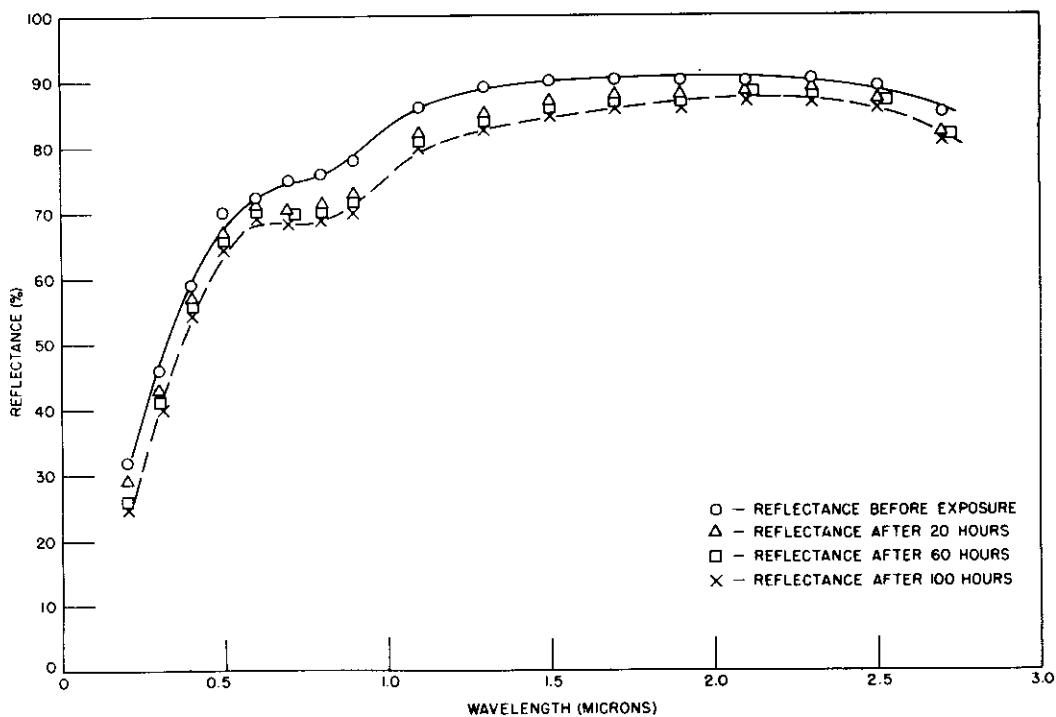
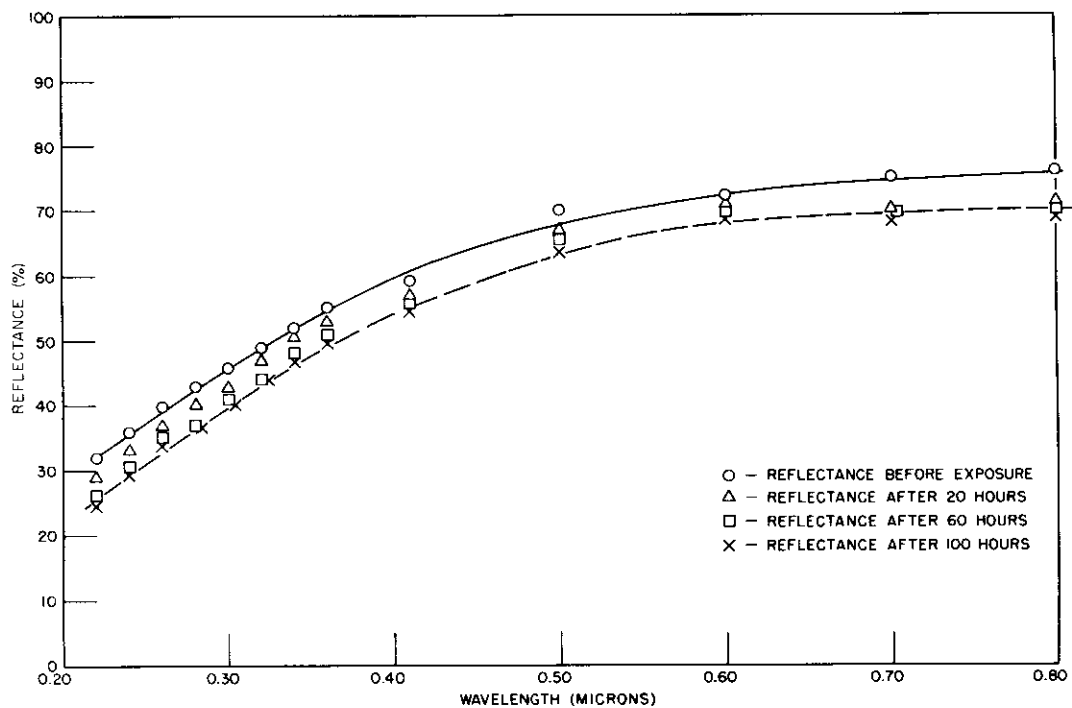


