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NRL Report 5737

THE PROPERTIES OF PAINTS AS AFFECTED BY ULTRAVIOLET RADIATION IN A VACUUM - PART 2

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ABSTRACT

Organic coatings are being studied as one possible means of achieving temperature control within space vehicles. However, their usefulness in the space environment may be limited by their physical and chemical stability in space. It is shown that the optical properties of most organic coatings are changed on exposure to intense ultraviolet radiation in high vacuum. Of the reflective pigments studied, those containing zinc sulfide and leafing aluminum are shown to be most stable to this radiation.

PROBLEM STATUS

This is an interim report; work on this problem is continuing.

AUTHORIZATION

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THE PROPERTIES OF PAINTS AS AFFECTED BY ULTRAVIOLET RADIATION IN A VACUUM - PART 2

INTRODUCTION

This report is the second in a series describing a number of experiments in which pigmented coatings have been exposed to intense ultraviolet radiation in a vacuum of 1×10^{-5} mm Hg. Also included in the studies are some unpigmented coatings, as well as several clean, bare metals, anodized aluminum (alloy 24S-T), and a ceramic. Since the main objectives of this research are concerned with the properties of organic materials, the inorganics are included only for comparison as a matter of interest. For the most part, this report describes experiments with pigmented coatings of high pigment volume. In all instances, the exposure of organic and anodized coatings to the stated conditions has resulted in a significant increase in the absorption of radiation below 0.5μ . However, the reflectance of clean, bright metals (aluminum, copper, and germanium) has not been changed in the course of identical exposure. This is of particular interest in the case of germanium which exhibits typical metallic properties toward relatively short wavelength radiation, but acts more like a nonmetal with regard to the absorption and emission of infrared energy.

SUMMARY OF PRIOR RESEARCH

Early work at this Laboratory demonstrated the deleterious effects of ultraviolet radiation on the optical characteristics of organic coatings in a vacuum (1,2). It also was shown that pigmentation with a properly chosen pigment improved the optical stability of organic film formers (2,3). The pigments most highly reflective to the solar spectrum are rutile titanium dioxide, high-purity zinc sulfide, and basic white lead carbonate. (Anatase TiO_2 has not yet been evaluated.) Coatings pigmented with carbon black or leafing aluminum are optically stable but, of course, exhibit spectral qualities very different from the white-pigmented formulations. Though each pigment has merit for specific applications, no coating formulation yet has been found which maintains a continued high order of reflectance to high-intensity ultraviolet energy during extended periods of exposure in vacuum.

In addition to various pigments, a number of different resins have been studied. It was discovered quite early that some silicones are relatively stable against the laboratory simulation of a space environment (2,4). As with many resins, a marked change in optical properties developed, but on the basis of other essential film properties the silicones are superior to all other resin types studied. With respect to optical properties, acrylic ester resins are superior to other types. Commercial melamine and urea formaldehyde resins also seem good in this respect, but these two types are relatively poor film formers unless copolymerized with other resins such as nondrying alkyds. This report deals with formulations based on only two types of binders - the silicones and the acrylics.

A disadvantage of the silicone polymers is the usual requirement for curing at relatively high temperatures. Typically, an hour or more at temperatures of 350°F and higher is a recommended curing schedule for most silicone coatings. However, in high-temperature applications it is not unusual for these coatings to be allowed to attain proper cure in service from the heat provided by the surfaces to which they are applied. Acrylic copolymers dry as lacquers, and heat usually is not necessary to develop their ultimate properties.

The acrylic of particular interest in the immediate studies is Acryloid A-10, a product of the Rohm and Haas Company. It has proven considerably more stable than other acrylic copolymers previously investigated (3,5).

EXPERIMENTAL PROCEDURE

The general approach in these experiments has been to expose experimental films to intense ultraviolet radiation in a vacuum for a considerable period of time. Figures 1 to 5, inclusive, illustrate the equipment used in these experiments. It is the same apparatus as used earlier (5). In this first group of experiments with pigmented films, the period of exposure was 100 hours in a vacuum of 1×10^{-6} mm Hg. The results of the initial studies indicated that an adequate comparison of coatings probably could be made on the basis of a shorter period of exposure. Also, it was evident that the intensity of light actually falling on the coatings should be determined. This point is particularly significant since it was found that very thin films of organic matter (products of outgassing) condensed on the interior surfaces of the quartz sample compartments and drastically reduced the transmission of ultraviolet radiation. Consequently, methods of monitoring the lamp intensity external to the test compartments are of little value.

The current studies have been designed with five primary objectives in mind. These are as follows:

- a. To determine the intensity of illumination impinging on the coatings under study.
- b. To determine the temperature of the experimental coatings during exposure to the simulated space environment.
- c. To evaluate further the significance of time of exposure on coating properties.

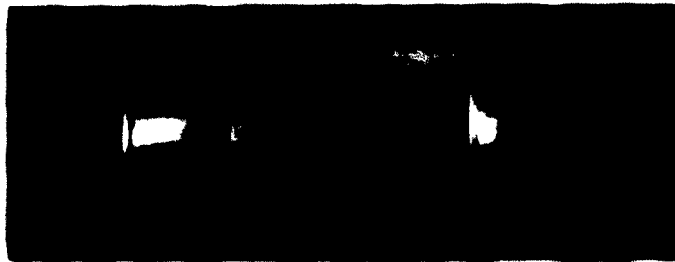


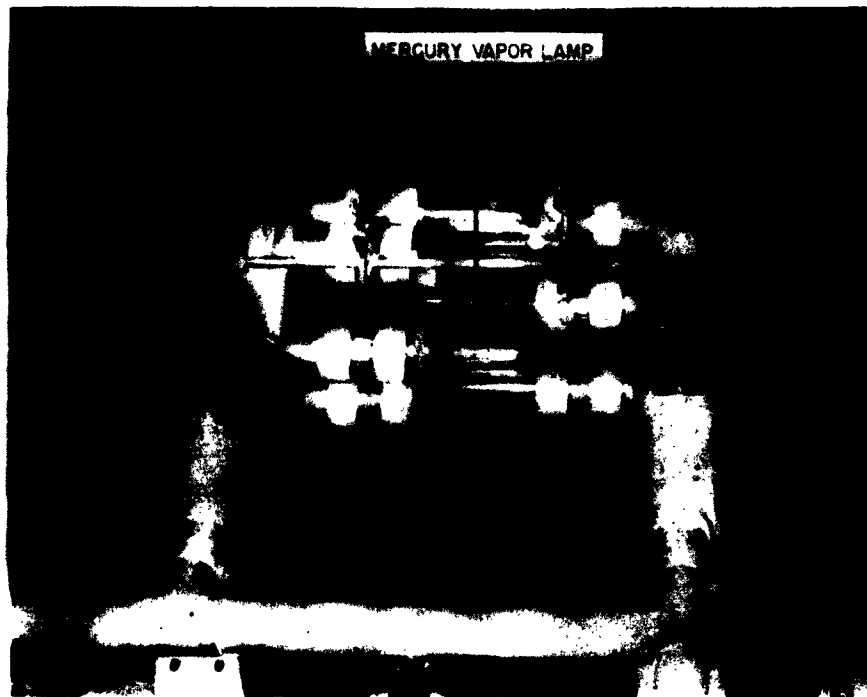
Fig. 1 - Disassembled sample compartment showing quartz tube and quick-coupling connector



Fig. 2 - Assembled sample compartment



**Fig. 3 - Vacuum manifold for twelve sample compartments
(quick-couplings in place)**



**Fig. 4 - Vacuum manifold and sample compartments
showing the position of the mercury vapor lamp**



Fig. 5 - Vacuum manifold and sample compartments showing quartz-water heat filter surrounding the mercury vapor lamp

- d. To continue the evaluation of pigments and pigment-volume ratios as they affect the properties of coatings subjected to the simulated space environment.
- e. To obtain guides for extending the research plan on this problem.

Among the first observations resulting from experiments in this program was the fact that many polymers showed a pronounced tendency to become insoluble. This was interpreted as indicating crosslinking under the influence of ultraviolet energy in a greatly reduced supply of oxygen (i.e., at vacuum of 1×10^{-5} mm Hg)(3). Therefore, it was logical to anticipate that films of silicone polymers might become "cured" as they undergo ultraviolet irradiation in the vacuum. This has been borne out in recent studies which subjected air-dried silicones to simulated space conditions. Only a minimum study has been made of this method of curing silicone coatings designed for use on the exteriors of spacecraft, but this finding appears to reduce considerably the disadvantages of using a so-called baking finish in satellite applications. The only noticeable difference in the properties of silicone coatings polymerized by ultraviolet, as compared to those precured by heat in a normal atmosphere, was the considerably greater outgassing of the air-dried silicone coatings at the outset of irradiation. This phenomenon is a logical expectation and is thought to be of no consequence in the true space environment (but of course, does constitute a problem in the laboratory apparatus). It appears reasonable, then, to formulate silicone coatings that will air-dry sufficiently to permit handling of space equipment to which the coatings are applied, assuming in confidence that adequate curing will be induced by the ultraviolet energy of sunlight in space.

It has been obvious from the outset that the temperature of each specimen in the laboratory would be influenced by many of the same factors that would determine its temperature were the specimen in a true space environment. The most significant factor in determining the equilibrium temperature of coatings in the laboratory, which is not a factor in the true space environment, is the conductive loss of energy through thermocouple

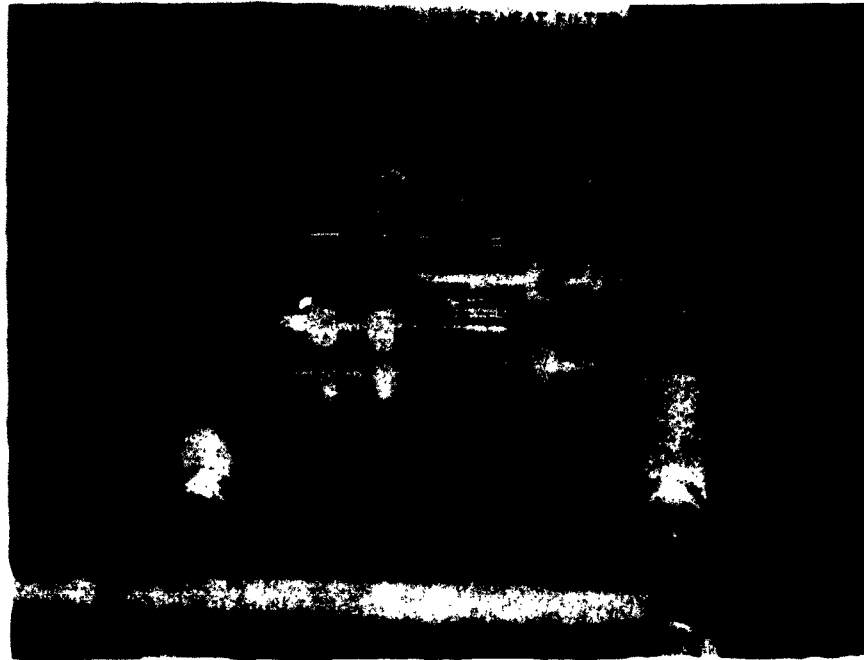


Fig. 5 - Vacuum manifold and sample compartments showing quartz-water heat filter surrounding the mercury vapor lamp

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leads and through the small, pointed springs used to hold each test panel in a fixed position. If the conductive energy loss could be determined, and if the absorptance and emittance of a sample were known, then it would be possible to calculate the intensity of radiant energy impinging on a specimen. Temperature equilibrium exists when the rate of absorption of energy by a specimen equals its rate of energy dissipation. With this concept in mind, an experiment was designed to determine the intensity of the radiation impinging on the coatings under study.

There are no established standard surfaces for which the total emittance is known over a range of moderate to low temperatures (0 to 100°C). It is believed, though, that a highly pigmented black silicone coating is an acceptable working standard for our studies. This coating was selected as an emittance standard, not because of its high emittance but because the initial experiments showed black silicone coatings to have a relatively uniform absorptance over the entire spectral range of interest. The total reflectance of the black reference coating between 0.22 and 2.7 μ is shown in Fig. 6. This determination was made using a Beckman Model DK-2 spectrophotometer with integrating sphere reflectance attachment. Freshly smoked magnesium oxide was the reflectance standard used for all coatings, including the black. Magnesium oxide is approximately 97 to 98 percent perfect as a reflector of the visible spectrum, but is known to be less efficient in reflecting ultraviolet and infrared energy (6). An overall reflectance value of 0.95 for MgO has been estimated for the purposes of these calculations.

