

## MATERIALS EFFECTS IN SPACECRAFT THERMAL CONTROL

by

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### INTRODUCTION

The work being conducted at LMSD to provide thermal control of satellites is discussed in this paper. For the electronic equipment aboard satellites to function properly, the equipment temperatures must be maintained within a range of approximately 0 to 60°C. Considerably more stringent requirements are imposed by certain payloads, which require temperature control as close as ±1°C.

As a consequence of this necessity for refined temperature control surfaces, LMSD is engaged in a broad program for developing materials which have the necessary characteristics for thermal radiation interchange and which, at the same time, manifest stability to prolonged exposure in the space environment. Primary effort at present is devoted to the development of paints, which have suitable radiation characteristics and which are resistant to both ascent heating conditions and ultraviolet irradiation in vacuum.

### ANALYTICAL BACKGROUND

The present design philosophy relies upon passive radiation techniques in which the desired average orbital temperature is achieved by properly balancing the absorptivity of the surfaces for solar radiation  $\alpha$  with their emissivity for infrared radiation  $\epsilon$ . Analysis reveals that the average orbital temperature varies as the fourth root of the  $\alpha/\epsilon$  ratio, as indicated by the following equation:

$$\sigma \bar{T}^4 = \frac{\alpha}{\epsilon} (\bar{F}_s S \bar{F}_r R) + \bar{F}_e E + \frac{1}{\epsilon} P_i$$

or, for a prescribed orbital geometry,

$$\bar{T}^4 = C_1 \frac{\alpha}{\epsilon} + C_2 \frac{P_i}{\epsilon} + C_3$$

where the term  $\alpha/\epsilon$  is normally dominant. The symbols used in the above equations are defined as follows:

- $\bar{T}$  = average orbital temperature of an external temperature control surface
- $\sigma$  = Stefan-Boltzmann radiation constant
- $\alpha$  = coefficient of solar absorptivity
- $\epsilon$  = coefficient of infrared emissivity

# Contrails

$F_s$ ,  $F_r$ ,  $F_e$  = radiant interchange geometrical factors for solar insolation,  
earth radiation, and albedo  
 $S$ ,  $R$ ,  $E$  = incident radiant energy due to solar insolation, earth emission,  
and albedo  
 $P_i$  = internal power generation

Different materials exhibit characteristically different values of the  $\alpha/\epsilon$  ratio; these values vary from 10.0 or more for polished metallic surfaces to 0.3 for certain classes of painted surfaces. The particular value of the  $\alpha/\epsilon$  ratio corresponding to a desired temperature is achieved by constructing a mosaic of materials that has the properly weighted average  $\alpha/\epsilon$  ratio. This concept has been discussed by Camack and Edwards (Ref. 1).

The four basic classes of thermal control surfaces from which a suitable mosaic may be constructed are indicated in Fig. 1. The solid lines indicate hypothetically perfect radiation control surfaces, while the dashed lines indicate the degree of present practical attainment.

The flat absorbers currently used are black paints and anodizing treatments resulting in black matte surfaces. Characteristic emissivities are 0.9 throughout the spectral range 0.2 to 25  $\mu$ . The flat reflector presently in use is an aluminum-pigmented silicone paint. Reflectance of incident energy is approximately 70 percent throughout the spectral range of interest.

Highly polished metallic surfaces are used as solar absorbers. As a representative material, polished aluminum surfaces have  $\alpha/\epsilon$  ratios between 6.0 and 12.0. The variation in  $\alpha/\epsilon$  ratio is indicative of the pronounced effect of surface finish and cleanliness. This class of thermal control surface requires specialized protection techniques throughout the manufacturing process.

At present, solar reflectors are approximated by white paints. Various pigment-vehicle combinations are used, and these will be discussed in more detail in a later section. Lowest practical values of  $\alpha/\epsilon$  are:  $\alpha/\epsilon \approx 0.24/0.90 = 0.27$ .

Solar reflectors are used in areas where it is desired to maintain a very low equilibrium temperature or where it is necessary to dissipate large amounts of internally generated power. Solar absorbers are, of course, used for exactly opposite reasons. Flat absorbers and reflectors are required to minimize orbital temperature fluctuations and, in conjunction with the solar reflectors and solar absorbers, to establish the temperature level.

## RADIATION CHARACTERISTICS OF MATERIALS

The radiation characteristics of materials for thermal control cannot be predicted theoretically, because present theory is limited largely to electrical conductors and neglects the effect of surface condition. Therefore, the solar absorptivity and infrared emissivity must be determined experimentally. At LMSD these determinations are made with the following standard equipment (Ref. 2) used in determining emissivity.

1. A Cary integrating sphere is used in conjunction with a double-beam spectrophotometer to determine solar absorptivity through the spectral range 0.2 to 1.8  $\mu$ .

