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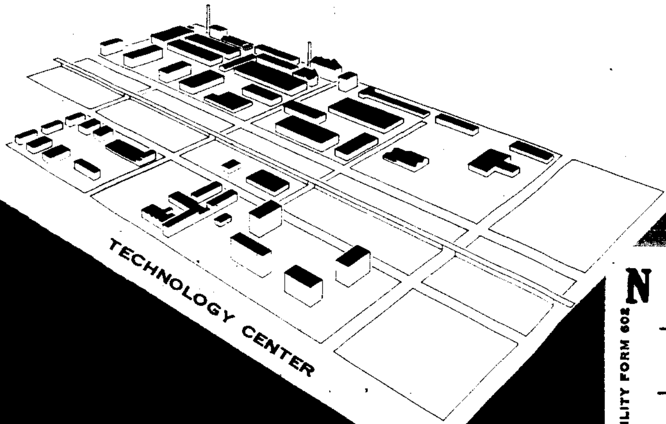

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Index JPL-950111

ARF Project C 207
JPL Contract ~~No.~~ 950111
(Subcontract under NASA Contract NAS7-100);

Title

STABLE WHITE COATINGS

Report No. ARF 3207-14
(Interim Report)
Title Suppl. Int. reps.
April 1 ~~to~~ October 1, 1962

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Nov. 13, 1962 102p 4 refs

for

Jet Propulsion Laboratory
Pasadena, California

Unclassified report

[redacted]

Copy No.________

November 13, 1962

FOREWORD

This is Report No. ARF 3207-14 (Interim Report) of ARF Project C 207, Contract No. 950111 (subcontract under NASA Contract NAS7-100), entitled "Stable White Coatings." The report covers the period from April 1 to October 1, 1962. A previous interim report, No. ARF 3207-5, was issued in April 1962.

Personnel who contributed to the program during this period include Gene A. Zerlaut (Project Leader and organic coatings formulation), Y. Harada and Harold L. Rechter (inorganic coatings formulation), Richard J. Larson (space-chamber operation and ion-pump solar-simulation design), O. Harry Olson (solar absorptance and emittance measurements), Dr. Caroline D. Miller (ultraviolet irradiation effects), Edwin H. Tompkins (zinc oxide photolysis studies), William L. Stepp (methyl silicone preparations), and Dr. Nicodemus E. Boyer (polyurea preparations). Major contributions to this report were made by C. D. Miller, E. H. Tompkins, and R. J. Larson.

Data are recorded in ARF Logbooks C 9164, C 11712, C 11934, C 12115, C 12238, C 12283, and C 12750.

Respectfully submitted,

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ABSTRACT

STABLE WHITE COATINGS 15369 10374

Investigation of the stability of various white materials as potential pigments for use on spacecraft was continued. Candidate coatings were exposed to an extraterrestrial ultraviolet environment for periods up to 3100 equivalent sun-hours. Emphasis was placed on developing usable zinc oxide-potassium silicate coatings and zinc oxide-pigmented methyl silicone polymers. The physical properties of these systems were studied in detail; in particular, torsion stress resistance, fatigue (vibration) resistance, abrasion resistance, temperature cycling, and soiling/cleaning operations, were investigated.

These studies showed that zinc oxide-potassium silicates possess ultraviolet stability superior to that of all other pigment/vehicle systems examined. Zinc oxide-methyl silicone paints were found to possess only slightly less stability than the inorganic silicate paints. The potassium silicate coatings are better solar reflectors than the methyl silicone paints, possessing solar absorptance of 0.15 versus 0.22 for the silicones.

An ion-pump space-simulation chamber was constructed, making possible longer, cleaner exposures at solar factors of 4 to 18 equivalent intensities.

Author

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STABLE WHITE COATINGS

I. INTRODUCTION

The principal objective of this program is the development of a white spacecraft coating with exceptionally high resistance to extraterrestrial solar radiation. Therefore, the primary requirements are that the coating possess a high degree of resistance to ultraviolet radiation in vacuum and that the maximum allowable change in α/ϵ, the ratio of solar absorptance to emittance, be only 10% after 1 year of exposure, with $\alpha/\epsilon \approx 0.2 \pm 0.05$ and $\epsilon \approx 0.9$. The other requirements are that the coating must cure at 300°F or less and that the coating must remain adherent to aluminum alloys and other spacecraft structural materials through temperature changes of 50°F/min between 200 and -100°F.

Work accomplished during the first interim report period provided a general basis for planning the remainder of the program. During the earlier portion of the work, a relatively wide range of organic and inorganic coatings, vehicles, and pigments were exposed in a vacuum for periods equivalent to 75 to 250 sun-hours. Spectral reflectance and solar absorptance determinations before and after exposure showed that no material was completely unaffected by the test conditions -- a fact which is consistent with the findings of other workers. This screening program did show, however, that zinc oxide and, to a lesser extent, zinc sulfide are unusually stable white pigments and that these pigments form relatively stable coatings when dispersed in pure potassium silicate and nonaromatic silicone vehicles. An analysis of the results of this earlier work indicated that coatings of still better stability could be developed.

Therefore, during the past six-month period, studies directed at finding new and better pigments and binder materials were continued. Increasing emphasis was placed on zinc oxide-potassium silicate coatings, which have been shown to be the most stable system in space-simulation experiments. With the exception of some preliminary syntheses of polyureas, the organic work was confined to evaluation of zinc oxide-pigmented methyl silicones. Various methyl silicone resins were synthesized in attempts to improve the film-forming characteristics of pigmented systems. In addition, greater emphasis was placed on the use of General Electric's LTV-602 elastomeric methyl silicone potting compound.

Studies during this period included determinations of physical and optical properties as functions of paint thickness and composition. The effects of soiling and cleaning candidate coatings were studied. The feasibility of eliminating heat curing of the potassium silicate coatings was investigated.

An ion-pump space-simulation system was constructed and was placed in operation during the past six months. In conjunction with the much longer tests now possible, the ion-pump system has served to permit irradiation at higher intensities than was practical with the larger diffusion-pump system described in the earlier report. The use of a special wide-angle thermopile, constructed for us by Eppley Laboratories, has made the estimates of solar ultraviolet intensity factors considerably more accurate.