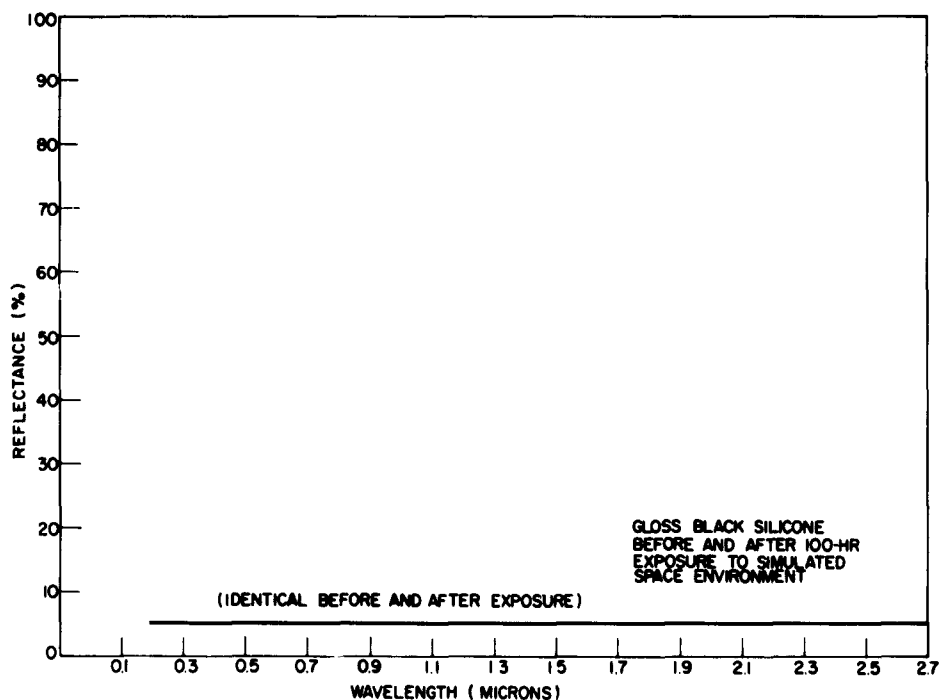


Fig. 6 - Total spectral reflectance of a gloss black silicone coating between 0.22 and 2.7 microns. The reflectance curve is based on smoked magnesium oxide as the reflectance standard and is expressed as percent of the total reflectance at each wavelength. This stable coating was in turn used as an emittance standard for all coatings (its normal emittance is 0.88, as compared to a cavity-type blackbody, for a 2-mil film at 100°C).

Jakob (7) has published some interesting and pertinent relationships between normal emissivity and total emissivity (i.e., hemispheric emissivity) for various substances. Using Jakob's findings, the hemispheric emittance of the black silicone reference coating should be about 0.94 times its normal emittance. The normal emittance was determined to be 0.88 for a 0.002-inch film at 100°C by comparison with a cavity-type blackbody at the same temperature. Hence, the hemispheric, or total, emittance is indicated to be approximately 0.83 by Jakob's relationships. It is believed that this value is correct within ± 5 percent, which is sufficiently accurate for making the calculations necessary to the current studies. The emissivity of this coating is not considered to vary significantly over the temperature range 0 to 100°C.

The emitted and conducted energy losses of panels bearing the black reference coating can be calculated from the cooling-rate curves. One-eighth-inch-thick copper panels of different overall area (and of different mass) were coated on all surfaces with a 2-mil thickness of the black reference coating. The panels were supported in identical fashion in their respective test cell compartments, thus insuring reasonably identical energy transfer by conduction for a given temperature, regardless of the fact that the panels were of different size. Copper was selected as the base metal because of its excellent conductivity and good heat capacity. A small thermocouple was placed in a cavity drilled $3/8$ inch deep in one end of each panel.

In the course of a typical laboratory experiment, the test panels absorb radiant energy from the surroundings, mainly from the UA-3 mercury vapor lamp, with a consequent rise in temperature until equilibrium is reached with the energy losses (these losses are almost wholly through the processes of emission and conduction; convective heat transfer is considered insignificant at the vacuum prevailing in these studies). Figure 7 illustrates a typical time-temperature relationship for two black-coated panels of different size. In studying the cooling-rate curves, it is difficult to obtain an accurate slope (rate of cooling) at the equilibrium temperature at the instant the UA-3 lamp is extinguished. This problem is overcome by making a special "run" of short duration in which the panels are heated approximately 20°C above their normal equilibrium temperature, then determining the slope of the cooling rate curves as they pass through the normal equilibrium temperatures in cooling. The higher initial temperature required by this procedure is easily reached by removing the quartz-water heat filter from around the lamp, allowing a considerably

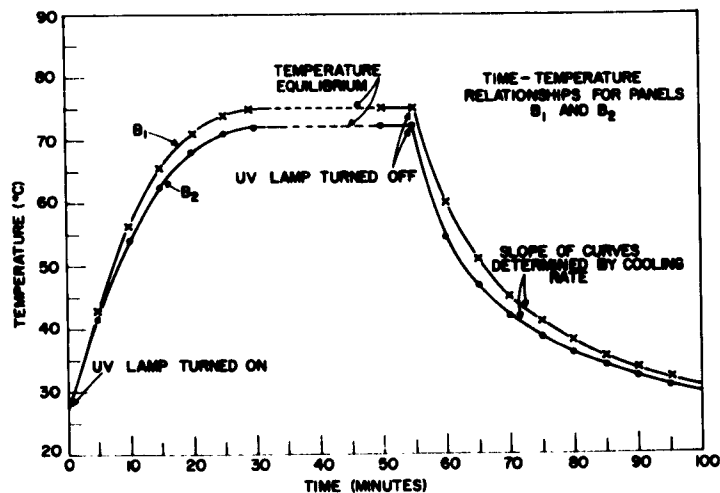


Fig. 7 - Typical heating and cooling-rate curves of two copper panels of different sizes, coated on all surfaces with gloss black silicone varnish

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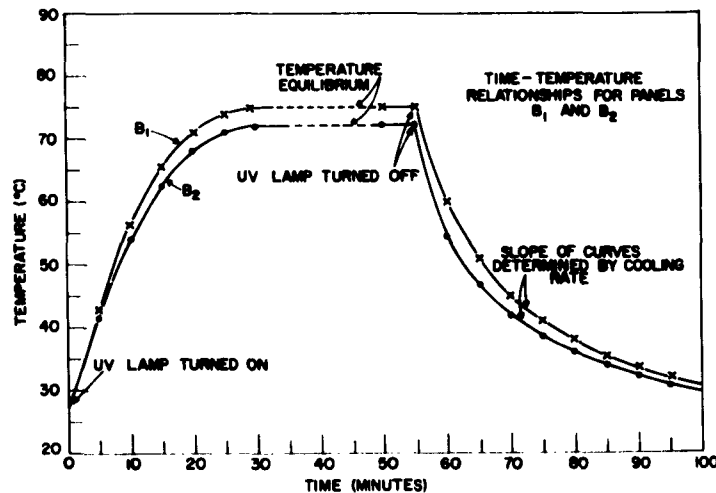


Fig. 7 - Typical heating and cooling-rate curves of two copper panels of different sizes, coated on all surfaces with gloss black silicone varnish

greater intensity of radiant energy to reach the panels. Another advantage of this technique is that within a few seconds after extinguishing the lamp, the quartz test chambers surrounding each panel are cooled to very near room temperature by the air circulated over the equipment. Under these conditions reasonable accuracy is attainable by assuming that the quartz chambers radiate energy as a function of the fourth power of their absolute temperature, with an emissive efficiency of approximately nine-tenths that of the theoretical blackbody. Since the quartz chambers are opaque to radiant energy above approximately 3.5μ and are nonconductors having refractive indexes of about 1.52, they should, according to Jakob (7), have an emissivity (and absorptivity) of approximately 0.90. At 300°K (27°C), over 99.9 percent of the energy radiated by a blackbody is of wavelengths longer than 3.5μ , which is in the region where quartz is opaque. Likewise, more than 99.5 percent of the energy that is radiated by a black-coated panel at 373°K (100°C) is in wavelengths longer than 3.5μ . It has been assumed that the black-coated panels and the quartz sufficiently approximate "gray"* bodies at these temperatures to use these facts without exceeding an error of ± 5 percent in making the calculations to follow. It is recognized that a more accurate evaluation could be made on the basis of integrated spectral emittance of the surfaces in question. However, this would entail the use of equipment capable of detecting extremely low intensities of infrared energy in narrow bandwidths over a range from approximately 3μ to more than 30μ . Such equipment is not yet available for these experiments.

Two copper panels of different mass and area were coated on all surfaces with 2 mils of a black-pigmented silicone paint. Thermocouples were imbedded in $3/8$ -inch-deep "wells" drilled into the edge of each panel. The example computation follows:

Panel B_1 = 55.43 gm with 46.5 cm^2 area

Panel B_2 = 26.11 gm with 24.3 cm^2 area .

From the plotted curve of temperature during cooling (i.e., with ultraviolet light off) the cooling rates at 71°C were

Panel B_1 = 16.1 cal/min

Panel B_2 = 8.6 cal/min .

The rate of cooling for each panel may be accounted for by the net energy loss due to radiation plus that lost conductively. (Convective heat losses are small and are not being considered.) Let R be the net energy transferred by radiation and C be the net energy transferred conductively. Since the method of supporting the panels is constant in all instances, it is assumed that the conductive heat transfer is solely a function of temperature gradient. Then at identical temperatures (71°C) the conductive energy loss should be the same for each panel. So, the total net energy loss is

$$R_{B_1} + C = 16.1 \text{ cal/min} \quad (1)$$

and

$$R_{B_2} + C = 8.6 \text{ cal/min} \quad (2)$$

from which $R_{B_1} - R_{B_2} = 7.5 \text{ cal/min}$.

*A "gray" body is defined as one with radiation properties differing from a blackbody by a constant factor at all wavelengths. Although such constancy is rarely, if ever, absolutely true, there is almost no other way to compare the emissivities of dielectrics in the far-infrared region.

Since identical coatings are used on each sample, the net energy losses ascribable to radiation are in proportion to their respective areas. Then,

$$R_{B_1} = A_{B_1} \epsilon \sigma (T^4 - T_o^4)$$

$$R_{B_2} = A_{B_2} \epsilon \sigma (T^4 - T_o^4)$$

where

A = area in cm^2

ϵ = emittance of coating as compared to a blackbody

σ = Stefan Boltzman constant

T = Temperature of coating in $^\circ\text{K}$

T_o = Temperature of surroundings in $^\circ\text{K}$ (-308°K)*

Therefore,

$$R_{B_1} - R_{B_2} = 7.5 = \epsilon \cdot \sigma (T^4 - T_o^4) (A_{B_1} - A_{B_2})$$

or

$$7.5 = \epsilon \cdot (1.35 \times 10^{-12} \times 60)(344^4 - 308^4)(22.2).$$

So

$$\epsilon = 0.83.$$

The conductive energy loss also may be calculated:

$$R_{B_1}/R_{B_2} = A_{B_1}/A_{B_2} = 46.5/24.3 = 1.91;$$

therefore,

$$R_{B_1} = 1.91 R_{B_2}.$$

Substituting this information in Eqs. (1) and (2) we obtain

$$1.91 R_{B_2} + C = 16.1$$

*The temperature of the quartz chamber surrounding each specimen slowly declines as the contained specimen cools. Over a number of runs this temperature has been observed to vary between 306°K and 309°K for specimen temperatures of approximately 345°K and a room temperature of 298°K . Further, it is difficult to achieve a high order of accuracy in sensing the temperature of these compartments in the present apparatus design. For an error of 1°K in the measurement of $(T^4 - T_o^4)$, an error of 0.017 in the calculation of coating emissivity results. Inasmuch as there is a possibility of making an error of several degrees in determining this temperature difference, this measurement probably accounts for much of whatever error exists in these determinations.