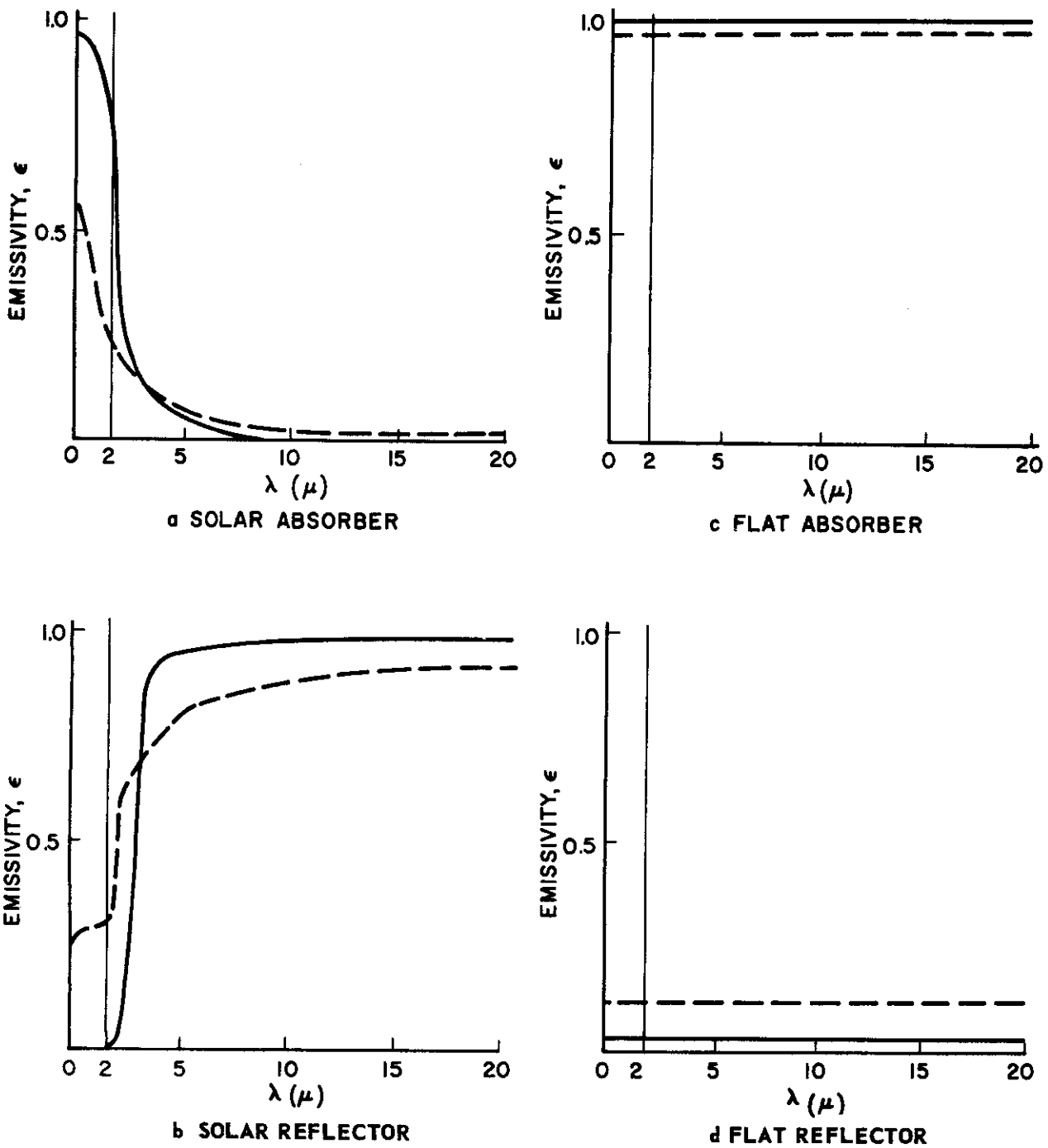


Fig. 1 Four Basic Thermal Control Surfaces

2. A Gier-Dunkle type Hohlraum is used, again in conjunction with a double-beam spectrophotometer, to determine spectral emissivity in the wavelength range 2 to 25  $\mu$ .

3. A calorimetric device consisting of concentric spheres with nitrogen cooling is used to determine total hemispherical emissivity as a function of temperature.

In addition to these basic instruments, equipment exists for measuring the angular dependence of emissivity and absorptivity, and for the determination of high-temperature emissivity (2000° F) utilizing a modified form of Mendenhall wedge.

A recently constructed device will be used to make direct measurements of the  $\alpha/\epsilon$  ratio and to augment the measurements of  $\alpha$  and  $\epsilon$  obtained using the standard equipment. The new device is shown schematically in Fig. 2. The surface under study is applied to both sides of a thin disk and suspended in an evacuated chamber. Incident solar radiation reaches the specimen through the quartz window at the top, and the radiation intensity is measured with a pyrliometer. Radiation from the specimen is absorbed by the chamber walls, which are cooled by immersion in liquid nitrogen. The  $\alpha/\epsilon$  ratio is computed from the steady-state temperature reached by the specimen. The value of  $\epsilon$  can also be determined in this equipment from the time rate of cooling when the source of radiation is removed. One advantage of using this equipment is that the value of the  $\alpha/\epsilon$  ratio for low values of  $\epsilon$  may be determined with greater accuracy than by conventional reflectance measurements.

The first three items of equipment have been used this year to determine the radiation characteristics of 500 different samples of materials being considered for spacecraft thermal control. Some of the more interesting experimental data are presented in Table 1. Flat absorbers are approximated most satisfactorily by black paints, such as vinyl-phenolic dull black Micobond and acrylic Kemacryl lacquer, and flat reflectors by the aluminum silicone paint. Solar absorbers, such as those listed under metals, show a pronounced effect of surface finish and cleanliness on the  $\alpha/\epsilon$  ratio and require close control by Materials and Processes groups. The chief difficulty is in the attainment of a solar reflecting material. At the present time, white paints are largely used as solar reflectors, but their  $\alpha/\epsilon$  ratio is about 0.27 and is not low enough for many practical applications, such as attaining low temperature for infrared sensors to operate efficiently. Considerable effort is being expended to develop a solar reflector with an  $\alpha/\epsilon$  ratio not greater than 0.1.

## FACTORS AFFECTING CHOICE OF MATERIALS

Although radiation characteristics are of primary importance, they are by no means the only factor involved in choosing a material for thermal control of spacecraft. The radiation characteristics must be reproducible in the shop, and they must be stable not only during the launch, orbit, and re-entry phases for which the vehicle is designed, but they must also be stable during all phases of manufacture, handling, checkout, and storage prior to the actual launch. Reproducibility of thermal control surfaces necessitates careful specification of substrate composition