II. EVALUATION OF INORGANIC PAINTS

A. Preparation of Materials

All paint formulations contained three ingredients: pigment, vehicle, and enough water to achieve a sprayable consistency. The only exceptions to this limited composition were a few paints which incorporated a wetting agent. Mixing was accomplished by ball-milling with porcelain balls for times ranging from 18 to 24 hours. Substrates for the paints were prepared in various sizes from type 6061 T6 aluminum. The panels were abraded by hand with No. 60 Aloxite metal cloth and cleaned by washing with detergent and water.

The paints were applied to the substrates by spraying with a Paasche type AUTF thumb-action airbrush. A pressure of 30 psi was generally used; the air source was a tank of compressed dry air. Two methods of curing were used. One was merely air drying, and the second was an 18-hour air drying followed by a 24-hour cure at 130 to 140°C.

Zinc oxide powders of various purities and particle sizes were investigated and are listed in Table 1. The vehicle which was used almost exclusively is PS7 potassium silicate, supplied by Sylvania Electric Products. The analysis for this binder is as follows:

Specific gravity	1.331
K_2O	11.38
SiO_2	23.83
Total solids	35.21
Mol ratio	1:3.28
Iron	.0027
Copper	$<4 \times 10^{-6}$

Table 1

ZINC OXIDE POWDERS INVESTIGATED

Material	Purity, %	Mean Particle Size, μ	Supplier
SP500	99.80	0.25-0.35	New Jersey Zinc
XX254	99.60	1.5	New Jersey Zinc
AZO 55-LO[a]	99.20	0.4	American Zinc Sales
E-P 414	99.40	1.0	Eagle-Picher
E-P 730	99.50	5.4	Eagle-Picher

[a]Low oil absorption.

B. Determination of Physical Properties

1. Thermal Shock

Initial thermal shock tests for the various paints involved elaborate methods for monitoring temperature and mounting samples in order to meet the requirements of the contract; i.e., the coating must withstand a change of 50°F/min between 200 and -100°F.

A simpler method was devised for more rapid testing of the majority of samples. This consisted of dropping the coating specimen directly into liquid nitrogen contained in a Dewar flask. Cessation of bubbling, in about 20 sec, indicated that the specimen had cooled to -320°F. The sample was then removed and placed in an oven at 200°F, a temperature which the sample attained in about 4 min. The severity as well as the simplicity of this test rendered it ideal for determining thermal shock resistance.

No damage to the silicate-bonded paints was evident after 10 cycles of the test. Compositions incorporating the zinc oxides listed in Table 1 and zirconium oxide also resisted the thermal shock successfully. A zinc sulfide-pigmented phenyl silicone panel furnished by the Jet Propulsion Laboratory failed on the first immersion.

2. Torsion

The torsion apparatus illustrated in Figure 1 was used to study adhesion of paints to substrates. One end of a 1 x 3-inch sample was held rigid while the other end was rotated through the longitudinal axis at a speed of approximately 1°/sec.

Shear failure in torsion usually occurred with initial separation from the substrate at points A and B (see Figure 2). Subsequent failure along the dotted diagonal line resulted almost immediately, except in a few cases. It is possible that the grips holding the sample in place at the ends may contribute additional stress which would not exist in pure torsion. The condition of loading in pure torsion implies that the end sections of the bar are free to warp, since there are no constraining forces to hold them in their respective planes.[1] Thus the angle-at-failure reported for various samples in torsion may actually be lower than the true values.

The data in Tables 2, 3, and 4 indicate that thermal shock had no deleterious effect on adhesion. Variations in pigment-to-binder ratio and solids content or omission of heat curing did not contribute to any significant change in the angle-at-failure. Coating thickness had an inverse relationship to torsional strength.

Calcination of SP500 zinc oxide yielded materials which required less diluent (distilled water) for satisfactory spraying viscosity (Table 3). Although good hardness was obtained by using powders calcined at 800 and 1000°C, they were visibly yellow. The powders calcined at 750°C also exhibited improved hardness. Incorporation of zinc oxides other than

[1] Roark, R. J., Formulas for Strees and Strain, McGraw-Hill Book Co., Inc., 1954.