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ϵ = emittance of coating as compared to a blackbody

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T = Temperature of coating in °K

T_o = Temperature of surroundings in °K (=308°K).*

Therefore,

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and

$$1.91 R_{B_2} + 1.91 C = 16.45.$$

So

$$0.91 C = 0.35$$

or

$$C = 0.385 \text{ cal/min.}$$

By a procedure similar to the above, the values of emittance of other surfaces have been calculated. From a large number of calculations, the following ranges of values have been found.

<u>Coating Material</u>	<u>Total Emittance</u>
Black silicone varnish of 2-mil thickness	0.77 to 0.83
White (zinc sulfide pigmented) silicone varnishes of 2- to 3-mil thickness and PV's of 30 to 50 percent	0.69 to 0.75*
Leafing aluminum (2.5 lb/gal) silicone varnish	0.33 (single determination)
Bright, clean copper	0.05 to 0.13

In evaluating these data, it is stressed that the primary objectives of this program do not necessarily include an intensive effort to determine the emittance of various surfaces. Rather, it is to compare coatings with one another and to determine the optimum formulations for various applications in the space environment.

The absolute values of emittance obtained with both black and white coatings are lower than anticipated. However, the relative values of the various surfaces (i.e., compared to each other) appear quite reasonable.

At the temperatures of this investigation, the conductive energy losses have consistently varied between approximately 0.4 and 1.3 cal/min. Compared to the cooling rates observed for pigmented coatings, this could indicate a possible maximum error of approximately 6 percent in the calculation of values of emittance.

Once the heat losses have been accounted for, it is possible to use this information in combination with the emission spectrum of the lamp and the reflectance spectrum of the coatings to make a determination of the intensity of incident radiation.

One of the variables not readily controllable in these experiments has been the light intensity. This is attributable to several factors. First of these is the decrease in the intensity of radiation from the UA-3 lamp as it ages. The manufacturer rates the life of

*It is noteworthy that no significant relationship yet has been observed between pigment-volume (PV) ratio, or pigment-volume concentration (PVC), and emittance of the zinc sulfide pigmented coatings. There is a good probability that the variation in emittance with pigment volume is comparable to or less than the range of experimental error inherent in the equipment and technique used in these experiments.

these lamps at 1000 hours, during which time output intensity may be expected to decrease approximately one-third. It is further indicated by the manufacturer that most of this decrease occurs in the first 200 hours of lamp life. Two other important factors affecting radiant intensity at the specimens are the absorption and the scattering of light by materials and surfaces between the lamp and specimen. New quartz transmits more than 90 percent of the radiant energy between 0.2 and 3.5μ in wavelength. However, as it ages under ultraviolet radiation the transmissivity of quartz declines, particularly in the ultraviolet portion of the spectrum. A heat-absorbing quartz-water filter is included in the design of this apparatus (see Fig. 5) to absorb infrared radiation above about 1.1μ . This filter is necessary to avoid overheating the specimens, but it also reduces the visible and ultraviolet energy intensity which otherwise would reach the samples. In addition, and as has been pointed out in earlier reports (2, 5), the condensation of a very thin film of organic matter on the inner surface of the quartz compartments containing each sample very substantially reduces the intensity of ultraviolet energy reaching the samples. Hence, it can be seen that a method of sensing the energy incident on the specimens within the individual quartz compartments is very desirable. Presently, it appears that the most practical way of doing this is by sensing the temperature of a "control" coating in each run. The black silicone has been chosen as a control for the reasons explained above. (A 10 percent variation in lamp intensity produces an equilibrium temperature change of the black-coated panel of about 4°C .)

Numerous calculations have shown that the radiant intensity incident on the test samples in the equipment 8.5 cm from the UA-3 lamp ranges between approximately 0.75 and 1.1 calories per square centimeter per minute. This lamp has about half of its emitted energy in the ultraviolet region (3). Thus, the test surfaces are subjected to from two to three times the intensity of ultraviolet energy anticipated in space for near-earth orbits (i.e. 8 to 10 percent of the sun's energy) but are required to withstand considerably less overall energy than the solar constant of 2 calories per square centimeter per minute.

While this knowledge of approximate energy intensity is useful, it appears that the principle basis for evaluation of coatings for the space environment must remain a comparison of one material with another with regard to those physical properties which are essential to serviceability.

Since the spectrum of the UA-3 lamp is not a reasonable approximation of sunlight, its effect on coatings cannot reasonably be extrapolated to an equivalent space-solar exposure. However, as shown in NRL Report 5503 (5) and as will be indicated in spectral data contained in subsequent portions of this report, it appears that a change in spectral reflectance of coatings will be relatively large during the early stages of exposure, after which further change occurs at a very slow rate. More data on this phenomenon will be obtained with an apparatus employing a GE-type AH-6 lamp which now is in final stages of assembly. The AH-6 lamp is a much better approximator for the solar spectrum than the UA-3. It also is several times as intense a source.

One way of comparing experimental coatings is on the basis of their "equilibrium" temperatures in the simulated space conditions. Since the manner of preparing and supporting the panels in their respective test chambers is reasonably reproducible and constant, it follows that the equilibrium temperatures of the panels are significantly determined by the ratio of their absorption and emission of radiant energy. The validity of comparing experimental coatings on this basis is dependent upon the ability to control the conductive heat losses, making them essentially constant for a given temperature differential between panel and surroundings in all instances.

Highly reproducible results have been obtained in the comparison of specimens on the basis of their equilibrium temperatures for a specific intensity of radiation. Table 1 compares a number of experimental coatings on the basis of temperature.

Table 1
Equilibrium Temperature of Test Panels with
0.002-Inch Coatings of the Type Indicated

Coating Material	Equil. Temp. (°C) *
Zinc sulfide pigment	
30% PV in silicone	59
40% PV in silicone	61
45% PV in silicone	66
50% PV in silicone	60
60% PV in silicone	58
Titanium dioxide (rutile)	
30% PV in silicone	64
40% PV in silicone	-
45% PV in silicone	57
50% PV in silicone	63
60% PV in silicone	64
Basic white lead carbonate	
30% PV in silicone	62
Basic white lead carbonate	
30% PV in Acryloid A10	66
Carbon black 10% PV in silicone	82
Clean rolled aluminum alloy 245T	127
Anodized (chromic acid process) aluminum alloy 245T	107

*The data do not indicate the precise temperatures that the sample coatings would have were they in a true space environment. One reason for this is the difference in the energy spectrum of the mercury vapor lamp as compared to that of the sun.

As a result of a large number of comparisons, such as illustrated above, it is obvious that with the existing experimental coatings the overall variation in temperature that can be achieved is rather small, though significant. Further, for white silicones the variation is even more limited, being less than 15°C in most instances.

The significant fact in analysis of the temperature data is that pigmented organic coatings (excepting those containing leafing metallic pigments), of sufficient thickness to be opaque, have a relatively high emittance. The ability to measure emittance has been limited, but it appears that typical values of total emittance range from about 0.70 to 0.83. Values of normal emittance are somewhat higher. Although other researchers occasionally report total (i.e., hemispheric) emissivity values for organic materials of above 0.9, an examination of results obtained at this Laboratory to date shows no instance where the temperatures obtained would involve total emissivities of more than 0.83.

Since the publication of Part 1 of this series (5), a number of experimental coatings have been exposed to ultraviolet radiation in vacuums of 1×10^{-6} mm Hg. In general, evaluation has been on the basis of physical properties, with particular emphasis on the

optical changes that have occurred in the course of the test exposure. Table 2 presents a summary of the most important physical properties (other than optical) before and after subjecting the coatings to the simulated space environment. Figures A1 to A12 show the spectral reflectance curves for these materials and are given in the Appendix.

There have been no findings which would alter the general conclusions reached at the end of the Part 1 studies. Those conclusions were that

1. on exposure to intense ultraviolet radiation, the reflectance of all white coatings decreases very significantly in the ultraviolet and visible spectral regions below approximately 0.6μ ;
2. the change in reflectance appears to be mainly attributable to photochemical reactions induced in the resinous binder of the coating;
3. by far the greatest change in spectral properties occurs during the first few hours of exposure to the simulated space conditions, after which further changes in optical characteristics develops quite slowly; and,
4. the photochemical reactions induced by ultraviolet irradiation, causing high absorption of the ultraviolet and the lower wavelength visible spectrum, are limited to a very thin surface layer of coating, which if removed by any means, exposes a fresh white under layer.

A primary object of the current studies was to compare zinc sulfide (Cryptone 800) and titanium dioxide (R 610) on the basis of medium-to-high pigment volumes in a silicone resin matrix. It also had been hoped that basic white lead carbonate could be included in the comparison. However, the latter pigment was found to be so reactive with the silicone that satisfactory films of high pigment volume could not be prepared. In fact, it appears that the 30 percent pigment volume, which was prepared, will have very limited package stability. This poor stability of the basic white lead carbonate in silicone, coupled with the strong absorption of ultraviolet energy by the silicone resins, prompted an additional survey of acrylic resin copolymers.

It was shown in Part 1 of these studies (5) that butyl acrylate polymers were wholly unsatisfactory in the simulated space environment. However, the acrylics as a class have the virtue of being good film formers and absorb very little ultraviolet energy of wavelengths above 0.25μ . Accordingly, an acrylic copolymer (Acryloid A-10) manufactured by the Rohm and Haas Company was selected for continuing the investigation of acrylic resins. The manufacturer did not reveal the composition of this polymer; however, it is a very hard, heat-resistant type and presumably contains a considerable proportion of the methyl and ethyl esters of acrylic acid.

Two formulations, one with zinc sulfide and the other with basic white lead carbonate, have been prepared at 30 percent pigment volume in Acryloid A-10. On exposure to the ultraviolet radiation in a vacuum, a considerable decrease in the reflectance of the white lead formulation was noted, but the zinc sulfide formulation was very resistant to a change in optical properties. These results are shown by Figs. A11 and A12.

DISCUSSION

Much of the present effort has been focused on the design of organic coatings having maximum reflectance to the solar spectrum. It also is desirable that such coatings have good infrared emission and long serviceable life in a space environment. The results to date indicate that white silicone coatings afford a very good combination of these properties, in spite of the fact that considerable discoloration develops under ultraviolet

Table 2
Physical Evaluation of Coatings Before and After Ultraviolet
Irradiation in a Vacuum of 1×10^{-5} mm Hg

Coating Formulation	Test Period (hr)	Flexibility - Mandrel Bend Test			Adhesion	Color	Quality - Remarks
		1/4 Inch	3/16 Inch	1/8 Inch			
Zinc sulfide (30% PV* in silicone †)	0	U †	U	U	G †	white	Cracks on bending
	100	S †	S	S	E †	light yellow	Hard and flexible
Zinc sulfide (40% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	light yellow	Hard and brittle
Zinc sulfide (45% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	pale yellow	Hard and brittle
Zinc sulfide (50% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	pale yellow	Hard and brittle
Zinc sulfide (60% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	pale yellow	Hard and brittle
Titanium dioxide (30% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	S	S	S	G	light yellow	Hard and flexible
Titanium dioxide (40% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	light yellow	Hard and flexible
Titanium dioxide (45% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	light yellow	Hard and brittle
Titanium dioxide (50% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	U	U	U	U	pale yellow	Hard and brittle
Titanium dioxide (60% PV in silicone)	0	U	U	U	U	white	Cracks on bending
	100	S	S	S	G	pale yellow	Hard and brittle
Basic white lead carbonate (30% PV in Acryloid A-10)	0	U	U	U	U	white	Hard and brittle
	100	S	S	S	G	pale yellow	Hard and flexible
Zinc sulfide (30% PV in Acryloid A-10)	0	U	U	U	U	white	Hard, very brittle
	100	U	U	U	U	pale yellow	Hard, very brittle

*PV: pigment-volume ratio.

†50/50 DCR 805/806A.

‡E: excellent, G: good, S: satisfactory, U: unsatisfactory.

irradiation. The recent favorable results of experiments which used Acryloid A-10 as the coating matrix justify further exploration of the use of this vehicle. In at least one instance, the acrylic formation with zinc sulfide pigmentation has proven superior to all silicone formulations. The best results continue to be obtained when using the high-purity zinc sulfide pigment Cryptone 800, supplied by the New Jersey Zinc Company. Anatase titanium dioxide may be superior to the rutile (8) and, consequently, will be evaluated in the near future. It appears that a significant benefit derived from high-pigment-volume formulations is the reduction in resin content, which therefore reduces the component most susceptible to discoloration.