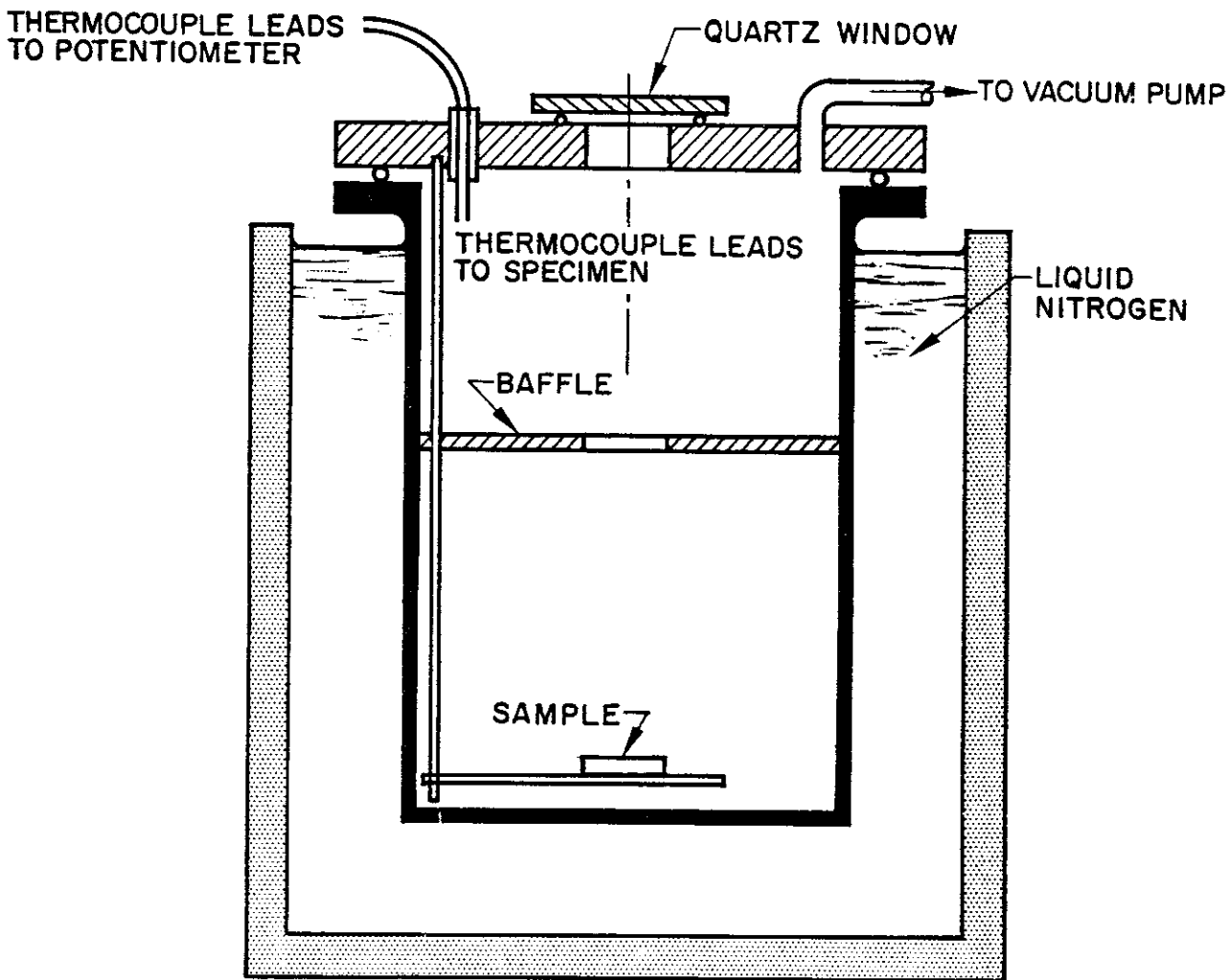


Fig. 2 Schematic of Apparatus for Direct Measurement of  $\alpha/\epsilon$  Ratio

Table 1  
**REPRESENTATIVE MATERIAL RADIATIVE PROPERTIES**

Material	$\alpha$	$\epsilon$	$\alpha/\epsilon$ Ratios
<b>Metals</b>			
Aluminum 6061 alloy			
As received	0.41	0.04	10.3
Machine polished and degreased	0.35	0.04	8.8
Sandblasted, 120 size grit	0.60	0.41	1.5
Aluminum 2024 alloy			
As received	0.27	0.02	13.5
Machine polished and degreased	0.31	0.06	5.2
QMU Beryllium alloy			
Rolled plate, chem. milled	0.48	0.11	4.4
Rolled plate, chem. milled, chem. polished	0.50	0.09	5.6
Gold			
Vacuum deposit gold on aluminum	0.24	0.04	6.0
Vacuum deposit gold on buffed titanium	0.33	0.05	6.6
Nickel			
Electroless nickel	0.45	0.17	2.6
Special surfaces on metals			
Dow 17 on magnesium	0.63	0.66	0.95
Foils and adhesive-backed metals	0.53-0.72	0.50-0.82	0.95
Fascal chrome aluminized mylar film	0.25	0.09	2.8
Bright gold foil	0.29	0.23	1.3
Paints (according to vehicle)			
Vinyl (phenolic)			
Dull black Micabond	0.93	0.84	1.1
Epoxy			
Skyspar (untinted white)	0.26	0.86	0.3
Silicone			
Fuller gloss white silicone	0.30	0.81	0.37
Fuller flat black silicone	0.89	0.81	1.1
Fuller aluminum silicone	0.23	0.20	1.2
Acrylic			
Kemacryl lacquer (white)	0.26	0.75	0.35
Kemacryl lacquer (black)	0.94	0.83	1.1
Miscellaneous			
Silica oxide			
5 mils of silica on magnesium	0.21	0.83	0.25
Adhesive-backed dielectrics			
Scotchcal (white) on aluminum	0.24	0.83	0.29
Ceramics			
Cermet (ceramic containing sintered metal)	0.65	0.58	1.1

$\epsilon$  = total hemispherical emissivity at 500°R

$\alpha$  = solar absorptivity, extraterrestrial

Values listed are averages of several determinations. Accuracy of the tabulated values is variable, but usually reliable to 10 percent, except for very low emissivities.

and finish, plating or coating processes, and all mechanical treatments to which the surface may be exposed.

Prelaunch environmental factors which affect the radiation characteristics of materials are:

1. High ambient temperatures
2. Mechanical wear and tear during handling, which necessitates both excellent adhesion and adequate abrasion resistance of a material
3. Oxidation in air, which causes the formation of a surface coating of oxide on a material with resultant change in the  $\alpha/\epsilon$  ratio
4. Corrosive atmospheres, which cause actual chemical changes in some materials, particularly magnesium
5. Physical contamination from dirt and dust, various organic oil film deposits, and perhaps most important, the fingerprints of workers handling thermal control materials

The launch, orbit, and re-entry stages are those that are usually discussed in connection with spacecraft materials work. Both the launch and re-entry stages are characterized by high temperatures produced by aerodynamic heating and by shear stresses due to atmospheric friction. The temperatures reached by external control surfaces during the ascent phase are frequently of the order of 1000° F. There is an urgent need to develop paints which are stable in this environment. Silicone-base paints, both white and black, which exhibit adequate stability up to about 800° F have been developed by LMSD.

The orbital stage subjects spacecraft to a number of important environmental factors that can affect the radiation parameters of materials. Arranged in order of increasing importance with regard to their effect upon thermal control materials, these factors are:

1. Micrometeorite erosion
2. Sputtering of materials by atmospheric ions and protons and possibly electrons
3. High-energy radiation and high-energy particles, both those in the Van Allen belt and corpuscular radiation emanating from the sun
4. Temperature extremes from -200° F to +600° F and the mechanical and thermal stresses induced by orbital cycling between these extremes
5. The high-vacuum environment ( $\approx 10^{-10}$  mm Hg) and resultant deterioration of volatile materials
6. The ultraviolet component of solar radiation and resultant changes in emissivity of most, if not all, materials exposed to ultraviolet for prolonged periods of time

## EXPOSURE TESTS TO ULTRAVIOLET RADIATION AND VACUUM

A series of tests are in progress at Lockheed in which specimens of temperature-control surfaces are being exposed to ultraviolet radiation in vacuum to evaluate their long-time stability under the last three environmental factors listed above.

The equipment for conducting the exposure tests is shown in Figs. 3, 4, and 5. The vacuum chamber consists of a closed cylinder of stainless steel, measuring 9 in. in diameter by 9.5 in. high. A VacIon pump (Varian model V-11404) with a pumping capacity of 40 liters per second is used to maintain pressures on the order of  $10^{-7}$  mm Hg during the tests. A mechanical pump (not shown in the figures) operates through a liquid nitrogen-cooled trap to lower the chamber pressure to about 5 to 10  $\mu$  before starting the VacIon pump. After the VacIon pump has been put into operation, the outlet from the chamber leading to the mechanical pump is closed and the mechanical pump is removed.