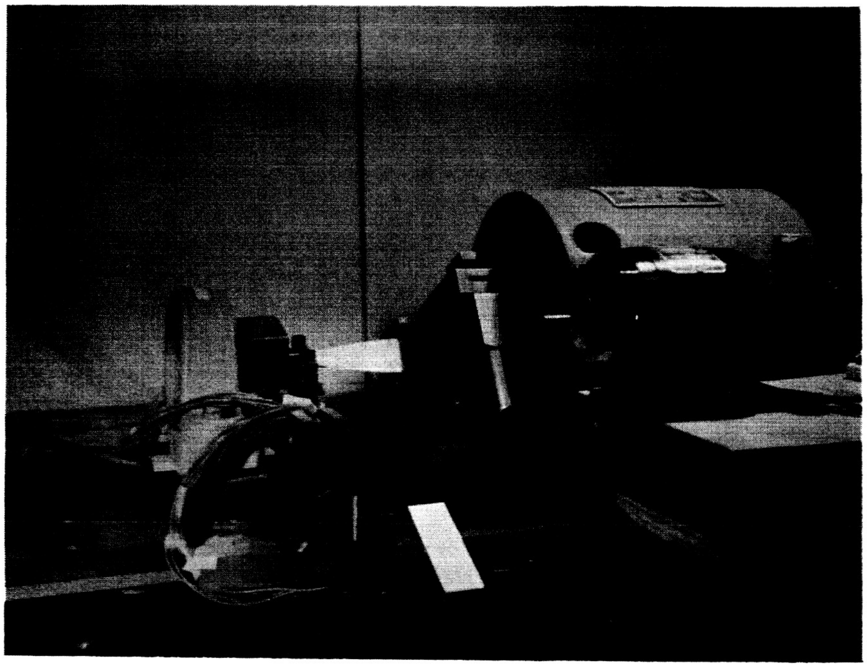

Figure 1

TORSION TEST APPARATUS

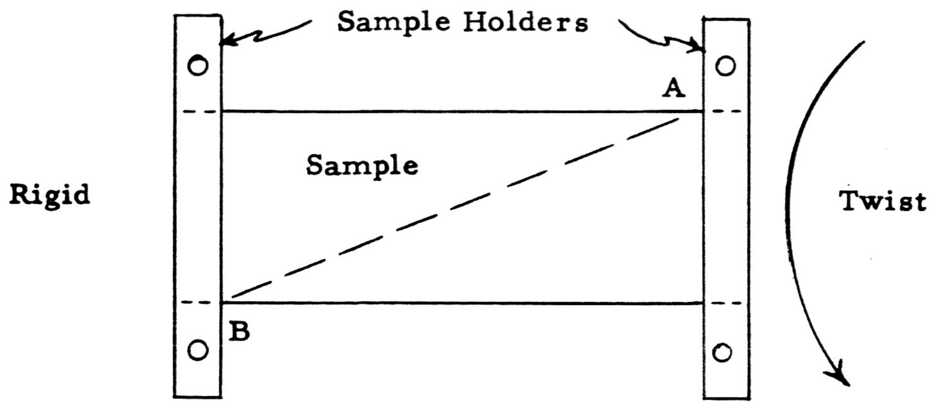

Figure 2

TORSIONAL FAILURE

Table 2

TORSIONAL STRESS RESISTANCE
OF SILICATE-BONDED SP500 ZINC OXIDE COATINGS
(composed of SP500 zinc oxide, PS7 potassium silicate, and distilled water)

Pigment-to-Binder Ratio	Solids, %	Cure	Sample	Thickness, mils	Angle-at-Failure, °
4.30	46.3	24 hr at 140°C	10-3a6	2	55
			10-3a7	2	64
			10-3a5[a]	2	54
			4-2c1	3	47
			4-2c2	4	44
			4-2c3[a]	3	49
			4-2c4[a]	2	62
			4-0b1[a]	2	54
			4-0b2[a]	3	49
4.30	46.3	Air dried only	10-3c1[a]	2	72
			10-3c2[a]	2	77[b]
			10-3c3	2	52
			4-2a1	3	52[b]
			4-2a2[a]	2	64[b]
			4-2a3	2	60[b]
			4-0a1	3	51
			4-0a2	3	39
			21-5f	6	35
			19-6b	5	37
4.30	51.1	24 hr at 140°C	10-1b1[c]	4	38
			10-1a2[c]	3	49
			10-1b6[a, c]	3	53
4.30	52.9	24 hr at 140°C	10-4d[c]	4	37
			10-4a[a, c]	4	33
3.22	51.3	24 hr at 140°C	14-0d	3	48
			14-0e	3	51
			14-0h[a]	3	52
3.58	49.3	24 hr at 140°C	14-4h	2	68
			14-4f	2	67
			14-4e[a]	2	70

[a] Thermally shocked: 10 cycles of 200 to -320°F in 5 min.

[b] Unlike the other samples, these experienced only minor chipping at corners and edges. The bulk of the coating remained intact on the aluminum substrate, even when further twisted to 90°.

[c] 2 drops Monamine AD-100 wetting agent added.

Table 3

TORSIONAL STRESS RESISTANCE
OF SILICATE-BONDED CALCINED SP500 ZINC OXIDE COATINGS
(composed of calcined SP500 zinc oxide, PS7 potassium silicate, and distilled water)

Calcination		Pigment-					
Temp., °C	Time, hr	to-Binder Ratio	Solids, %	Cure	Sample	Thickness, mils	Angle-at-Failure, °
500	66	4.30	52.9	24 hr at 140°C	12-1c	3	40
					12-1a[a]	4	47
650	18	4.30	56.9	24 hr at 140°C	13-6a[a]	5	36
					13-6b[a]	4	52
700	2	4.30	52.9	24 hr at 140°C	12-42	2	60
					12-48	2	76
					12-41[a]	2	64
700	16	4.30	56.9	24 hr at 140°C	14-2a	5	44
					14-2c	4	50
					14-2d	5	53
750	2	4.30	56.9	24 hr at 140°C	13-5b	3	61
					13-5a[a]	3	53
800	12	4.30	64.4	24 hr at 140°C	10-6b	3	27
1000	1	4.30	64.4	24 hr at 140°C	12-2b[a]	2	49

[a]Thermally shocked: 10 cycles of 200 to -320 to 200°F in 5 min.

Table 4

TORSIONAL STRESS RESISTANCE
OF SILICATE-BONDED ZINC OXIDE COATINGS
(composed of various zinc oxides, PS7 potassium silicate, and distilled water)

Pigment	Pigment-to-Binder Ratio	Solids, %	Cure	Sample	Thickness, mils	Angle-at-Failure, °
AZO 55-LO	4.30	56.9	24 hr at 140°C	4-6c1	2	52
				4-6c2	3	47
AZO 55-LO	4.30	56.9	Air dried only	4-6a1	2	50
				4-6a2	3	52
AZO 55-LO	3.22	59.0	24 hr at 140°C	14-1e	2	47
				14-1f	3	28
				14-1a[a]	2	47
AZO 55-LO[b]	4.30	61.7	24 hr at 140°C	14-3d	3	46
				14-3a[a]	4	42
E-P 730	4.30	73.0	24 hr at 140°C	15-04	3	41
				15-01[a]	3	41
E-P 414	4.30	56.9	24 hr at 140°C	15-1e	3	73
				15-1f	3	58
				15-1b[a]	3	68
XX254	4.30	61.7	24 hr at 140°C	15-2a	4	45
				15-2b	2	48
				15-2e[a]	3	50
XX254	4.30	73.0	24 hr at 140°C	15-3a	5	36
				15-3b[a]	3	37
XX504	4.30	60.4	24 hr at 140°C	4-7c1	2	31
				4-7c2	3	24
XX504	4.30	60.4	Air dried only	4-7a1	3	25
				4-7a2	1	42

[a]Thermally shocked: 10 cycles of 200 to -320°F in 5 min.