In order to minimize the number of variables in the experiments thus far conducted, pigmentation has been limited to a single pigment. It is believed, however, that this has yielded coatings of somewhat less than optimum optical properties. It has been shown by other researchers (9, 10) that noticeable pigment agglomeration sets in at pigment volumes above about 10 percent (9, 10), and agglomeration may be assumed to be a very significant factor at high pigmentations (i.e., 40 to 60 percent PVC). This observation is strengthened by reflectance measurements which show only a slight increase in the reflectance of a coating by increasing the pigment volume above 40 percent (Appendix Figs. A2 through A5). In the case of titanium dioxide the reflectance of coatings above 40 percent PVC decreases (Figs. A7 through A10). Since this small, if any, increase in reflectance and resistance to discoloration from exposure is obtained at a great sacrifice in the coating's other properties, pigmentations above 40 percent are not recommended.

Work is now in progress to evaluate coatings containing certain extender pigments in combination with the hiding pigment to reduce pigment agglomeration. The ideal matrix for such a coating would be one that would absorb no ultraviolet or visible energy. However, since no such material exists, compromise must be effected between the absorption of radiation by the vehicle and its serviceability in a prolonged space-environment exposure. The silicones which the Laboratory has been using are relatively unattractive from the standpoint of light absorption, but have appeared to offer good film properties over a long period of time. At least one of the acrylic resin copolymers appears interesting as an alternative consideration. Also, the family of silicone resins may yet provide some materials superior to those examined to date.

The only surfaces which have maintained a high reflectivity to the ultraviolet spectrum over an extended period in the simulated space environment are clean, bare metals (aluminum and copper). Similarly, the only highly reflective, pigmented coatings which have remained reasonably stable optically during similar exposure have been those coatings pigmented with leafing aluminum (5). It is well known that such coatings containing leafing, metallic pigment expose a minimum of organic material and a maximum of metal to their surroundings; thus, they represent a paint technologist's way of laying down a semimetallic film. Unfortunately, leafing aluminum is a good reflector and, therefore, a poor emitter of the infrared as well as the visible and ultraviolet regions of the spectrum.

REFERENCES

1. Crecellius, S.B., Alexander, A.L., and Kagarise, R.E., "Mechanism of Linseed Oil Film Degradation Under Ultraviolet Irradiation," NRL Report 4803, July 31, 1956
2. Alexander, A.L., Noonan, F.M., Cowling, J.E., and Stokes, S., "The Degradation of Polymers by Ultraviolet Irradiation. Part II - (a) Radiation in the 'Near' Ultraviolet Region in Air; (b) Radiation in the 'Far' Ultraviolet Region in High Vacuum," NRL Memo Report 914, 1959
3. Cowling, J.E., Alexander, A., Noonan, F., Kagarise, R., and Stokes, S., "The Effects of Ultraviolet Radiation on Organic, Film-Forming Polymers," First Symposium, Surface Effects on Spacecraft Materials, Palo Alto, California, May 1959; New York: Wiley, pp. 364-377, 1960
4. Alexander, A.L., Noonan, F.M., Cowling, J.E., and Kagarise, R.E., "The Degradation of Polymers by Ultraviolet Irradiation. Part I - When Subjected to Radiation of the 'Near' Ultraviolet Region in Air," NRL Report 5257, Feb. 6, 1959
5. Noonan, F.M., Alexander, A.L., and Cowling, J.E., "The Properties of Paints as Affected by Ultraviolet Radiation in a Vacuum - Part 1," NRL Report 5503, July 13, 1960
6. Middleton, W.E.K., and Sanders, C.L., "The Absolute Spectral Diffuse Reflectance of Magnesium Oxide," J. Opt. Soc. Am. 41(No.6):419-424 (1951)
7. Jakob, M., "Heat Transfer," Vol. I, New York:Wiley, 1949
8. Von Fischer, W., and Bobalek, E.G., eds., "Organic Protective Coatings," New York: Reinhold, 1953
9. Stieg, F.B., Jr., "The Effect of Extenders on the Hiding Power of Titanium Pigments," Official Digest, Federation of Paint and Varnish Production Clubs, Vol. 31, Jan. 1959
10. Stieg, F.B., Jr., and Enswinger, R.L., "The Production and Control of High Dry Hiding," Official Digest, Federation of Paint and Varnish Production Clubs, Vol. 33, July 1961

APPENDIX
SPECTRAL REFLECTANCE CURVES*

On the following pages the curves on the upper part of each figure show the spectral reflectances measured from 0.22 to 0.76 micron. The curves on the lower part of each figure show the spectral reflectances measured from 0.22 to 2.7 microns.

- Fig. A1 - Zinc sulfide (30% PV[†] in silicone)**
- Fig. A2 - Zinc sulfide (40% PV in silicone)**
- Fig. A3 - Zinc sulfide (45% PV in silicone)**
- Fig. A4 - Zinc sulfide (50% PV in silicone)**
- Fig. A5 - Zinc sulfide (60% PV in silicone)**
- Fig. A6 - Titanium dioxide (30% PV in silicone)**
- Fig. A7 - Titanium dioxide (40% PV in silicone)**
- Fig. A8 - Titanium dioxide (45% PV in silicone)**
- Fig. A9 - Titanium dioxide (50% PV in silicone)**
- Fig. A10 - Titanium dioxide (60% PV in silicone)**
- Fig. A11 - Basic white lead carbonate (30% PV in Acryloid A-10)**
- Fig. A12 - Zinc sulfide (30% PV in Acryloid A-10)**

***Comparison with MgO as the standard.**

†PV (or PVC): pigment-volume ratio (concentration).

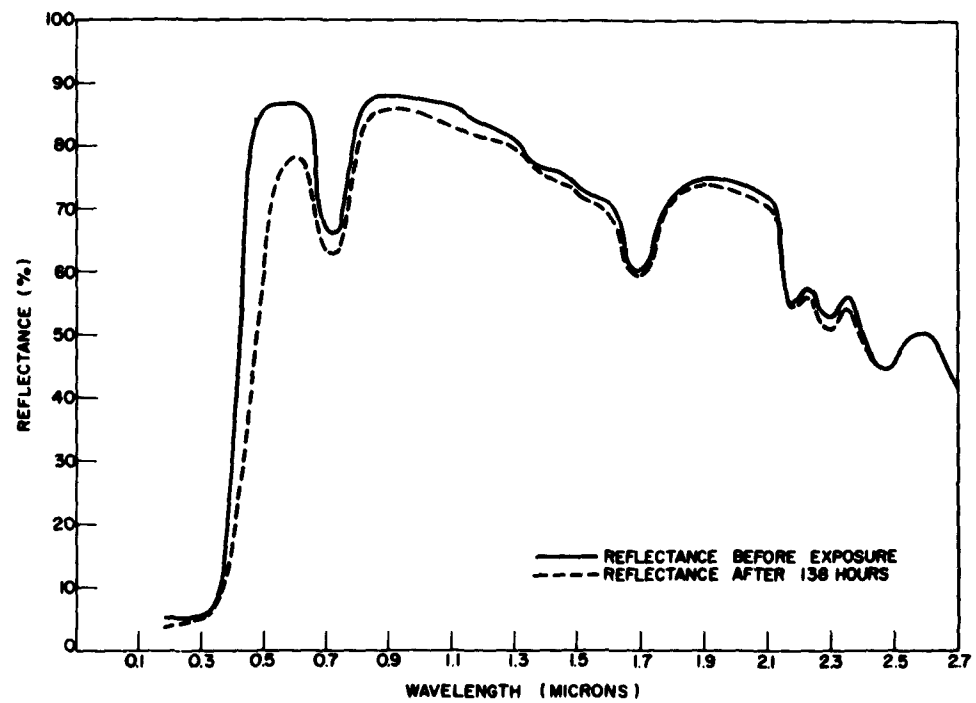
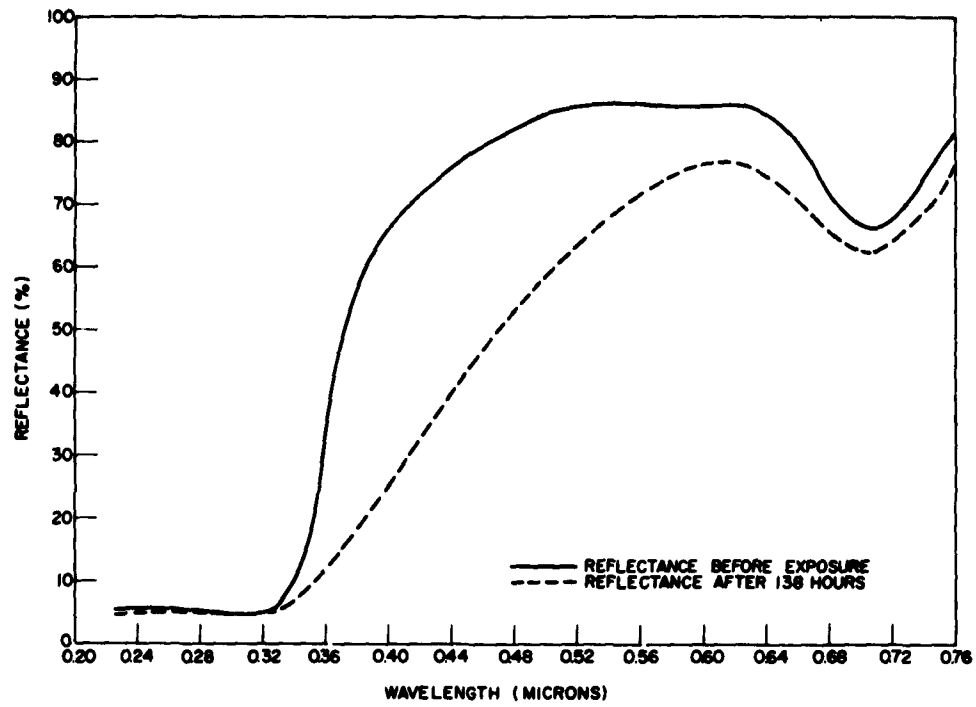


Fig. A1 - Zinc sulfide (30% PV in silicone)