The source of ultraviolet radiation is an argon-filled A-H6 high-pressure mercury arc lamp. It operates with an input of 1000 w. The total radiant output is 65,000 lu, and consists of a continuous spectrum with superimposed lines. The mercury-argon mixture is held in a quartz tube, so that wavelengths less than 2000 A are absorbed by the envelope. The lamp is held in a water-cooled quartz envelope, which absorbs most of the infrared radiation. The lamp assembly is placed in a quartz finger which is sealed through the center of the top of the vacuum chamber. The vacuum chamber is water cooled by a double shell arrangement during the tests.

Specimens for testing are magnesium disks, 1-in. in diameter by approximately 0.125-in. thick, whose surfaces are coated with the appropriate temperature-control material. The disks are affixed to specimen holders, which are water-cooled copper blocks with a depression for accommodating the disks. The single holder shown in Fig. 3 is at a distance such that the intensity of ultraviolet radiation between 2000 and 4000 A is 20 times greater than that which the surface would experience in space. A second holder (not shown in the figures) accommodates 6 specimens and is at such a distance from the ultraviolet source that the specimens attached to it are exposed to an intensity 6 times the solar ultraviolet radiation. In the exposure tests performed to date, the temperature of the specimens was maintained at that of the cooling water during radiation exposure.

Temperature-control surfaces exposed to vacuum and ultraviolet radiation are listed in Tables 2 and 3, and include a number of commercial white paints with  $\text{TiO}_2$  pigment and binders of silicone, acrylic, and epoxy resins, several experimental white paints with various inorganic pigments and sodium silicate binders, and Dow 15 bright metal finish.

The results of exposure tests are summarized in Table 4. Typical spectral curves for a white organic-base paint before and after exposure are shown in Fig. 6. Of the commercial, white organic-base paints, the acrylic-base paints are more resistant to visible yellowing than either the epoxy- or silicone-base paints. For many of the organic-base paints, there is an increase of approximately 50 percent in the solar absorptivity  $\alpha$ , while the infrared emissivity  $\epsilon$  remains almost constant; this significantly increases the  $\alpha/\epsilon$  ratio and, consequently, the average temperature. As is evident from visible changes, inorganic paints with sodium silicate binders appear more stable than the organic-base paints.



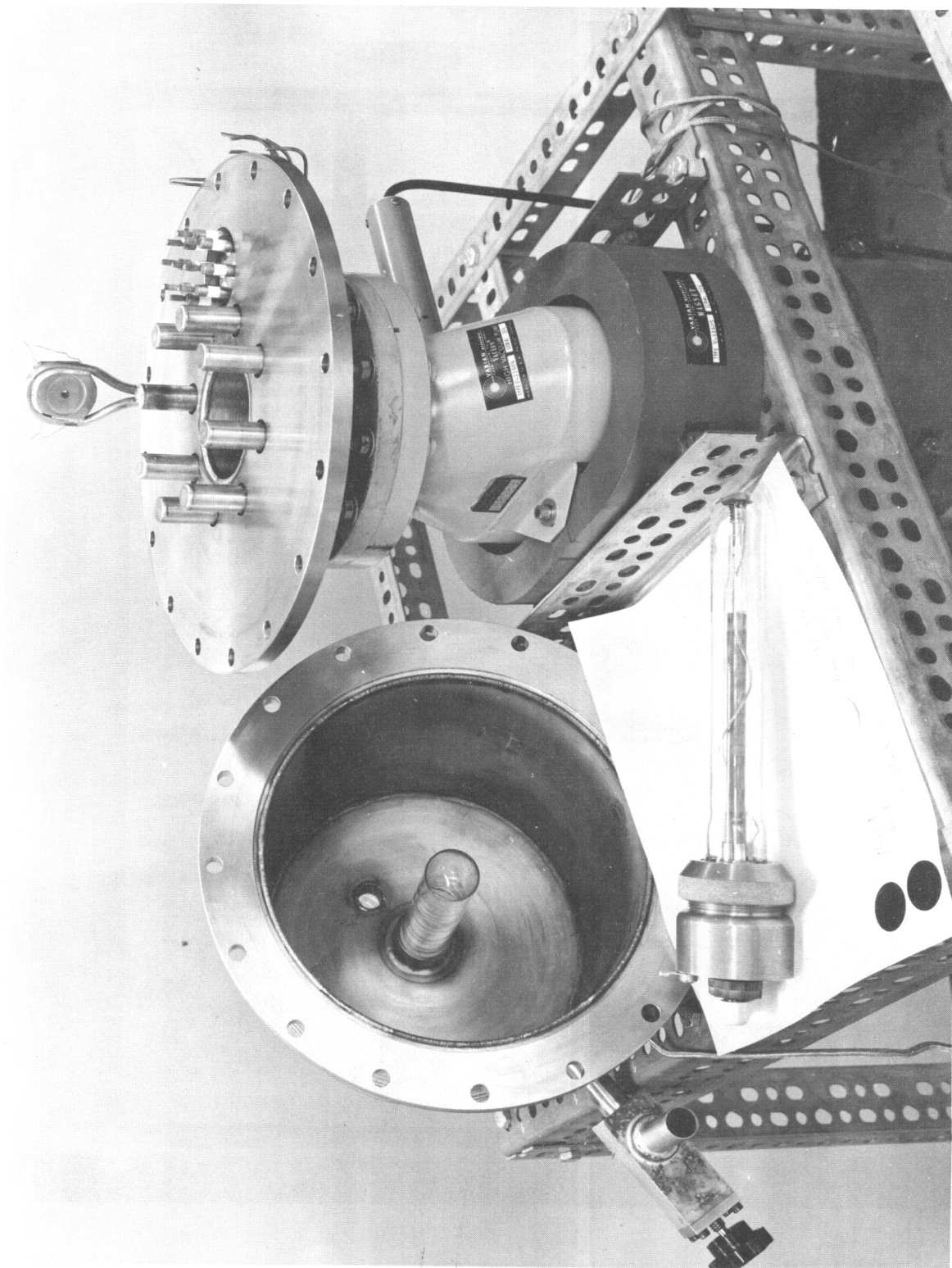


Fig. 3 Equipment for Exposure Tests to Ultraviolet Radiation and Vacuum (Disassembled)