Fig. 10 - Spectral Reflectance of Clean Rolled Aluminum Alloy 24S-T



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in the reflectance of ultraviolet energy by most of these surfaces as exposure progressed is most striking in those coatings which contain the granular type pigments. In contrast, the reflectance of the coating pigmented with a leafing aluminum decreases very little over the 100-hour exposure period. The large decrease in the reflectance of anodized aluminum was a surprise finding. This result has been obtained with aluminum anodized by both the chromic acid and sulfuric acid processes. The slight decrease in reflectance of the clean 24S-T alloy is possibly attributable to condensation of volatiles evolved elsewhere in the vacuum equipment.

In general, the weight loss through volatilization of pigmented coatings has been insignificant. Table 1 presents typical results of weight loss studies conducted on the coatings subjected to the simulated space "atmosphere" for 100 hours. Table 1 also presents an evaluation of other essential film properties following the period of irradiation.

There is considerable visible evidence that the effect of ultraviolet energy on pigmented coatings in a vacuum is limited to the surface region of the coatings, and that the properties of the films are not deleteriously affected below the depth penetrated by the ultraviolet radiation. If the irradiated coatings are abraded with a knife or fine sandpaper, a fresh, white surface is again exposed.

Although a very large amount of the work to date has been carried out using coatings having a pigment-volume content of 30%, a few studies have been completed on the effect of variations in the pigment volume content. As would be a logical expectation, the efficiency of a coating in reflecting light energy may be improved if its content of an appropriate pigment is increased. However, experience has shown that such an increase in pigmentation is likely to be accompanied by a sacrifice in adhesion and flexibility. Just how great a compromise of this sort can be made is yet to be determined, but the requirements for adhesion and flexibility in a spacecraft coating may not be so exacting as for an aircraft coating.

The theoretical solar absorptance of a coating can be determined with good accuracy by subtracting the integrated solar reflectance from the integrated solar emission spectrum. The computed values, of course, should be corrected for the reflectance of the reference standard, magnesium oxide. Since the sum of the reflected and absorbed energy by a surface coating at each wavelength equals the total energy of each wavelength falling on the surface, the spectral absorptance can be obtained indirectly from the reflectance measurements. The significance of such data with respect to the probable efficacy of two of the experimental coatings, if used on spacecraft, is shown by Figures 11 and 12. The curves in these two figures are based upon reflectance measurements on the two coatings after exposure to the experimental space environment for 100 hours.

The hemispherical emittance (primarily infrared emittance) of a spacecraft material is relatively difficult to obtain. The Laboratory

Table 1  
Physical Evaluation of Coatings Before and After Ultraviolet Irradiation in a Vacuum of  $1 \times 10^{-5}$  mm Hg