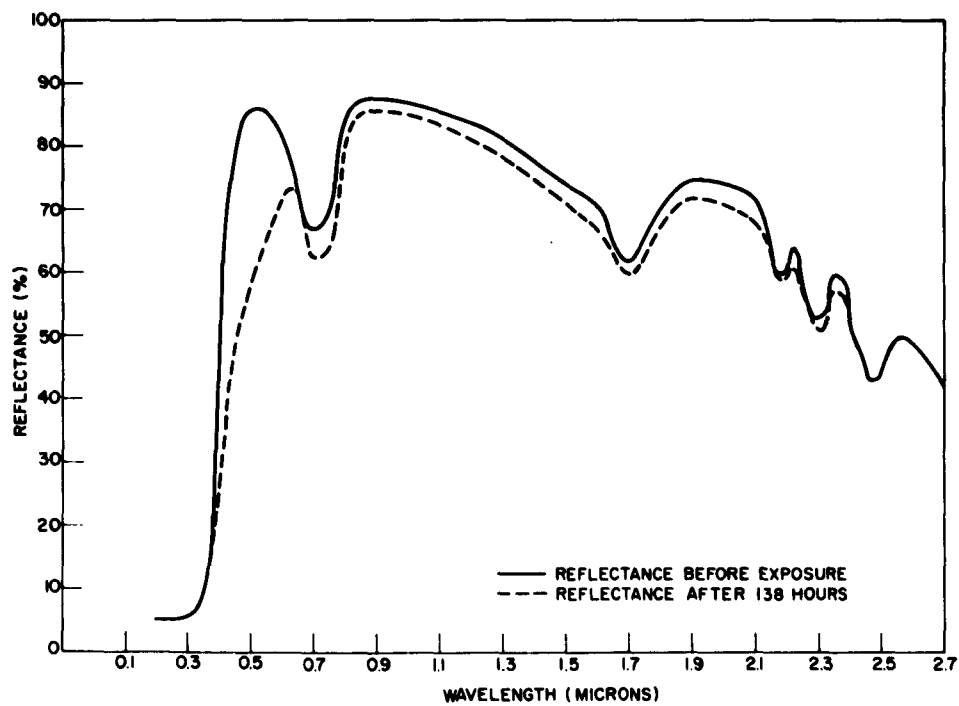
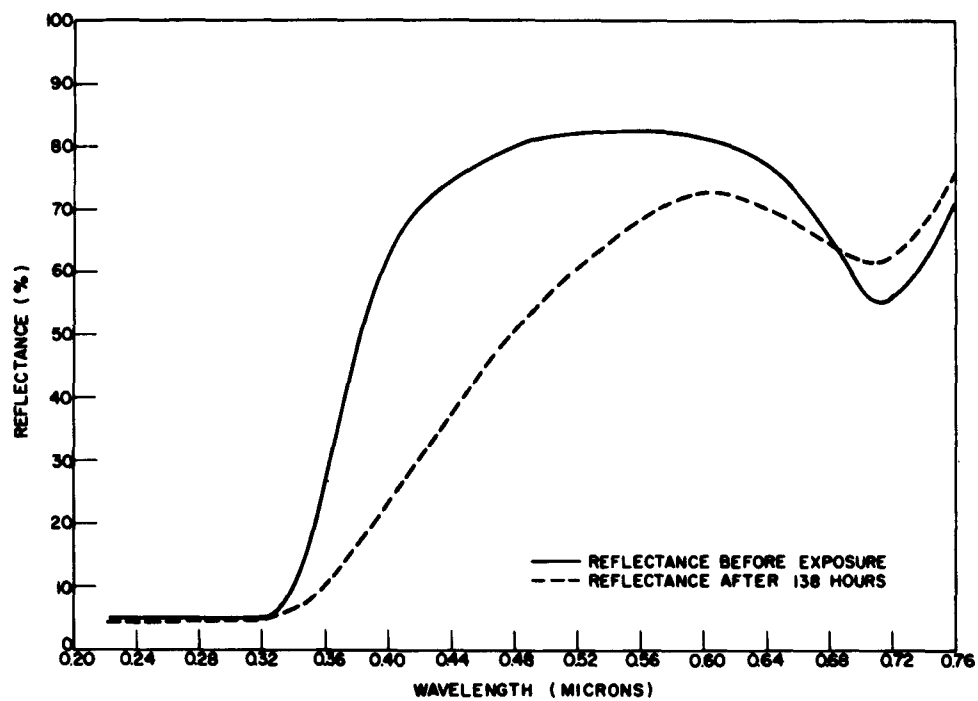


Fig. A2 - Zinc sulfide (40% PV in silicone)

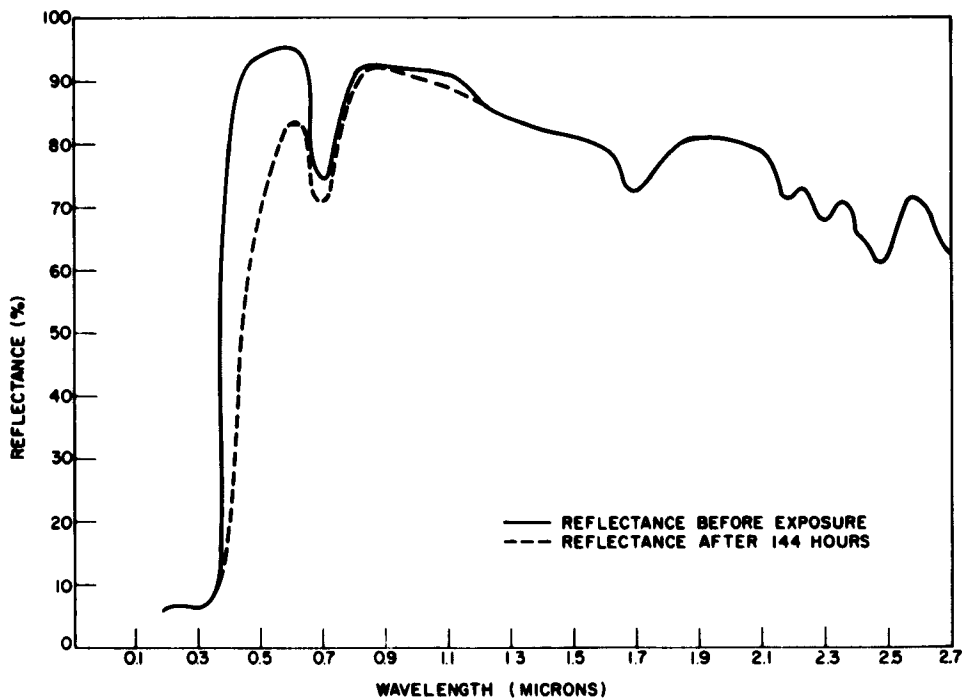
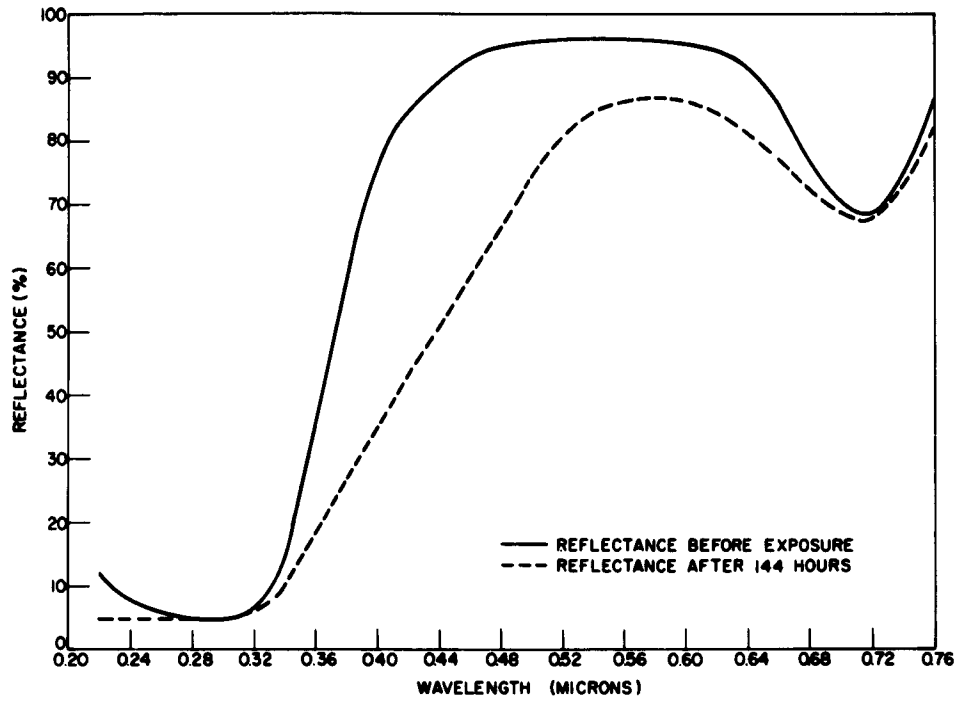


Fig. A3 - Zinc sulfide (45% PV in silicone)

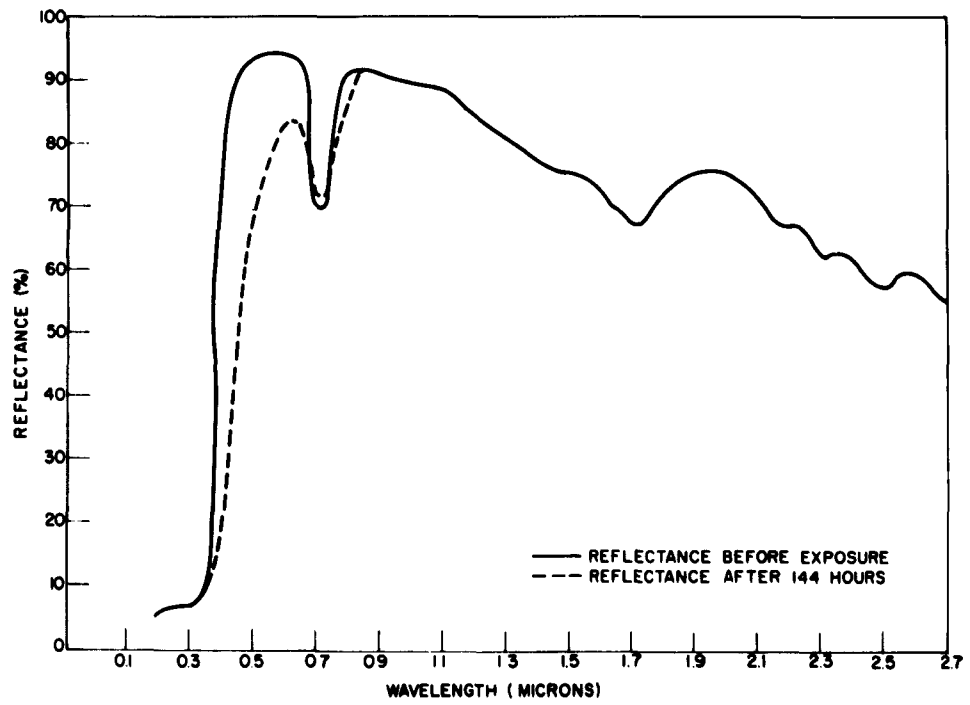
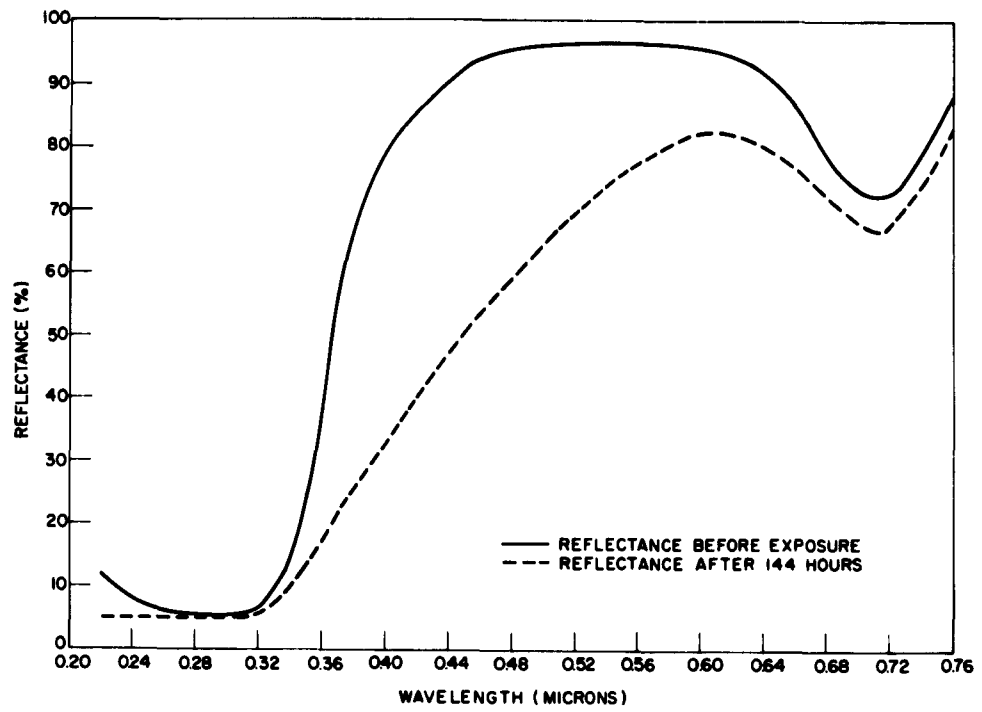


Fig. A4 - Zinc sulfide (50% PV in silicone)