[b]Calcined at 700°C for 16 hr.

SP500 yielded coatings which exhibited hardness and torsional stress resistance comparable with those of calcined SP500.

Torsional stress resistance of all silicate-bonded zinc oxide coatings appeared to be primarily a function of thickness. There were indications that the harder, more brittle samples were slightly more susceptible to physical distortion. As in the thermal shock tests, the samples all survived a stress condition much more severe than might be expected in actual practice.

3. Fatigue

A test method which may more closely simulate actual launch and flight conditions consists of subjecting a sample first to fatigue and then to thermal shocking. The fatigue machine rapidly vibrated one end of a 1 x 3-inch coated specimen while the other end was held rigid (Figure 3). The distance of travel of the free end (0.01 inch) was determined from the formula for end-loading of a cantilever:

$$d = \frac{P L^3}{3 E I}$$

where P = load

L = length

E = modulus of elasticity

I = moment of inertia.

The use of a strain value of 1500×10^{-6} inches/inch (75% of the yield strength of aluminum) in the calculation precluded plastic deformation of the aluminum.

The various samples were each subjected to over 10,000 cycles in a 6-min period (1725 cycles/min). They were then thermally shock tested for 10 cycles by immersion in liquid nitrogen followed by rapid heating to 200°F. None of the specimens (listed in Table 5) were visibly affected by this combination of physical and thermal stresses.

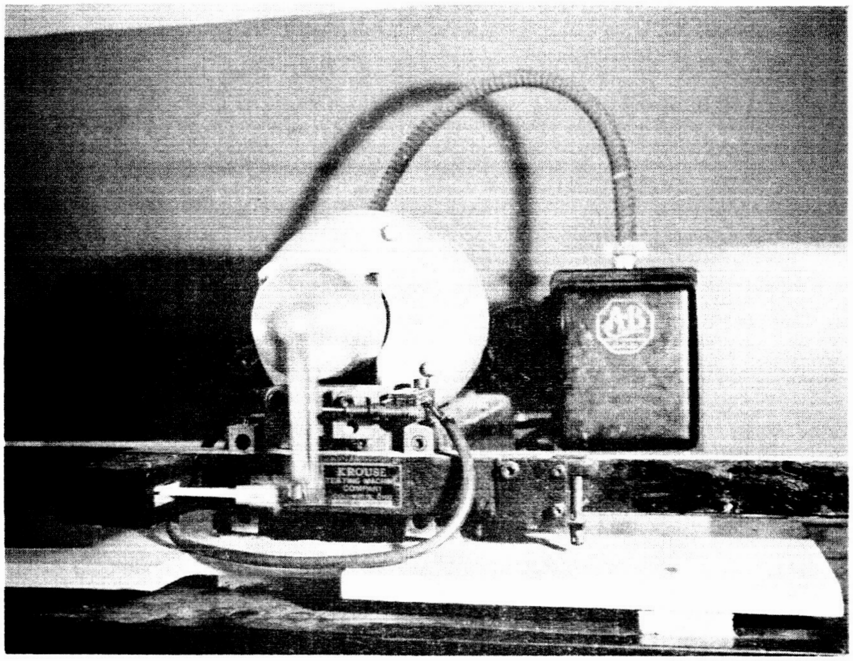

Figure 3

FATIGUE TEST APPARATUS

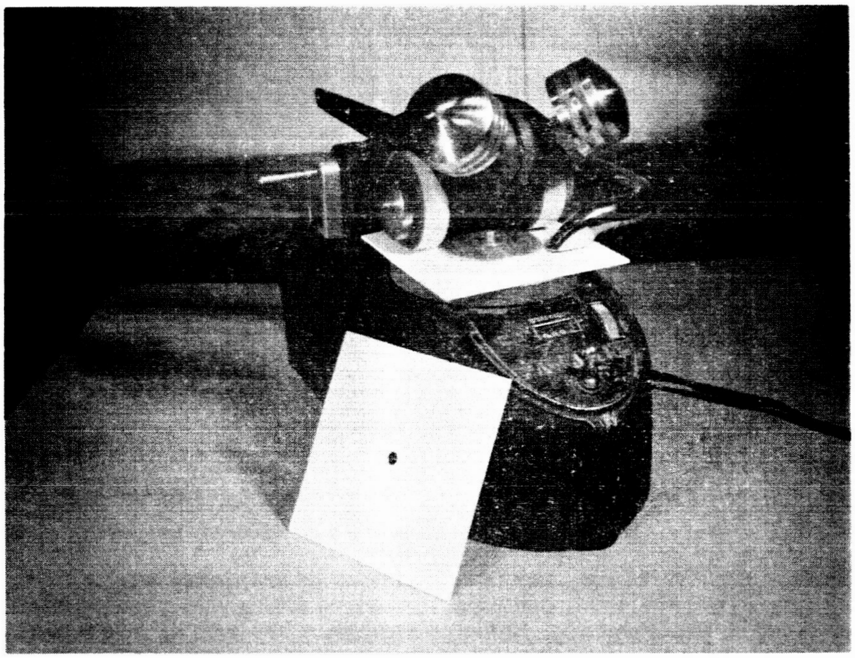

Figure 4

TABER ABRASER

Table 5

COATINGS WHICH WITHSTOOD FATIGUE AND THERMAL-SHOCK TESTS

Pigment	Pigment-to-Binder Ratio	Solids, %	Cure	Sample	Thickness, mils
SP500	4.30	46.3	Air dried only	3-19-6a 3-19-6b	4 4
SP500	3.22	51.3	18 hr at 140°C	3-14-0c	3
SP500[a]	3.58	49.3	18 hr at 140°C	3-14-4a	2
SP500[a]	4.30	52.9	18 hr at 140°C	3-12-43	2
AZO 55-LO	3.22	59.0	18 hr at 140°C	3-14-1b	2
E-P 414	4.30	56.9	18 hr at 140°C	3-15-1c	3
TAM c.p. ZrO_2	4.30	64.4	18 hr at 140°C	3-21-6b	5

[a]Calcined at 500°C for 2 hr.