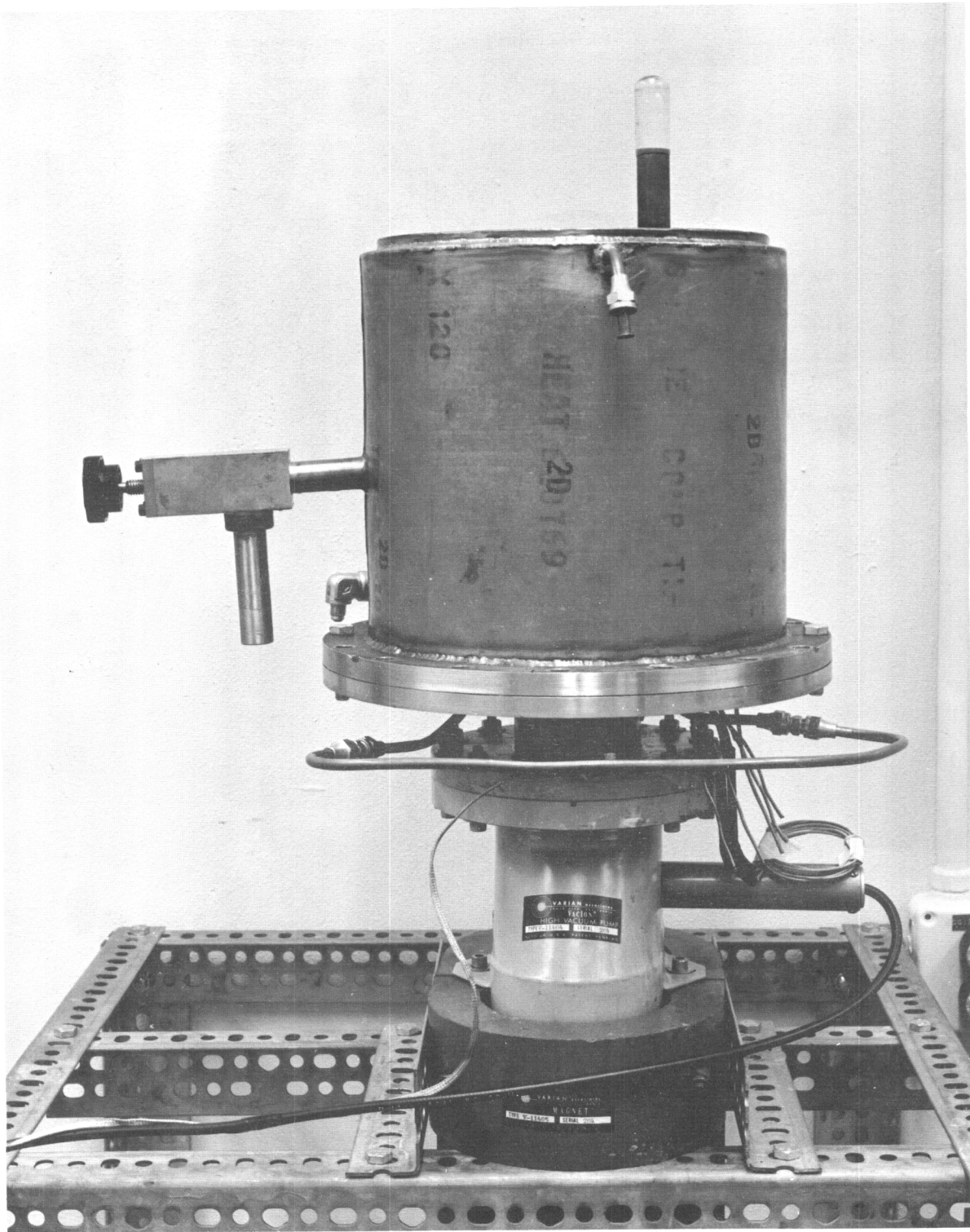


Fig. 4 Vacuum Chamber for Exposure Tests to Ultraviolet Radiation and Vacuum

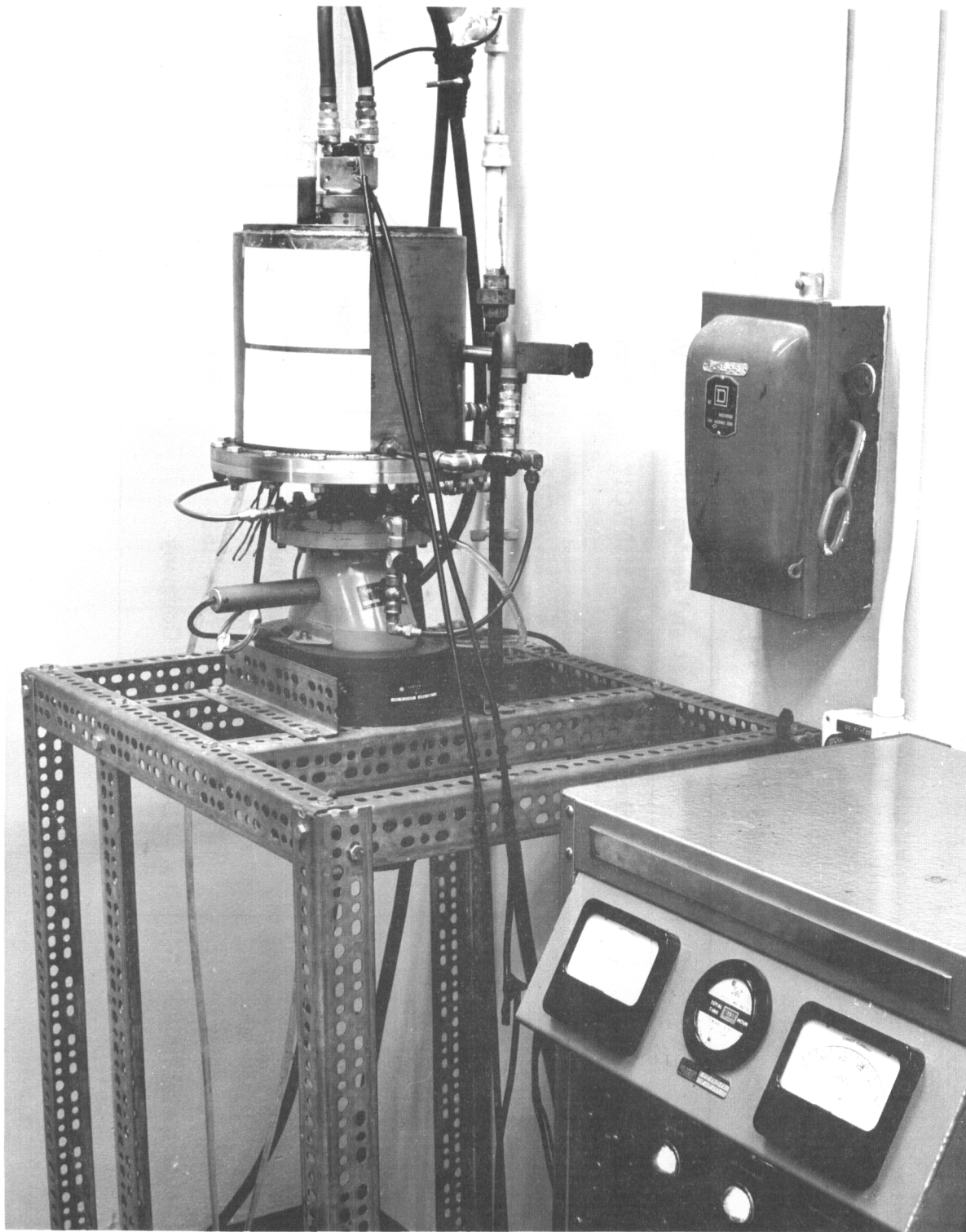


Fig. 5 Equipment for Exposure Tests to Ultraviolet Radiation and Vacuum (Assembled)