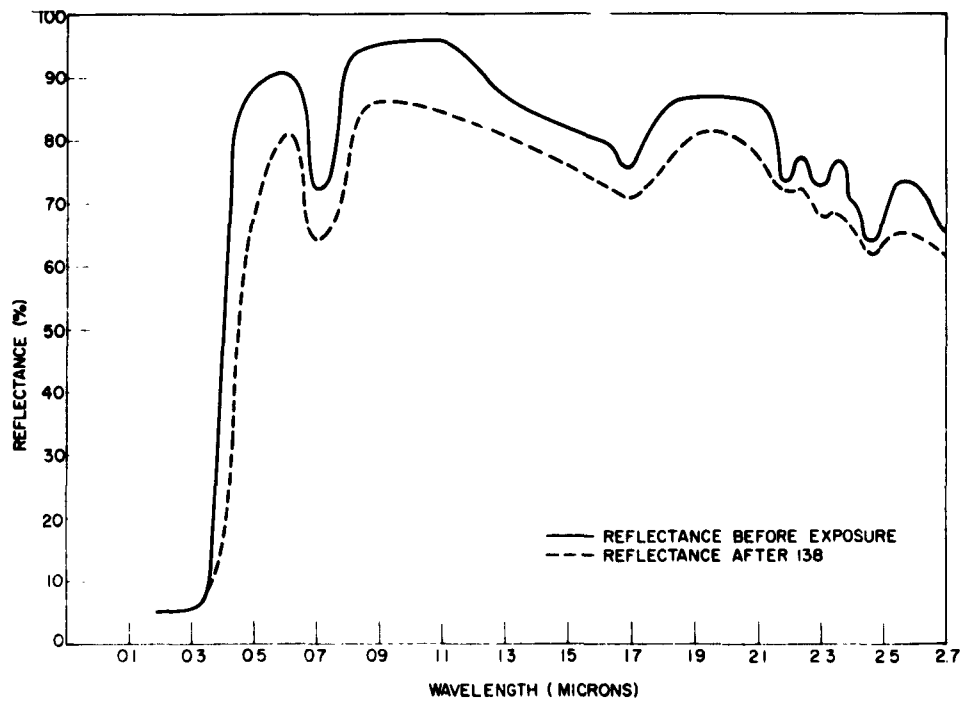
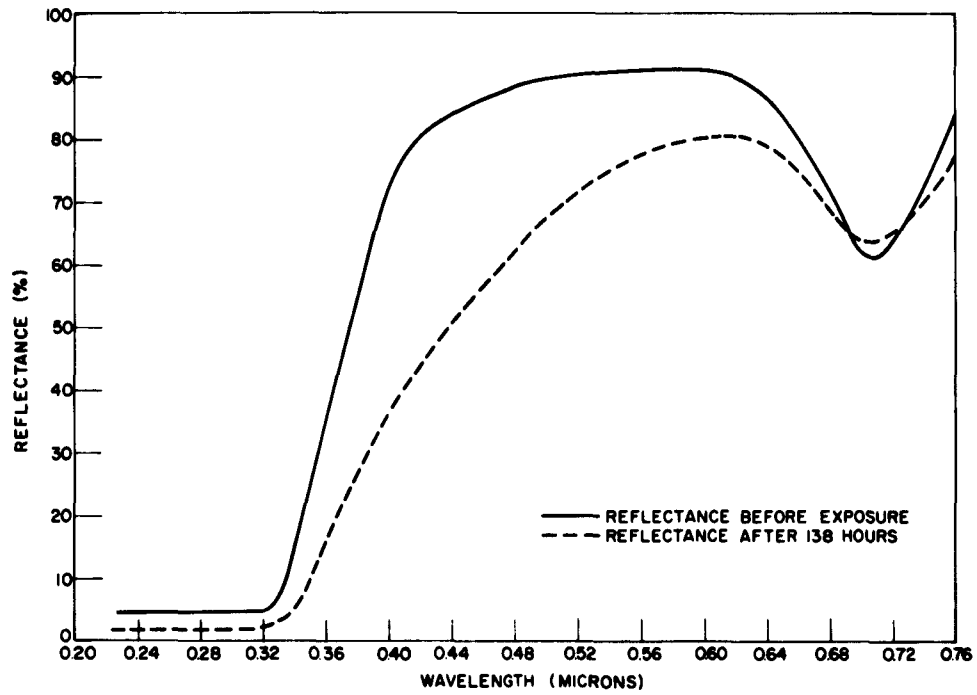


Fig. A5 - Zinc sulfide (60% PV in silicone)

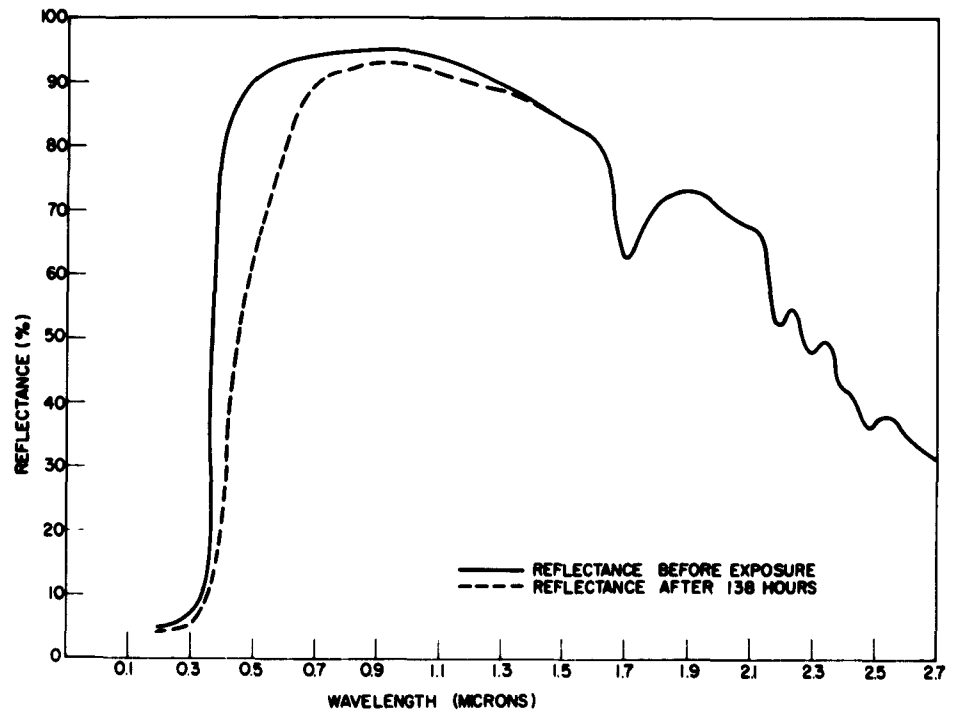
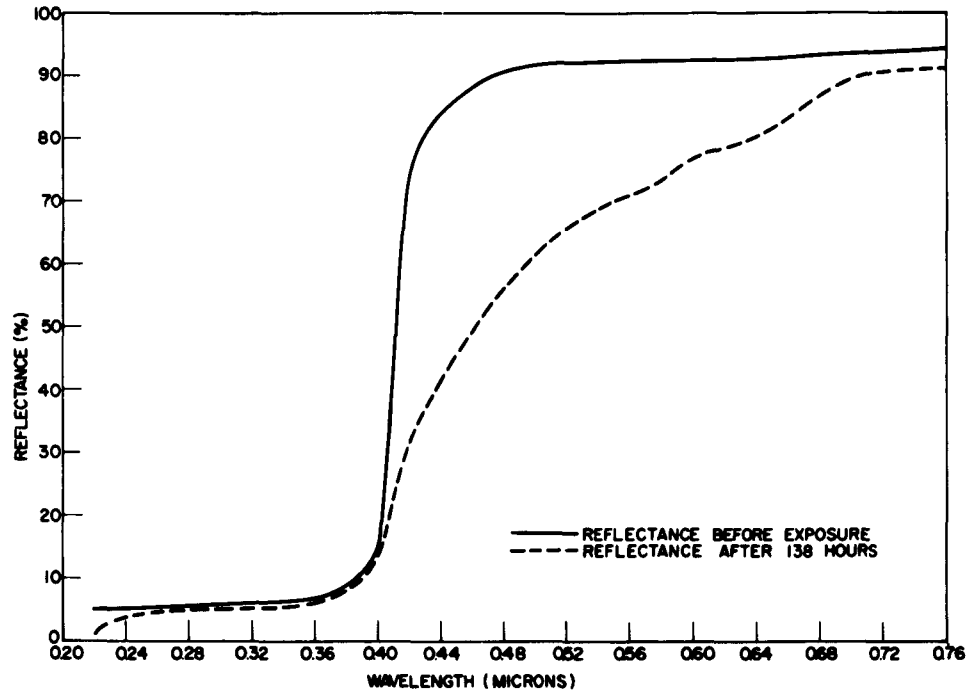


Fig. A6 - Titanium dioxide (30% PV in silicone)

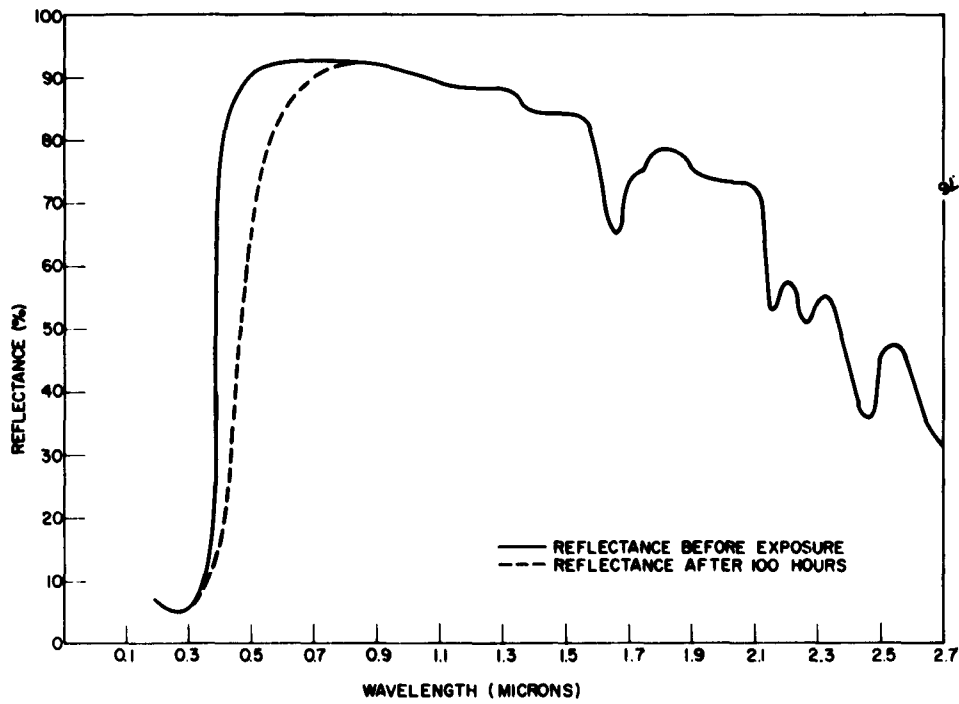
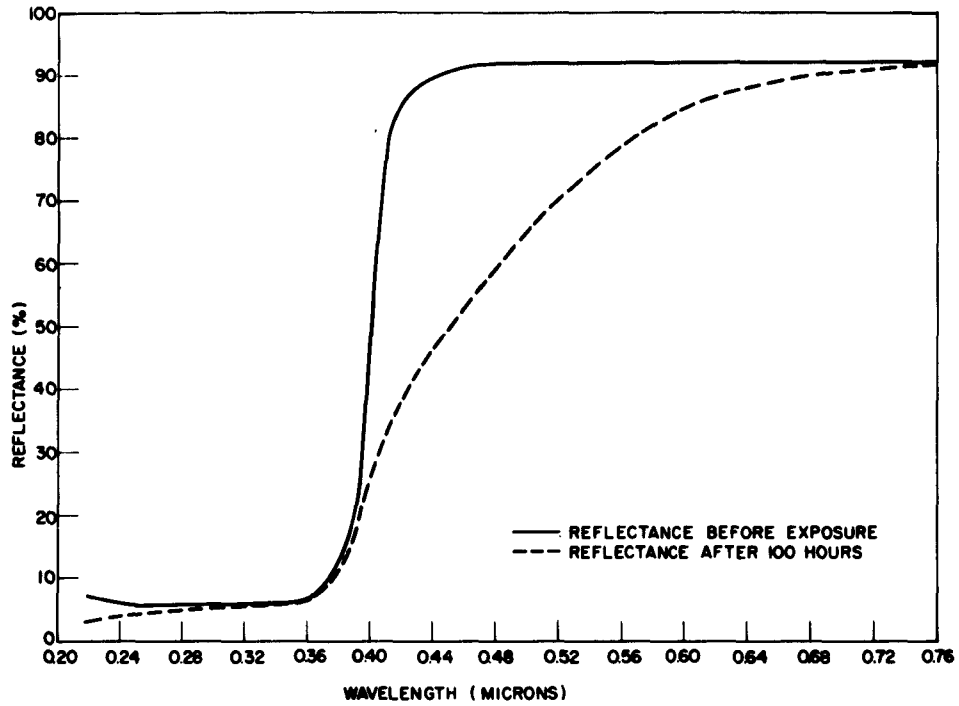