4. Abrasion

Paints incorporating various zinc oxides were applied on 4 x 4-inch panels for abrasion resistance tests with a Taber Abraser (Figure 4). Each sample received 1000 revolutions on the Abraser with the same abrading wheels at either of two forces, 125 or 500 g. The data in Table 6 show the abrasion resistance of the different zinc oxides used. The softest coatings were those pigmented with SP500 zinc oxide, and the hardest finish was displayed by XX254 zinc oxide. The abrasion resistance of SP500 samples was improved by precalcination of the pigment, decreasing the pigment-to-binder ratio, and heat curing. Although zinc oxide coatings are relatively soft, this very softness may be advantageous because stripping by abrasion would not be difficult should repainting be necessary.

Table 6

ABRASION RESISTANCE OF SILICATE-BONDED ZINC OXIDE COATINGS

Pigment	Pigment-to-Binder Ratio	Solids, %	Cure	Sample	Wt. Loss, grams At 125 g	Wt. Loss, grams At 500 g
SP500	4.30	46.3	18 hr at 140°C	3-19-6	0.0167	
SP500	4.30	46.3	Air dried only	4-12-0AD		0.3365
SP500	4.30	46.3	18 hr at 140°C	4-12-0HC		0.3123
SP500	3.58	49.3	18 hr at 140°C	3-24-0	0.0145	
SP500	3.22	51.3	18 hr at 140°C	3-24-1	0.0030	
SP500[a]	4.30	56.9	18 hr at 140°C	3-24-2	0.0012	
SP500[a]	4.30	56.9	18 hr at 140°C	4-14-3AD		0.1978
SP500[a]	4.30	56.9	18 hr at 140°C	4-14-3HC		0.0708
SP500[b]	4.30	56.9	18 hr at 140°C	3-24-3	0.0044	
E-P 414	4.30	56.9	18 hr at 140°C	3-24-4	0.0113	
XX254	4.30	61.7	18 hr at 140°C	3-24-5		0.047
AZO 55-LO	4.30	56.9	18 hr at 140°C	3-24-6	0.0092	0.302
E-P 730 and SP500, 2/1 wt. ratio	4.30	61.7	18 hr at 140. C	3-24-7		0.087

[a]Calcined at 700°C for 16 hr.

[b]Calcined at 750°C for 2 hr.

C. Determination of Optical Properties

Studies were conducted to determine the effect of coating thickness on solar absorptance and emittance.

Figure 5 graphically illustrates the solar absorptance of an SP500 zinc oxide-PS7 potassium silicate coating which had a pigment-to-binder ratio of 4.30 and a solids content of 46.3%. The data reveal that minimum α is obtained at a coating thickness of more than 4 mils. The randomness of points can be attributed to slight variations in the hand-spraying technique, which could introduce minor dissimilarities in surface pigment concentration, porosity, and other factors.

Emittance is relatively insensitive to coating thickness. Ten samples which ranged from 1 to 5 mils exhibited ϵ's of 0.94 to 0.98. Thus the deciding criteria for thickness requirements is the solar absorptance desired. Representative absorptance curves appear in Figures 6 through 11.

D. Thermal Treatment of Zinc Oxide

It was noted that various procedures produced yellowing of zinc oxide coatings: scratching of the surface, grinding with an agate mortar and pestle, and compacting at high pressure. This yellow did not appear on the bottom surface of the coating adjacent to the substrate when the coating was removed in one piece.

Pellets of SP500 and E-P 730 zinc oxide were compacted at pressures of 10,000 and 50,000 psi. The yellowing phenomenon is evident from the total reflectance measurements listed in Table 7. A Photovolt photoelectric reflection meter utilizing a green filter was used for the optical determinations. The samples were heated for 16 hours each, in argon with titanium sponge