Table 2  
 COMMERCIAL MATERIALS EXPOSED TO ULTRAVIOLET RADIATION AND VACUUM

Material	Manufacturer and designation	Vehicle	Pigment
White Kemacryl laquer	Sherwin Williams, M49WC17	Acrylic resin	50 percent TiO <sub>2</sub> , 50 percent talc
Black Kemacryl laquer	Sherwin Williams, M49BC12	Acrylic resin	Carbon black
White Skyspar enamel, A	Andrew Brown, SA-8818 A423-SA8818	Epoxy resin	TiO <sub>2</sub> , tinted
White Skyspar enamel, B	Andrew Brown, A423-SA9185	Epoxy resin	TiO <sub>2</sub> , untinted
Gloss white silicone	H. B. Fuller, 517-W-1	Silicone resin	TiO <sub>2</sub> , untinted
Sicon white, A	Midland Industrial Finishes Co., 7X1153	Silicone	TiO <sub>2</sub> , tinted
Sicon white, B	Midland Industrial Finishes Co., 7X1120	Silicone	TiO <sub>2</sub> , tinted
Aluminum silicone paint	H. B. Fuller, 171-A-152	Silicone	Aluminum
Dow 15 bright metal finish	Dow Chemical Company	Chemical treatment; no vehicle or pigment	

Table 3

LABORATORY-PREPARED PAINTS EXPOSED TO ULTRAVIOLET RADIATION AND VACUUM

Coating Composition (parts by weight)	Curing Cycle
146 parts sodium silicate K 356 parts zircon 890 parts water	0.5 hr 20° C, 1 hr 110° C, 2 hr 150° C, 1.5 hr 250° C, 1 hr 400° C
120 parts silicone resin 40 parts xylene	2 hr 20° C, 0.5 hr 85° C, 0.5 hr 120° C, 16 hr 155° C, 1 hr 210° C, 1 hr 265° C, 1 hr 325° C
120 parts silicone resin 70 parts barium titanate 40 parts xylene	2 hr 20° C, 0.5 hr 85° C, 0.5 hr 120° C, 16 hr 155° C, 1 hr 210° C, 1 hr 265° C, 1 hr 325° C
120 parts silicone resin 70 parts strontium zirconate 40 parts xylene	2 hr 20° C, 0.5 hr 85° C, 0.5 hr 120° C, 16 hr 155° C, 1 hr 210° C, 1 hr 265° C, 1 hr 325° C
120 parts silicone resin 70 parts zircon 40 parts xylene	2 hr 20° C, 0.5 hr 85° C, 0.5 hr 120° C, 16 hr 155° C, 1 hr 210° C, 1 hr 265° C, 1 hr 325° C
100 parts sodium silicate K 57 parts Aquablack B 50 parts water	88 hr 20° C, 1 hr 65° C, 1 hr 110° C, 2 hr 150° C
142 parts sodium silicate D 356 parts zircon 890 parts water	0.5 hr 20° C, 1 hr 110° C, 2 hr 150° C, 1.5 hr 250° C, 1 hr 400° C

Sodium silicate D has Na<sub>2</sub>O:SiO<sub>2</sub> ratio of 1:2.00; sodium silicate K, 1:2.90

Silicone resin was Dow Corning No. 805

Table 4

RESULTS OF EXPOSURE TO ULTRAVIOLET RADIATION AND VACUUM

Test No.	Exposure Time (hr)	Material	Substrate	Visible Changes	Measured Radiation Characteristics			
					Before		After	
					$\alpha$	$\epsilon$	$\alpha$	$\epsilon$
1	46	White Skyspar enamel, A Gloss white silicone	Dow 15 treated magnesium alloy	yellowed	0.25	0.85	0.37	0.87
					0.280	0.83	0.293	0.82
2	80	White Skyspar enamel, A (2 samples) White Kemacryl lacquer Black Kemacryl lacquer Aluminum silicone paint (2 samples)	Dow 17 treated magnesium alloy	yellowish brown	0.22-0.23	0.82-0.85	0.39	0.82
			Dow 17 treated magnesium alloy	very slight yellowing	0.26	0.73	0.33	0.78
			Dow 17 treated magnesium alloy	very slight change	0.94	0.81	0.92	0.79
			Bare, untreated magnesium alloy	slight crackling	0.21-0.22	0.20-0.19	0.30-0.33	0.23-0.27
3	26	White Skyspar enamel, B Gloss white silicone (2 samples) Gloss white silicone White Kemacryl lacquer (2 samples) White Kemacryl lacquer (20 times intensity)	Dow 17 treated magnesium alloy	yellowish brown	0.24	0.83	0.37	0.85
			Bare, untreated magnesium alloy	yellowish brown	0.27-0.33	0.83	0.30-0.35	---
			Dow 15 treated magnesium alloy	yellowish brown	0.30	0.81	0.34	0.78
			Dow 17 treated magnesium alloy	very little change	0.27	0.73	0.32	0.76
			Dow 17 treated magnesium alloy	very little change	0.27	0.73	0.35	0.75
			Dow 15 treated magnesium alloy	yellowish brown	0.26	0.86	0.31	0.84
4	12	White Skyspar enamel, B (2 samples) Gloss silicone white Sicon white, A Dow 15 finish on magnesium (2 samples) Dow 15 finish on magnesium (20 times intensity)	Bare, untreated magnesium alloy	yellowish brown	0.30	0.81	0.29	0.83
			Dow 15 treated magnesium alloy	yellowish brown	0.25	0.83	0.33	0.83
			---	no change	0.23-0.17	0.06-0.07	0.28	0.07-0.08
			---	no change	0.18	0.09	0.38	0.14
5	100	Gloss white silicone (2 samples) Sicon white, A White Kemacryl lacquer (2 samples) White Skyspar enamel, B Sicon white, (20 times intensity)	Bare, untreated magnesium alloy	yellowish brown	0.30	0.81	0.33	0.84
			Dow 15 treated magnesium alloy	yellowish brown	0.26	0.84	0.37	0.83
			Dow 17 treated magnesium alloy	no change	0.74	0.35-0.32	0.76	---
			Bare, untreated magnesium alloy	yellowish brown	0.26	0.86	0.36	0.82
			Dow 17 treated magnesium alloy	very dark brown	0.31	0.83	0.60	0.83
			Dow 17 treated magnesium alloy	slight yellowing	---	---	---	---
6	127	Unpigmented silicone resin Barium titanate pigment, silicone resin Stroptium zirconate pigment, silicone resin Zircon pigment, silicone resin Zircon pigment, sodium silicate K binder Aquablack B, sodium silicate binder Zircon pigment, sodium silicate D binder (20 times intensity)	Dow 17 treated magnesium alloy	yellowed	---	---	0.34	0.84
			Dow 17 treated magnesium alloy	severe yellowing	---	---	0.47	0.85
			Dow 17 treated magnesium alloy	severe yellowing	---	---	0.45	0.85
			Dow 17 treated magnesium alloy	slight yellowing	0.20	0.84	0.21	0.83
			Dow 17 treated magnesium alloy	slight lightening	---	---	0.91	0.78
			Dow 17 treated magnesium alloy	slight yellowing	0.184	---	0.22	0.83