Fig. A7 - Titanium dioxide (40% PV in silicone)

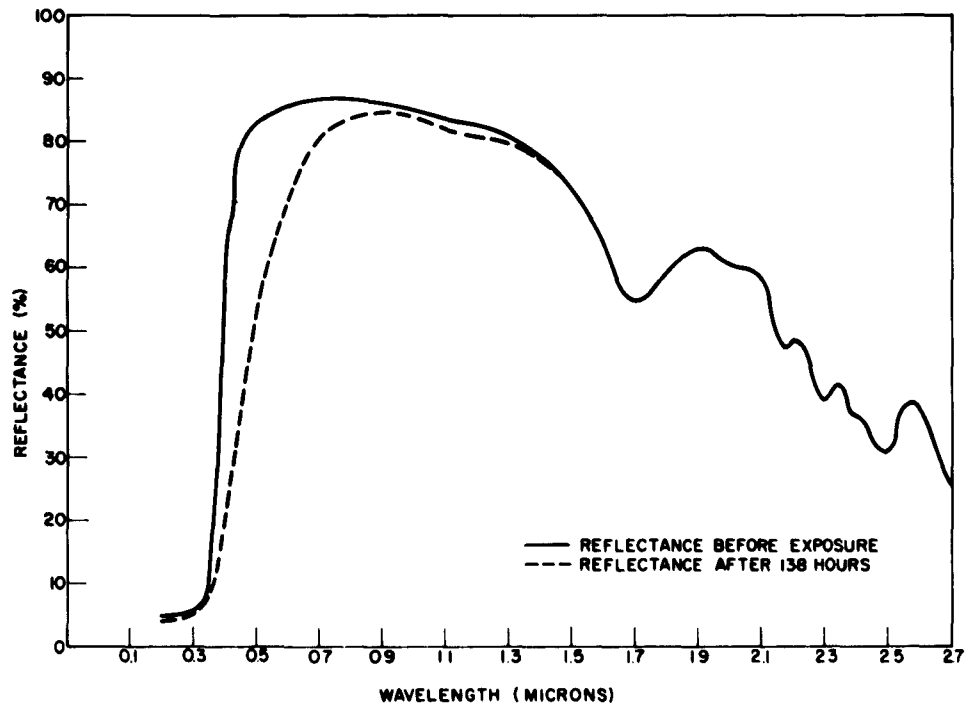
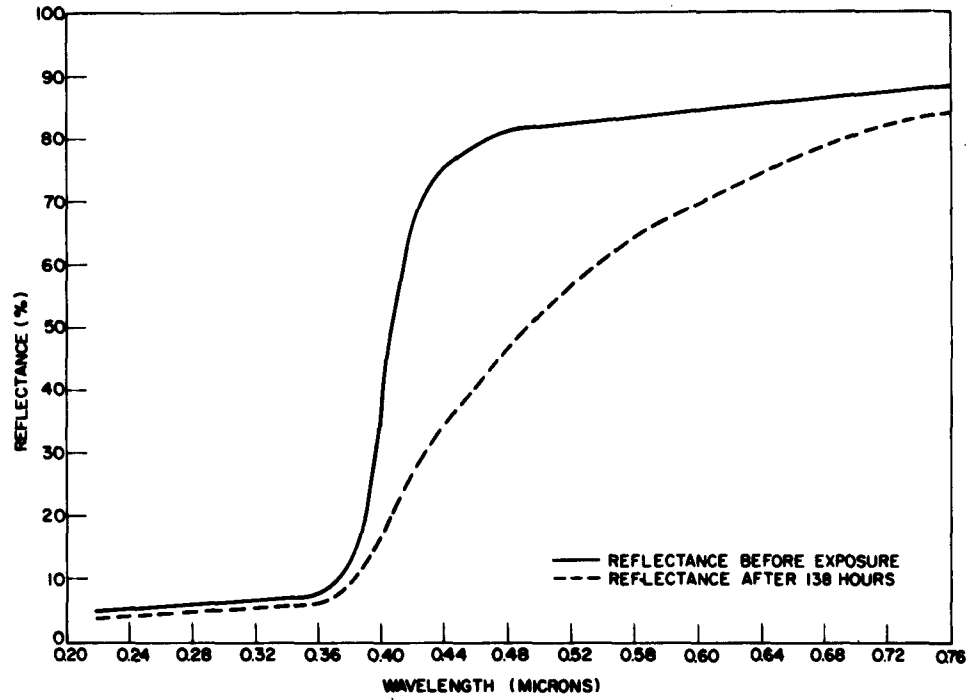


Fig. A8 - Titanium dioxide (45% PV in silicone)

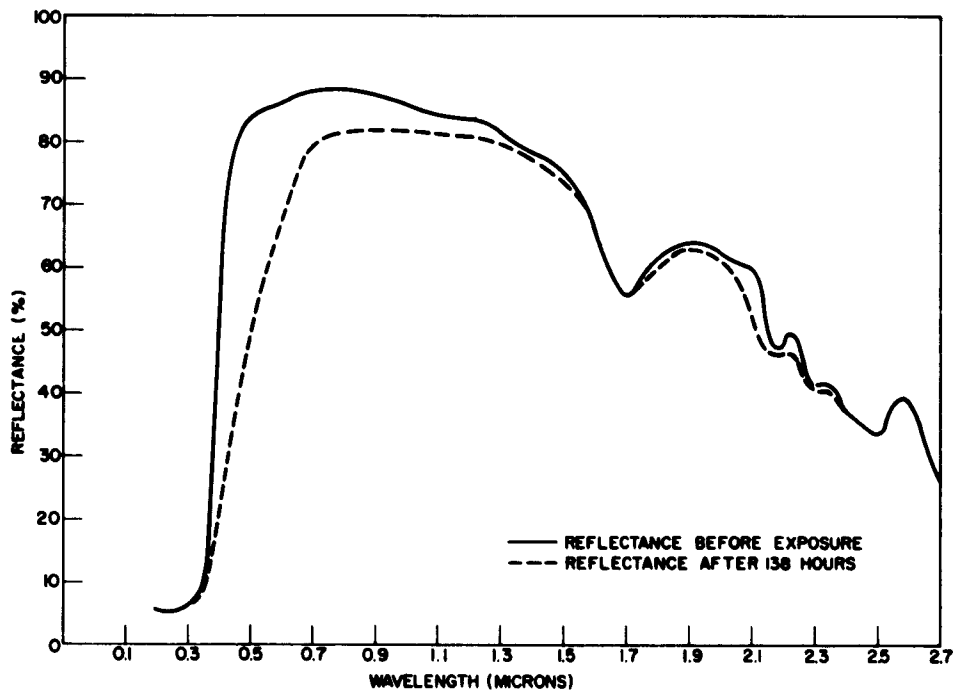
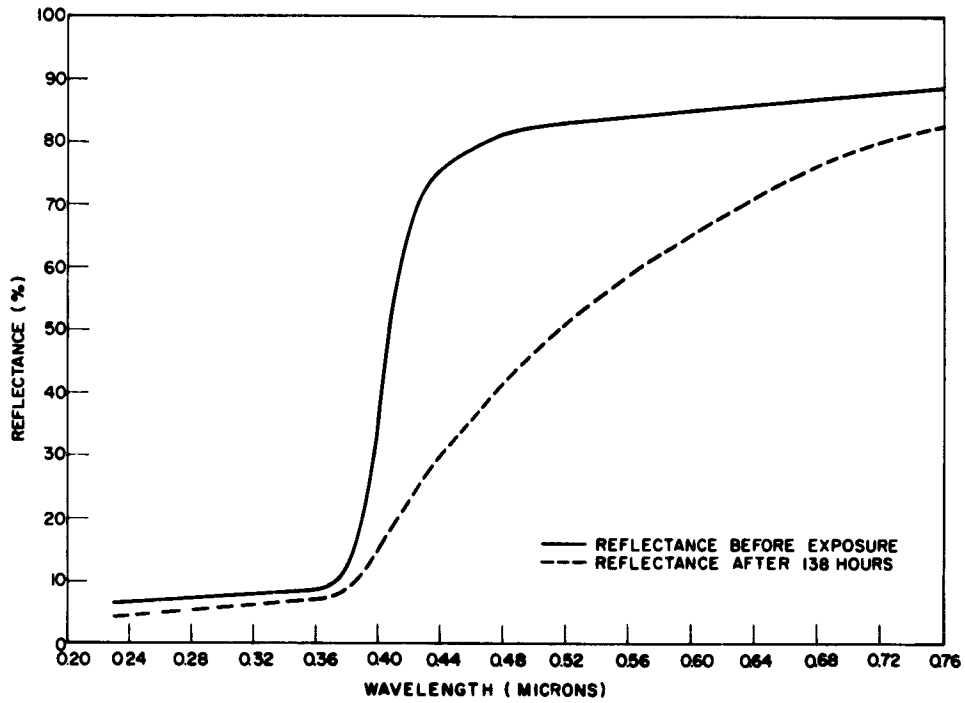


Fig. A9 - Titanium dioxide (50% PV in silicone)

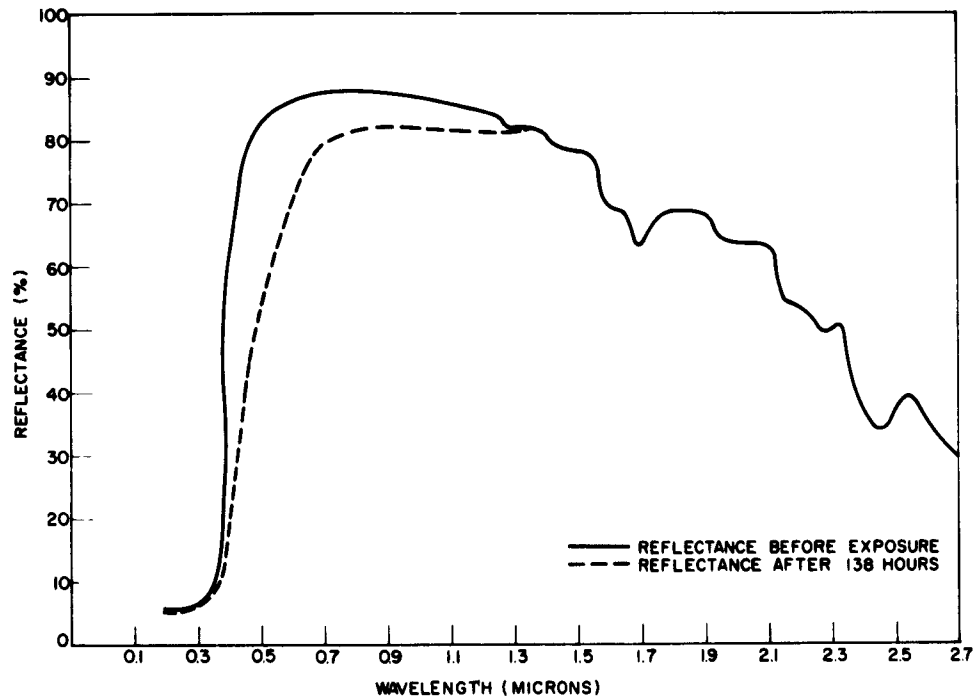
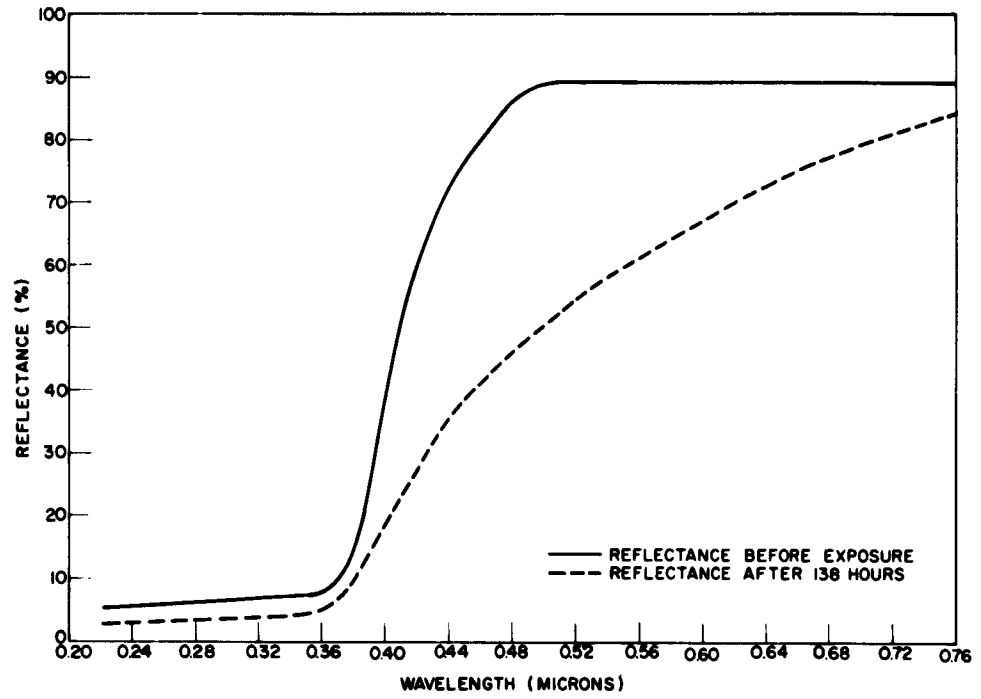