Coating Formulation	Test period (hr)	Flexibility - Mandrel:			Adhesion (a)	Color	Weight loss (%)	Quality - Remarks
		1/4 inch	3/16 inch	1/8 inch				
Phenylmethyl silicone (unpigmented)	0	S	S	S	E	Colorless	-	Tough & flexible
	100	U	U	U	G	Amber	0.63	Hard - brittle
Leafing aluminum in silicone	0	S	S	S	G	Metalllic	-	Tough & flexible
	100	S	S	S	G	Metalllic	0.08	Tough & flexible
Zinc sulfide (30% PV in silicone) (b)	0	U	U	U	E	White	-	Cracks on bending
	100	S	S	U	E	Slight yellow	0.05	Hard
Antimony oxide (30% PV in silicone)	0	S	U(c)	U(c)	E	White	-	Hard & slightly brittle
	100	S	U(c)	U(c)	E	Slight yellow	1.27	Hard & brittle
Calcium carbonate (30% PV in silicone)	0	S	S	S	E	Grayish	-	Tough & flexible
	100	S	S	U	E	Dark amber	0.34	Hard & slightly brittle
China clay (30% PV in silicone)	0	S	S	S	G	Dark gray	-	Tough & flexible
	100	S	S	S	G	Dark amber	0.80	Tough & flexible
Basic white lead carbonate (30% PV in silicone)	0	S	S	U	E	White	-	Hard & slightly brittle
	100	S	S	U	G	Slight yellow	2.92	Hard & slightly brittle

(Continued)

Table 1 - Continued

Coating Formulation	Test period (hr)	Flexibility - Mandrel:			Adhesion (a)	Color	Weight loss (%)	Quality - Remarks
		1/4 inch	3/16 inch	1/8 inch				
Basic white lead carbonate (40% PV in silicone)	0	U	U	U	White	-	Hard & brittle	
	105	U	U	U	White	0.89	Hard & brittle	
Butyl methacrylate (unpigmented)	0	S	S	S	Colorless	-	Soft	
	105	S	U	U	Amber	62%	Brittle	
Basic white lead carbonate (40% PV in butyl methacrylate)	0	S	S	U	White	-	Slightly brittle	
	105	S	S	S	White	4.26	Slightly brittle	
Butylated urea formaldehyde (unpigmented)	0	S	S	S	Colorless	-	Hard & flexible	
	105	U	U	U	Amber	14.8	Hard & brittle	
Basic white lead carbonate (40% PV in urea formaldehyde)	0	U	U	U	White	-	Brittle	
	105	U	U	U	White	5.81	Brittle	

(a) E: excellent, G: good, S: satisfactory, U: unsatisfactory.

(b) PV: pigment-volume ratio.

(c) Slight surface cracks not extending through the coating.

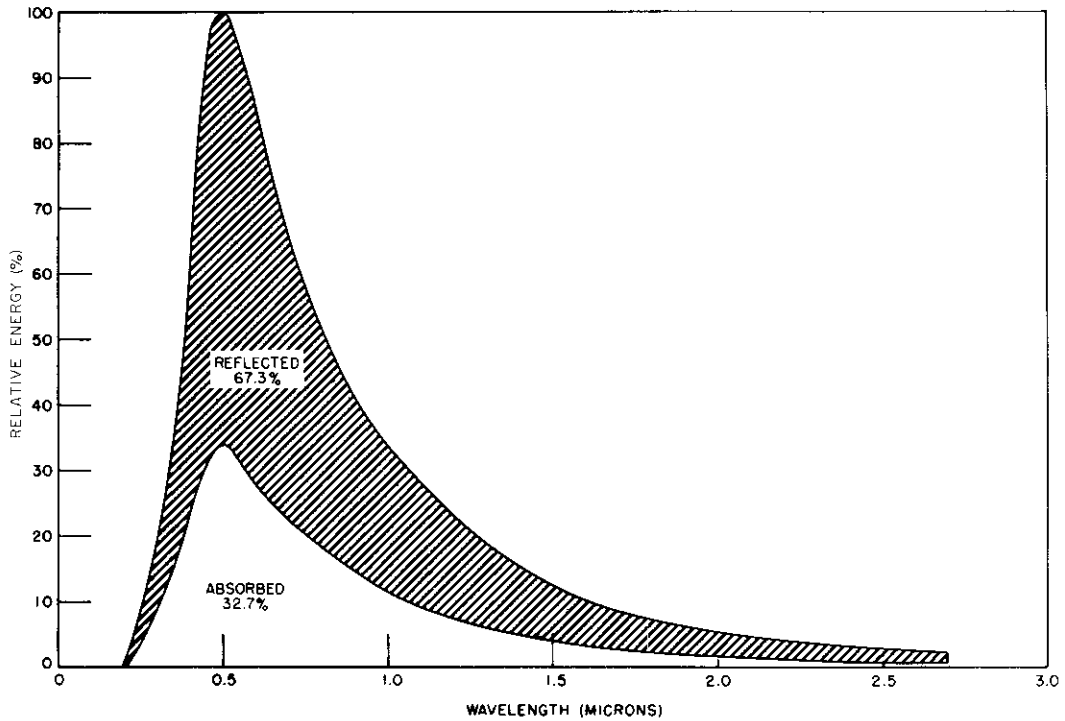


Fig. 11 - Proportion of Solar Energy Reflected vs Absorbed by Leafing Aluminum in Silicone Varnish