Note: Intensity of ultraviolet radiation was six times solar ultraviolet intensity in space, except as noted. Vacuum generally improved with time during each test, beginning at about 8 X 10<sup>-6</sup> mm Hg and ending at about 1 X 10<sup>-6</sup>.

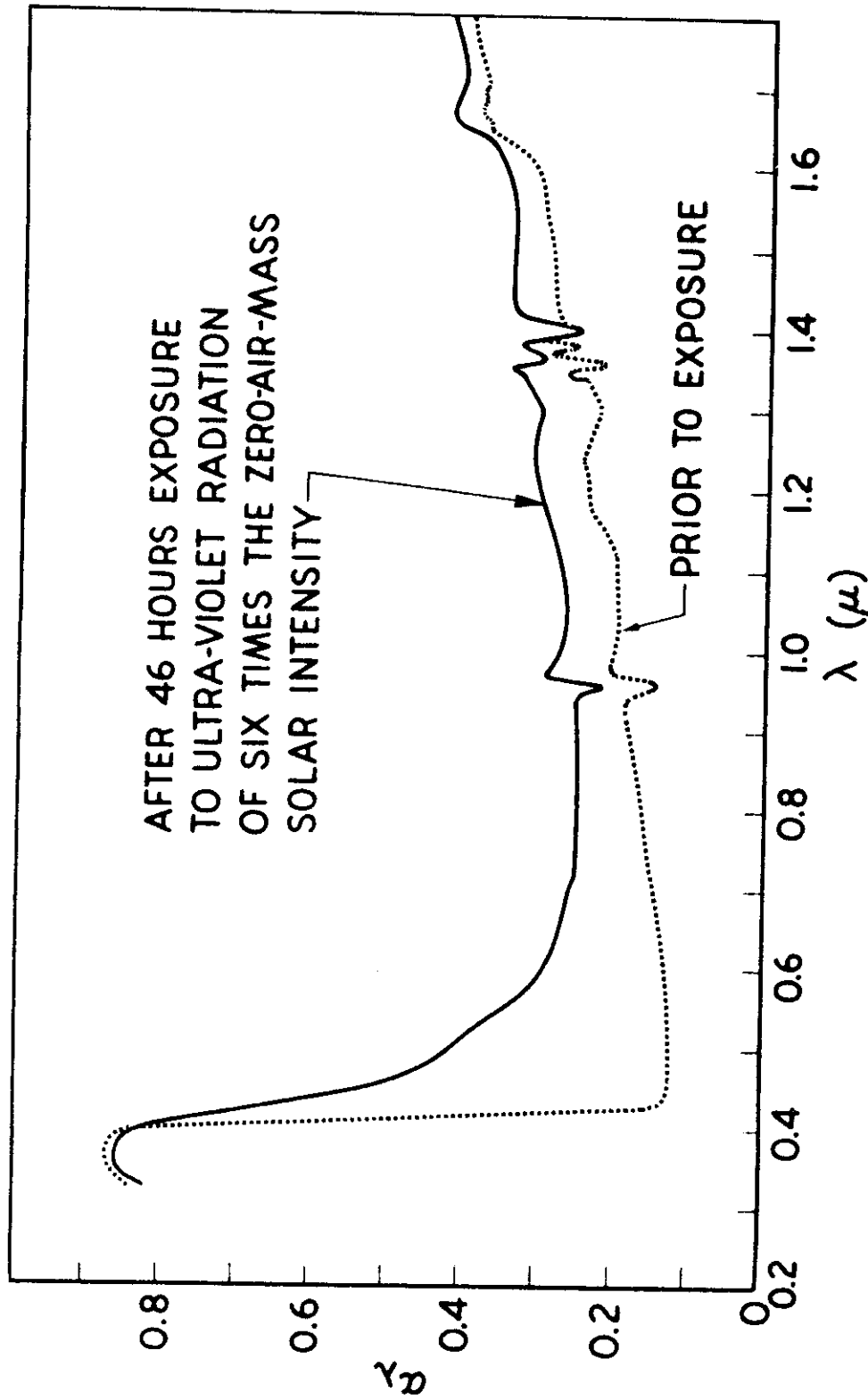


Fig. 6 Spectral Absorptivity  $\alpha_\lambda$  Versus Wavelength  $\lambda$  for  $TiO_2$ -Pigmented Epoxy-Base Paint (Dips in the curve at approximately 1.0 and 1.4  $\mu$  are probably due to absorption in the reference and not true characteristics of the paint itself)

## INORGANIC TEMPERATURE-CONTROL PAINTS

Because of the poor stability of paints with organic vehicles, LMSD is engaged in a program to develop temperature-control paints of inorganic materials with greater stability. Much of the present program was based on work initiated by the late Dr. L. Whitby (Ref. 3). For current application, the paints must be compatible with magnesium and have the usual requirements of adherence and emissivity. The stability of these paints under vacuum, ultraviolet radiation, and aerodynamic heating is being determined as part of the overall effort.

Vehicles under consideration include silicates and phosphates. Pigments include oxides, double oxides, refractory silicates, and sulfides, as well as carbon black, graphite, and carbides. Such other agents as dispersants, anticoagulants, and buffers are also used in some of the compositions. Tables 5, 6, and 7 list typical vehicles and pigments being studied, and Tables 4 and 8 list typical paint formulations and curing cycles, respectively.

In addition to the materials, the investigation is concerned with the vehicle-to-pigment ratio, particle size of pigment, viscosity, pH, and methods of mixing, application, and curing.