Fig. A10 - Titanium dioxide (60% PV in silicone)

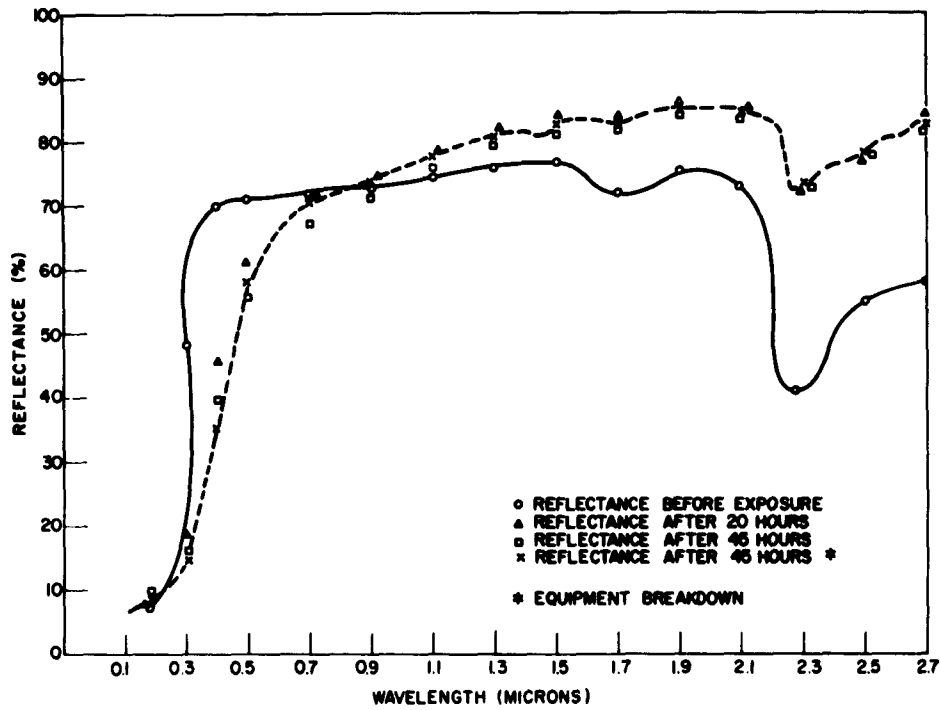
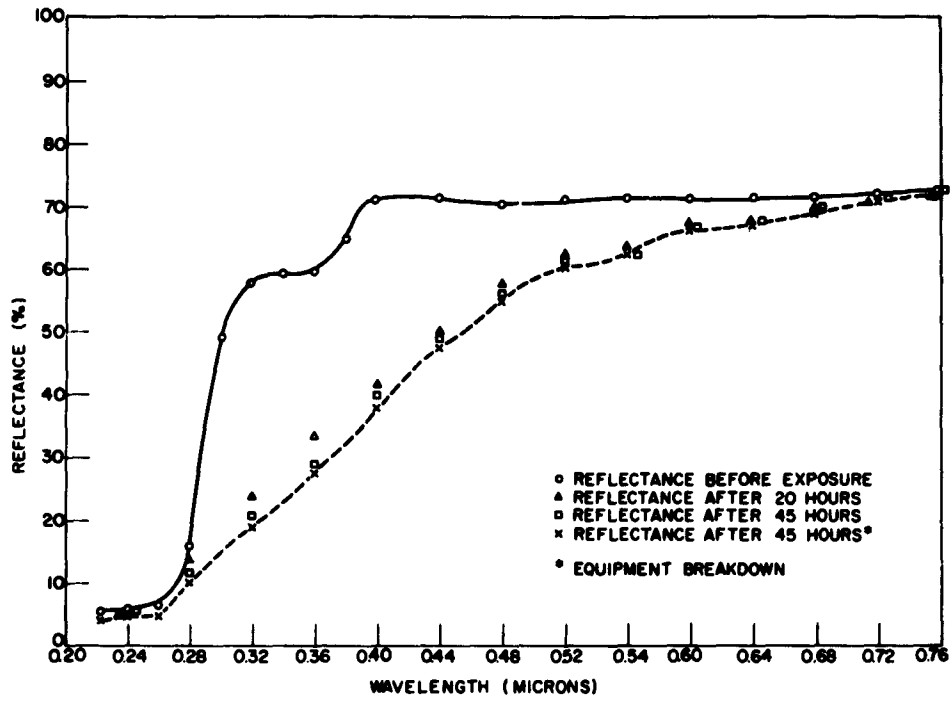


Fig. A11 - Basic white lead carbonate (30% PV in Acryloid A-10)

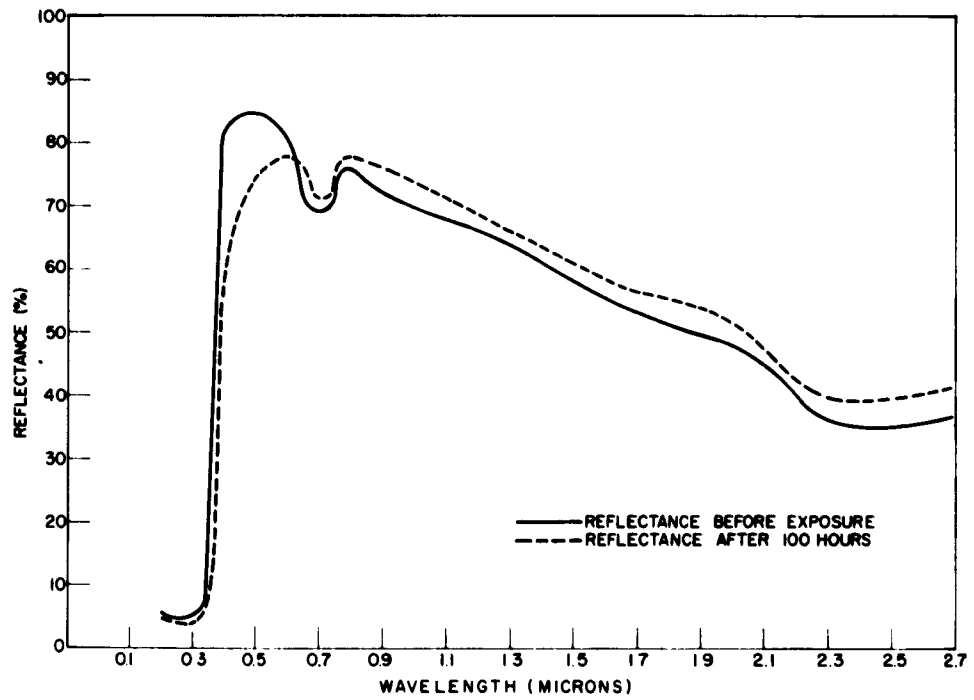
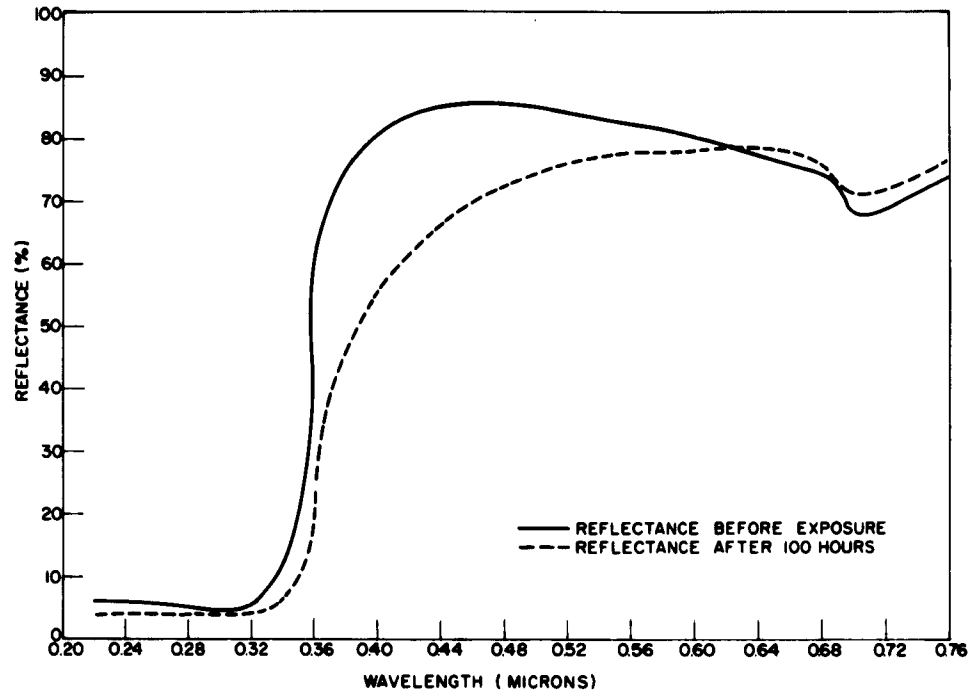


Fig. A12 - Zinc sulfide (30% PV in Acryloid A-10)

<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5737. THE PROPERTIES OF PAINTS AS AFFECTED BY ULTRAVIOLET RADIATION IN A VACUUM - PART 2, by D.E. Field, J.E. Cowling, and F.M. Noonan. 28 pp. and figs., March 8, 1962</p> <p>Organic coatings are being studied as one possible means of achieving temperature control within space vehicles. However, their usefulness in the space environment may be limited by their physical and chemical stability in space. It is shown that the optical properties of most organic coatings are changed on exposure to intense ultraviolet radiation in high vacuum. Of the reflective pigments studied, those containing zinc sulfide and leafing aluminum are shown to be most stable to this radiation.</p> <p style="text-align: center;">UNCLASSIFIED</p>	<p style="text-align: center;">UNCLASSIFIED</p> <p>Naval Research Laboratory. Report 5737. THE PROPERTIES OF PAINTS AS AFFECTED BY ULTRAVIOLET RADIATION IN A VACUUM - PART 2, by D.E. Field, J.E. Cowling, and F.M. Noonan. 28 pp. and figs., March 8, 1962</p> <p>Organic coatings are being studied as one possible means of achieving temperature control within space vehicles. However, their usefulness in the space environment may be limited by their physical and chemical stability in space. It is shown that the optical properties of most organic coatings are changed on exposure to intense ultraviolet radiation in high vacuum. Of the reflective pigments studied, those containing zinc sulfide and leafing aluminum are shown to be most stable to this radiation.</p> <p style="text-align: center;">UNCLASSIFIED</p>
<p style="text-align: center;">UNCLASSIFIED</p> <p>1. Paints - Physical properties</p> <p>2. Paints - Effects of radiation</p> <p>I. Field, D.E. II. Cowling, J.E. III. Noonan, F.</p>	<p style="text-align: center;">UNCLASSIFIED</p> <p>1. Paints - Physical properties</p> <p>2. Paints - Effects of radiation</p> <p>I. Field, D.E. II. Cowling, J.E. III. Noonan, F.</p>
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