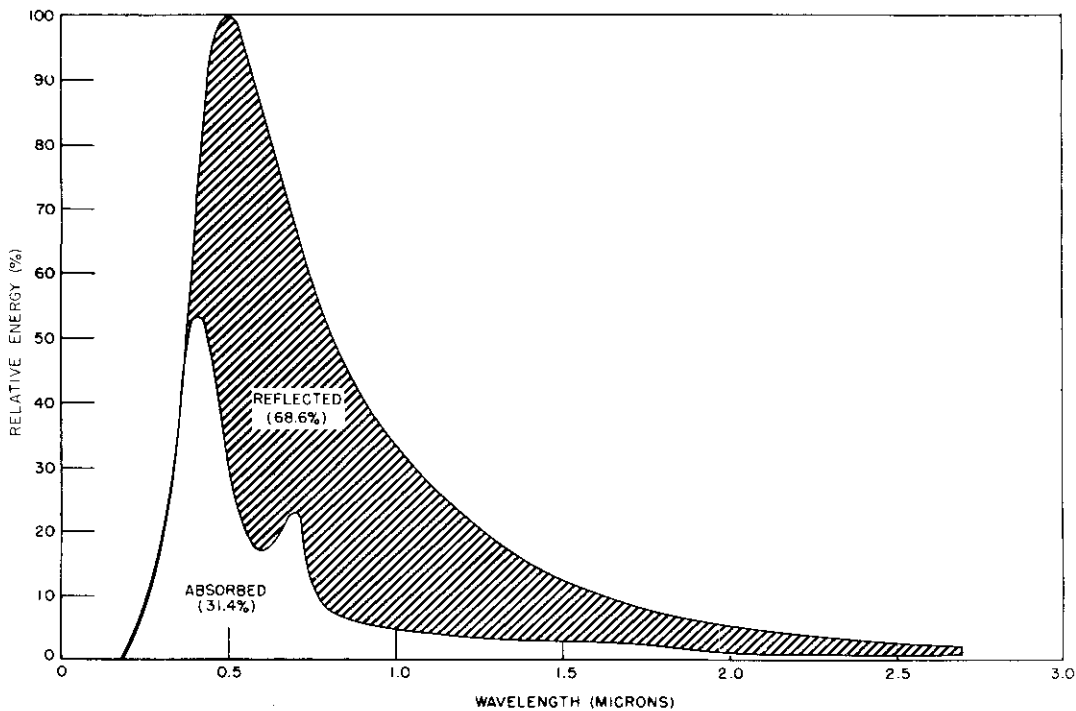


Fig. 12 - Proportion of Solar Energy Reflected vs Absorbed by 30% PV Zinc Sulfide in Silicone Varnish



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has determined the normal emittance of some of its experimental coatings for the temperature of 100°C (7). According to Jakob (8), hemispheric emittance bears a rather precise relation to the normal emittance, and therefore can be computed. Table 2 gives the normal emittance values of some typical coatings.

Table 2

The Normal Emissivities of Typical Surface Materials  
at 100°C. (Not exposed to ultraviolet irradiation  
in a vacuum)

<u>Sample</u>	<u>Emissivity</u>
(All organic coatings of 2 mil thickness on anodized aluminum)	
Black silicone paint	0.88
White (30% PV zinc sulfide) silicone paint	0.77
Clear (unpigmented) silicone varnish	0.74
Anodized 24S-T aluminum (uncoated; chromic acid process)	0.55
Aluminum (leafing pigment) silicone paint	0.33
Krylon (control)*	0.90

\* This coating, used by the Division of the Laboratory making these measurements, may have been of greater thickness than 2 mils.