The sodium silicates listed in Table 4 provide a wide range of  $\text{Na}_2\text{O}:\text{SiO}_2$  ratios. The lower  $\text{SiO}_2$  contents give the most desirable properties. These vehicles show good adhesion and cohesion when properly applied in thin coats. Although firing at  $300^\circ\text{C}$  to  $350^\circ\text{C}$  ( $575^\circ\text{F}$  to  $660^\circ\text{F}$ ) has been generally thought necessary to impart stability against moisture, a properly pigmented sodium silicate seems to stabilize at about one-half of this temperature, so that very high curing temperatures are not necessary.

The aluminum phosphates listed in Table 4 adhere better than the silicates to many metals. The higher  $\text{P}_2\text{O}_5$  contents appear preferable, probably because of their higher concentration of  $\text{Al}(\text{H}_2\text{PO}_4)_3$ , which is the active vehicle. Pigmentation results in a liberation of gas and an increase in the pH to about 3 to 5, depending on the amount and particle size of the pigment. The high acidity of the aluminum phosphates makes them too reactive to be used directly on magnesium. For use on magnesium, these vehicles have been buffered with ammonium compounds such as ammonium hydroxide. The ammonia is lost in the early stages of curing, so that there is no net change in the paint formulation.

Of the various oxide and silicate pigments studied thus far, zircon ( $\text{ZrSiO}_4$ ) has shown the greatest resistance to ultraviolet radiation. Commercial titania ( $\text{TiO}_2$ ) undergoes severe yellowing. This yellowing may be caused by the formation of color centers resulting from impurities in commercial titania. It is likely that other pigments listed in Tables 5 and 6 will prove to have equal value to zircon as the program progresses.

Inorganic paints are prepared in the conventional manner by ball milling with porcelain mills and balls. The milling operation requires from 12 to 72 hours to obtain a uniform consistency suitable for spray application. Phosphate-based paints, in general, require longer milling than silicate types. Small evaluation samples have been prepared rapidly with a high-speed blender.



Table 5

**SODIUM SILICATE VEHICLES**

Ratio Na <sub>2</sub> O·SiO <sub>2</sub>	Na <sub>2</sub> O Content (%)	SiO <sub>2</sub> Content (%)	Density (g/cc)	Viscosity (P)
1:3.75	6.75	25.3	1.318	2.2
1:3.22	8.90	28.7	1.394	1.8
1:2.90	11.00	31.9	1.480	9.6
1:2.00	14.70	29.4	1.534	3.5
1:1.60	19.50	31.9	1.676	7.0

Table 6

**ALUMINUM PHOSPHATE VEHICLES**

P <sub>2</sub> O <sub>5</sub> Content (%)	Al <sub>2</sub> O <sub>3</sub> Content (%)	H <sub>2</sub> O Content (%)	Viscosity (cp)	Acidity (pH)
16	13	71	—	1.0
20	12	68	—	0.8
24	11	65	1500	0.5
31	9	60	—	0.5
33	9	58	60	2.6 (1% solution)
33	13	54	—	0.4
36	11	53	1000	2.6 (1% solution)

Table 7  
INORGANIC PIGMENTS FOR LMSD LABORATORY PREPARED PAINTS

Material	Melting Point (°C)	Mesh Size Range	Density (g/cc)
BeO	2530	-325	3.01
ZrO <sub>2</sub>	2715	-200 to +325	5.6
Nb <sub>2</sub> O <sub>5</sub>	1520	—	4.47
Ta <sub>2</sub> O <sub>5</sub>	1470 <sup>(a)</sup>	—	8.735
ThO <sub>2</sub>	3050	-200 to +325	10.03
BaTiO <sub>3</sub>	—	-100 to +200	—
SrTiO <sub>3</sub> <sup>(c)</sup>	—	—	—
BaZrO <sub>3</sub>	—	-200	—
MgSiO <sub>3</sub>	1557 <sup>(a)</sup>	—	3.28
CaSiO <sub>3</sub>	1200 <sup>(b)</sup>	-325	2.915
Al <sub>6</sub> Si <sub>12</sub> O <sub>13</sub>	1810 <sup>(a)</sup>	—	3.15
ZrSiO <sub>4</sub>	2550	—	4.56
CaTiO <sub>3</sub>	—	—	4.10

- (a) decomposes
- (b) transforms
- (c) to be investigated

Table 8  
CURING CYCLES

Vehicle	Paint Pigment	Time (hr)	Temperature (oC)	Remarks
Na <sub>2</sub> SiO <sub>2</sub> (1: 2.90)	ZrSiO <sub>4</sub>	0.5	20	No change after 250° C
		1.0	110	
		2.0	150	
		1.5	250	
		1.0	400	
Na <sub>2</sub> O.SiO <sub>2</sub> (1: 2.00)	BaTiO <sub>3</sub>	1.0	20	
		1.0	80	
		1.0	150	
		0.5	200	
		0.5	260	
		0.5	370	
Na <sub>2</sub> O.SiO <sub>2</sub> (1: 2.90)	Carbon Black	8.0	20	Loss of pigment above 350° C
		1.0	65	
		1.0	110	
		2.0	150	
Al <sub>2</sub> O <sub>3</sub> , H <sub>3</sub> PO <sub>4</sub> BaTiO <sub>3</sub>	BaTiO <sub>3</sub>	2.0	20	No change above 200° C
		0.5	80	
		0.5	115	
		16.0	150	
		1.0	200	
		1.0	260	
		1.0	315	

# Contrails

In the case of the phosphates, it is helpful to mill the vehicle before adding the pigment.

All paints are applied by standard spray techniques to 3 by 5 or 2 by 4 in. panels of magnesium that have received a Dow 17 treatment. The rate of paint application, optimum thickness, and number of coats are determined for each composition.

Both silicate- and phosphate-based paints must be applied in relatively thin coats (approximately 1 mil) to prevent crazing during the curing cycle. Two or three coats with intermediate low-temperature cures are required to obtain a good coating over the magnesium panels. There are indications that room-temperature drying is an adequate between-coat cure.

Both silicate and phosphate paints require a thermal curing cycle to eliminate free moisture and to form a stable film. Because most of the water is lost during the spray application, relatively short heat treatments are sufficient.

Several successful curing cycles for these classes of paints are given in Table 8. In all cases, these samples were carried beyond the limits required for stability, and temperature can probably be reduced by as much as 50 percent. Further quantitative studies are required in this area.

Temperature stability is determined as part of the curing cycle in most cases. Using the silicate and phosphate compositions discussed, there has been no detectable change in coatings up to 500°C. In a few cases checked, the silicate materials exhibited no significant deterioration up to the melting point point of the metal substrate (651°C).

The only white compositions thus far evaluated which have shown high-radiation resistance are zircon pigmented silicates. The carbon black pigmented silicate also shows favorable characteristics. Titania pigmented vehicles are poor in radiation resistance.

## REFERENCES

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