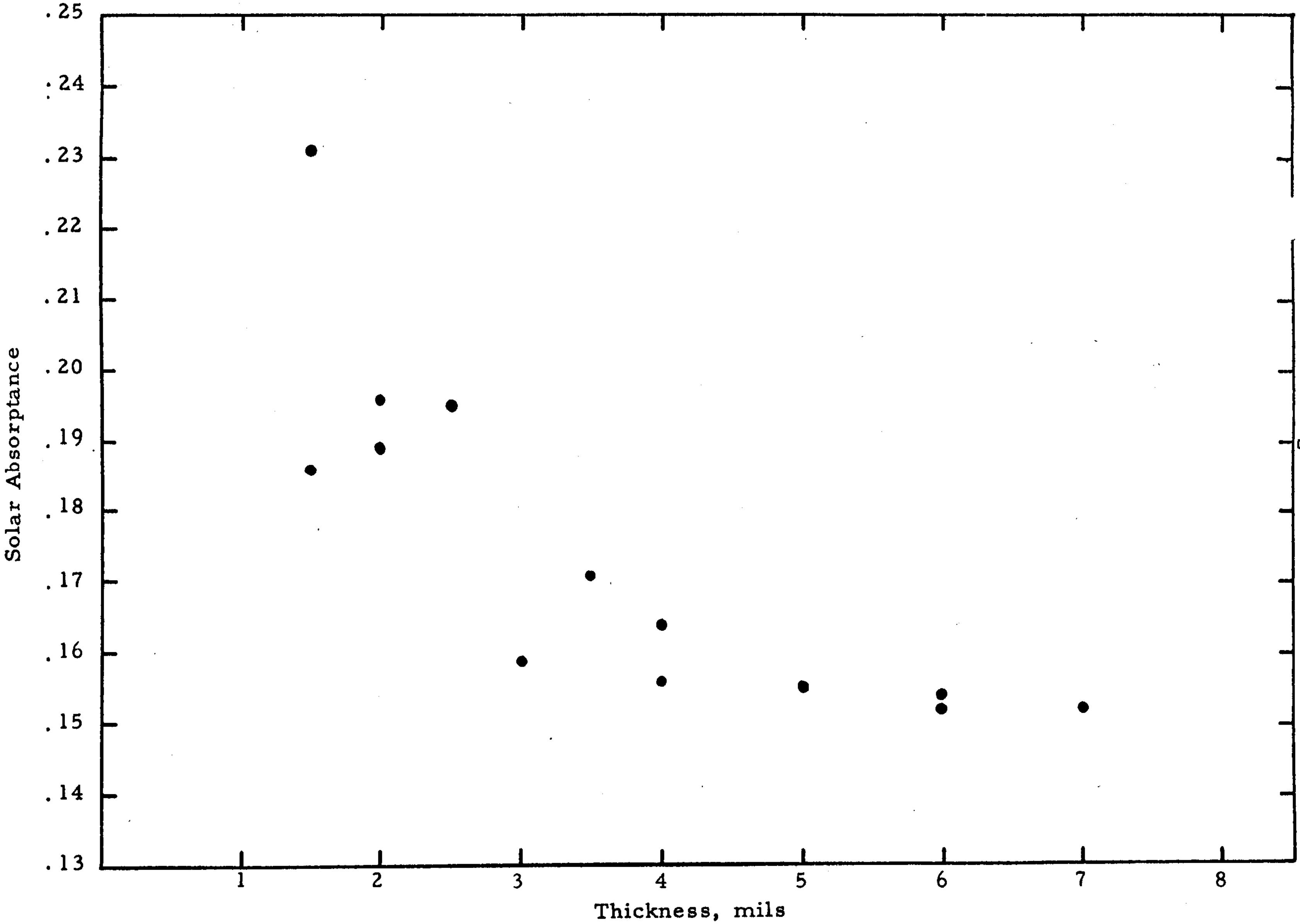

Figure 5

SOLAR ABSORPTANCE VERSUS THICKNESS OF SILICATE-BONDED ZINC OXIDE COATINGS
(pigment-to-binder ratio 4.30; solids content 46.3%)

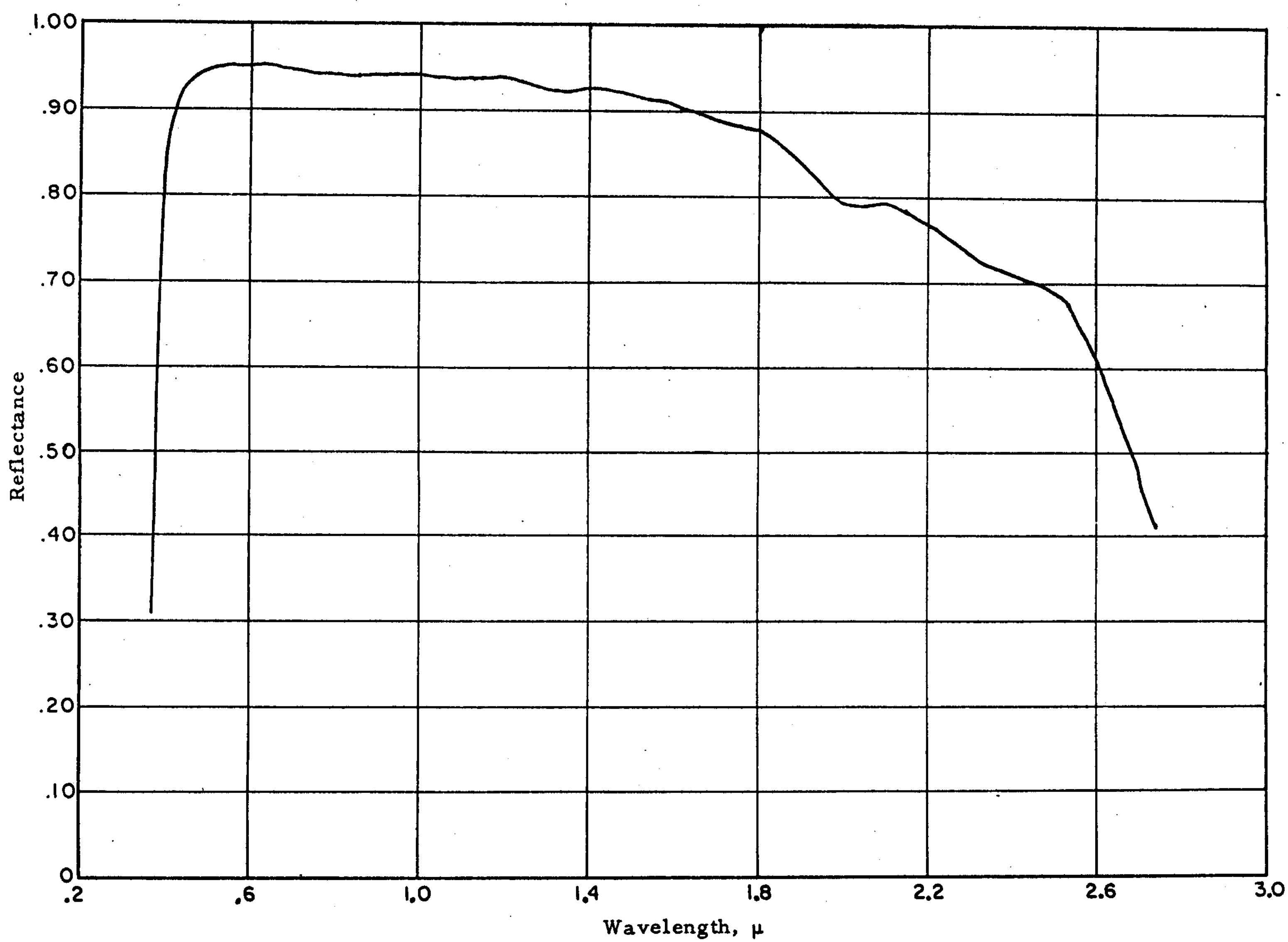

Figure 6

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 6 MILS THICK
(sample 3-21-5f; 0.154 absorptance)