Other interesting observations made in course of these studies are the temperatures of the various specimens as they undergo irradiation. Obviously the relationship between the absorptance and emittance of each specimen significantly affects its temperature in the test equipment, just as it will determine the equilibrium temperature of a similar body in space. In these experiments each coating has been applied to a 1" x 3" anodized aluminum strip which is .020 inches thick. Temperature is sensed by a thermocouple attached to the non-irradiated side of the panel. There is, of course, some loss of energy from the specimen by the conductive process, but such loss is not great in comparison with energy which is radiated by surfaces that are good emitters (i.e., paints, organic materials, and numerous metal oxides). However, the conductive heat losses are great in comparison with the emission of energy by a clean, smooth metallic surface. The temperatures which have been noted for several of the sample materials as they undergo irradiation in the vacuum chambers are given in table 3.

Table 3

Temperature of Sample Materials when Exposed in  
The Laboratory's Simulated Space Environment

(All organic coatings of 2 mil thickness on anodized aluminum,  
facing lamp, unless otherwise indicated)

<u>Sample</u>	<u>Temperature</u> (°C)
1. Black silicone paint	87°
2. Black silicone paint on <u>both</u> sides of panel	84°
3. White (30% PV zinc sulfide) silicone paint	84°
4. White (30% PV zinc sulfide) silicone paint on both sides of panel	73°
5. Aluminum (leafing type) silicone paint	97°
6. Unpigmented silicone varnish	89°
7. Anodized aluminum (uncoated)	107°
8. Anodized aluminum panel with black silicone paint on reverse side	78°
9. Clean, rolled, nonanodized 24S-T alloy	127°

The "a/e" values for the black, aluminum, and zinc sulfide pigmented coatings are approximately 1.1, 1.0, and 0.4, respectively. The values for the other surfaces have not been determined. The temperatures indicated in table 3 are not an indication of the equilibrium temperatures of these samples were they in a true space environment, because of great differences in the spectral distribution and intensity of the Laboratory's source of irradiation as compared to the sun's energy beyond the earth's atmosphere.

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\*It appears that several logical conclusions can be drawn from the experimental results thus far obtained. On the basis of our present technical knowledge, it is practical to formulate organic coatings having "a/e" values ranging between 0.4 and 1.1. Other researchers have reported pigmented organic coatings which provide "a/e" values as low as 0.17 (9) and as high as 1.2 (10). Undoubtedly the ultimate choice of any pigmented coating must be something of a compromise between essential physical properties, such as flexibility and adhesion, versus its optical characteristics.

It is apparent that much additional study is required before an accurate answer can be given to the question of how long an organic coating can be expected to perform its intended role on the exterior of a space vehicle. Because of the great difficulty, if not impossibility, of accurately simulating a space environment in the laboratory, it appears that ultimately an experiment must be designed to evaluate the most promising coatings on a vehicle in space.

While a precise answer to the question of coating serviceability in space is not yet at hand, the Laboratory's experiments have turned up some facts which certainly will have a bearing on the eventual answer. Probably the most significant finding of this research to date is the fact that, with exception of the coatings pigmented with leafing aluminum, the effectiveness of all organic coatings in reflecting ultraviolet energy diminishes rapidly on exposure. In most cases, 80-90% of the decrease in reflectance of ultraviolet energy occurs during the first 10-20 hours of exposure to the simulated space conditions. Furthermore, in many cases the efficacy of the coatings in reflecting the lower wavelength visible spectrum concurrently decrease substantially. Coatings containing leafing aluminum as a pigment show a relatively slight (5-10%) decrease in reflectance under the conditions of the experiment.

It is the Laboratory's opinion that the two silicone coatings containing leafing aluminum and zinc sulfide pigments are suitable for use on the exteriors of some space vehicles, even though their very long term serviceability in a space environment has not yet been established. The white coating is particularly suitable where a "cold" surface is needed to counterbalance a "hot" surface area such as results from the use of solar cells, and unpainted metal.

\*The quantity of data collected from these experiments is too voluminous for its complete presentation in this paper. Some of it has been published recently in NRL Report 5503 (6), and the remainder will appear in subsequent NRL reports. Those observations which are believed to be most significant have been presented.

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## ACKNOWLEDGMENT

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