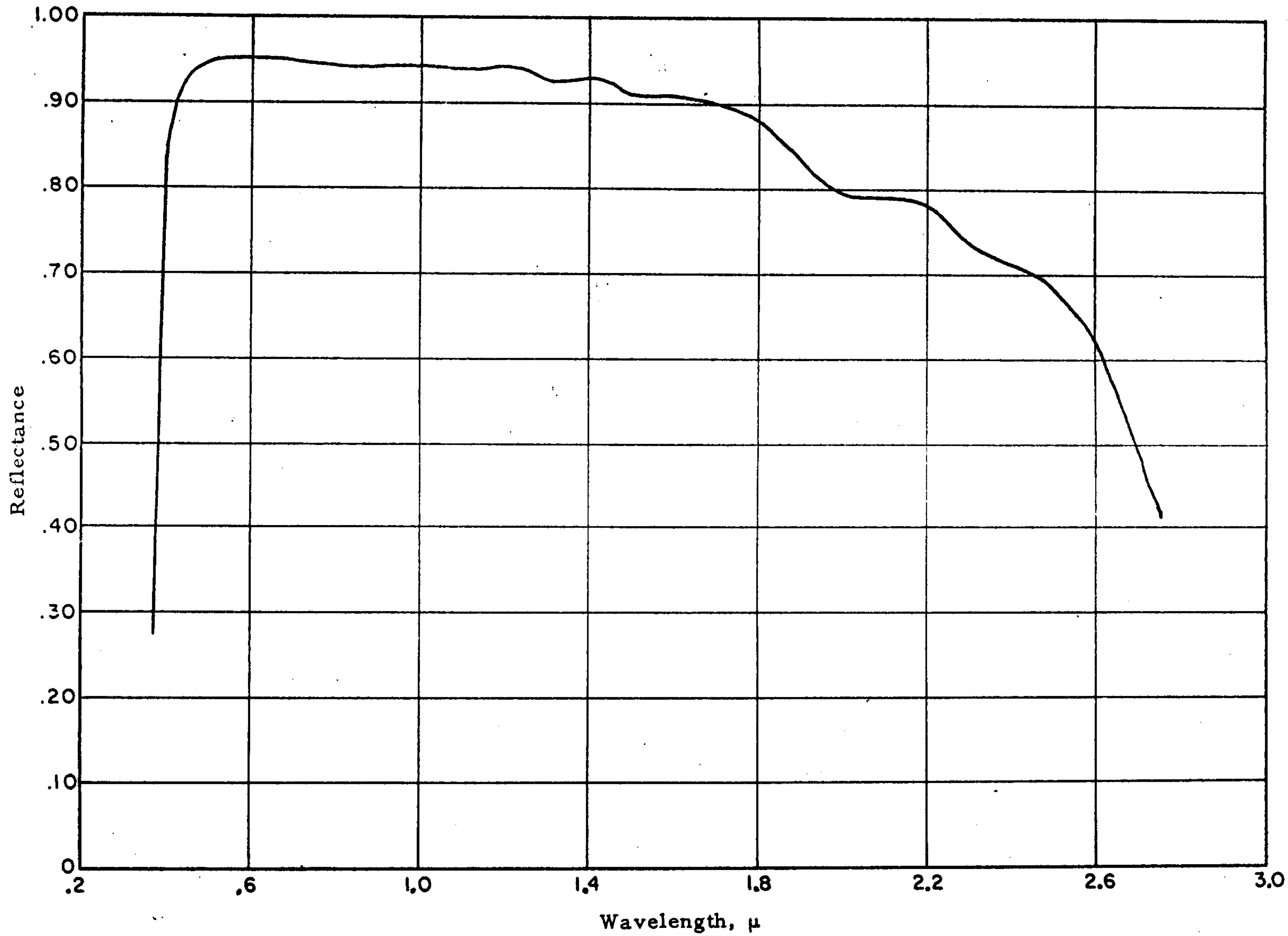

Figure 7

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 5 MILS THICK
(sample 3-21-5e; 0.155 absorptance)

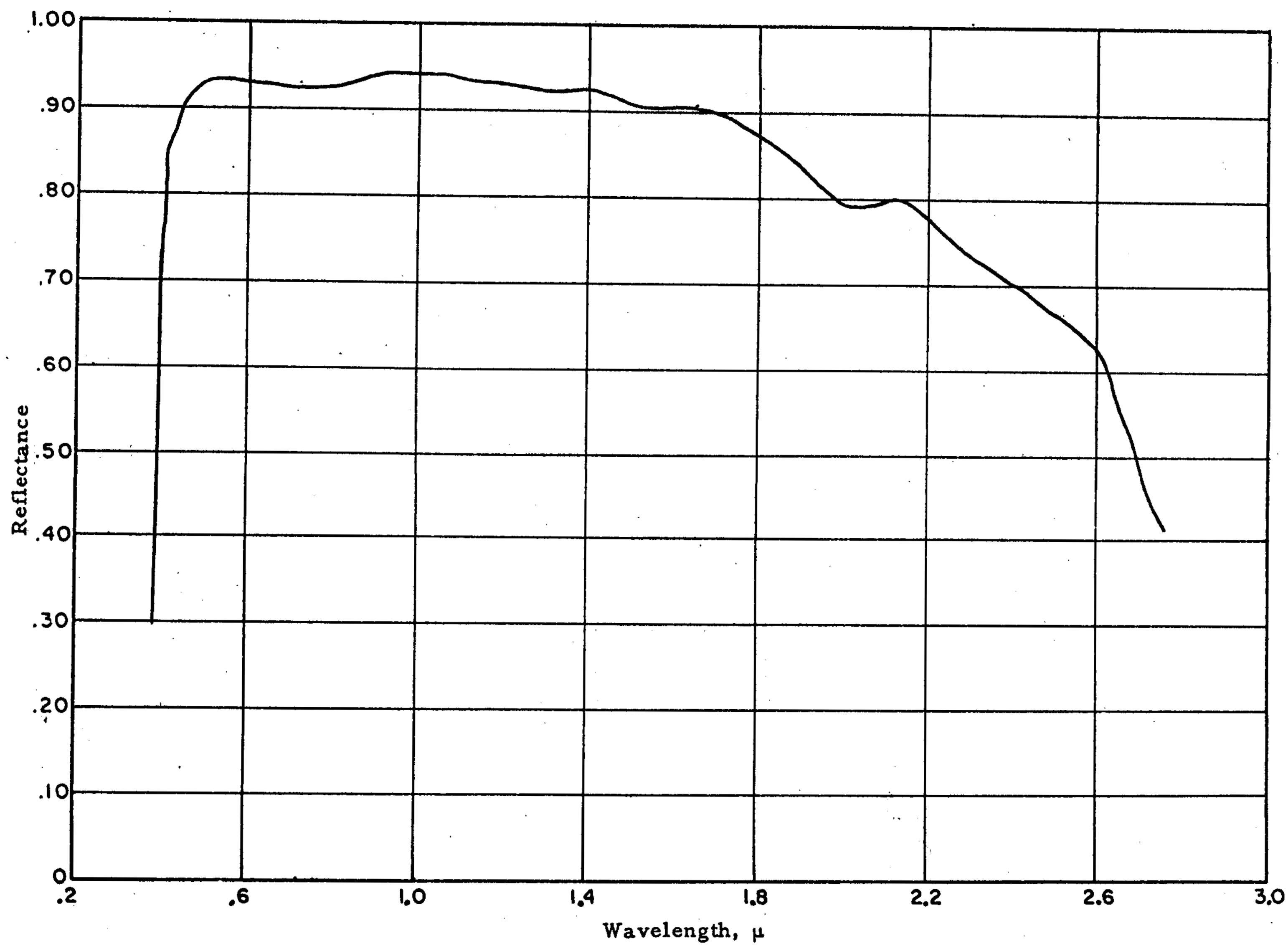

Figure 8

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 4 MILS THICK
(sample 3-21-5d; 0.163 absorptance)

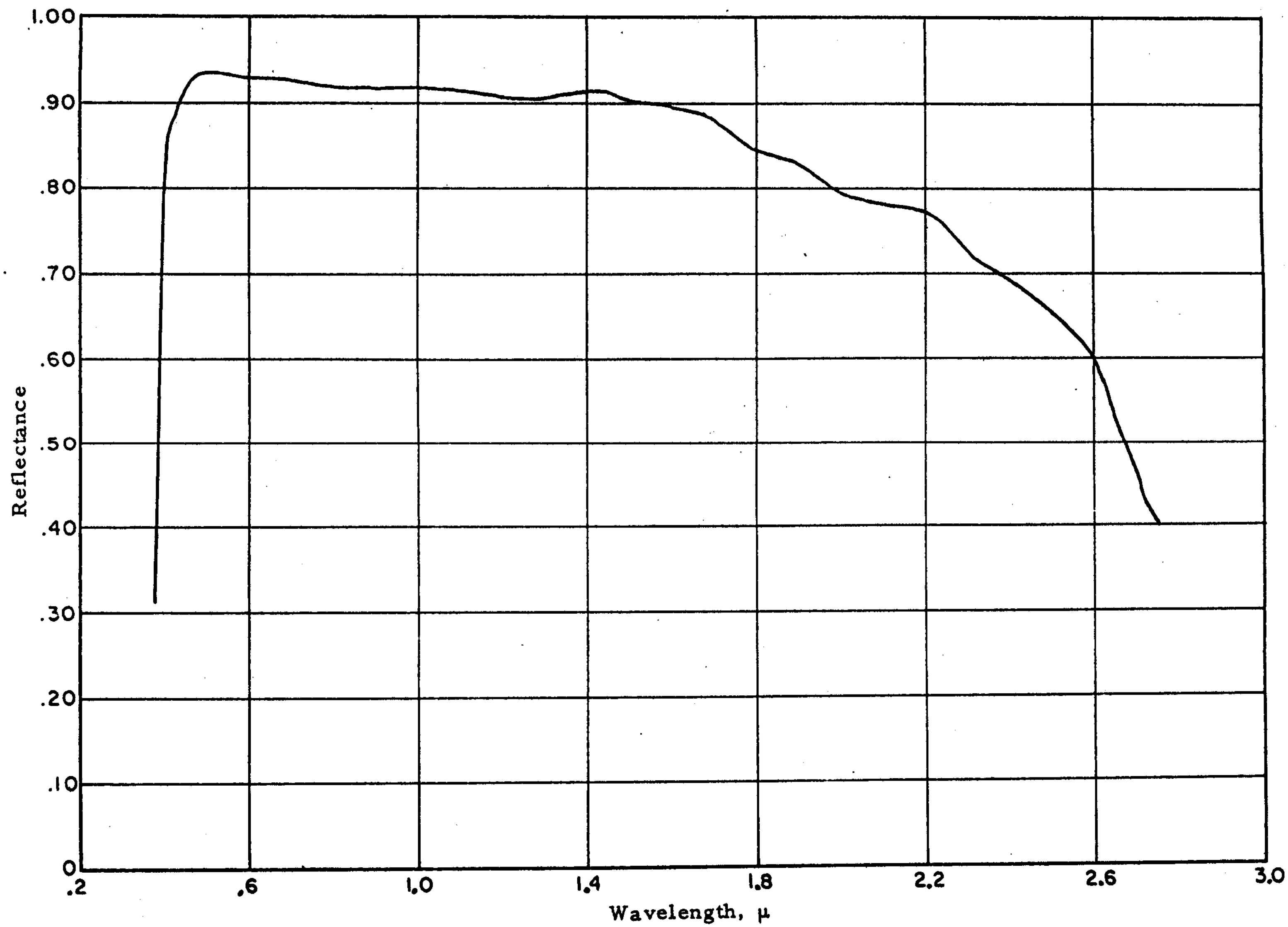

Figure 9

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 3.5 MILS THICK
(sample 3-21-5c; 0.171 absorptance)

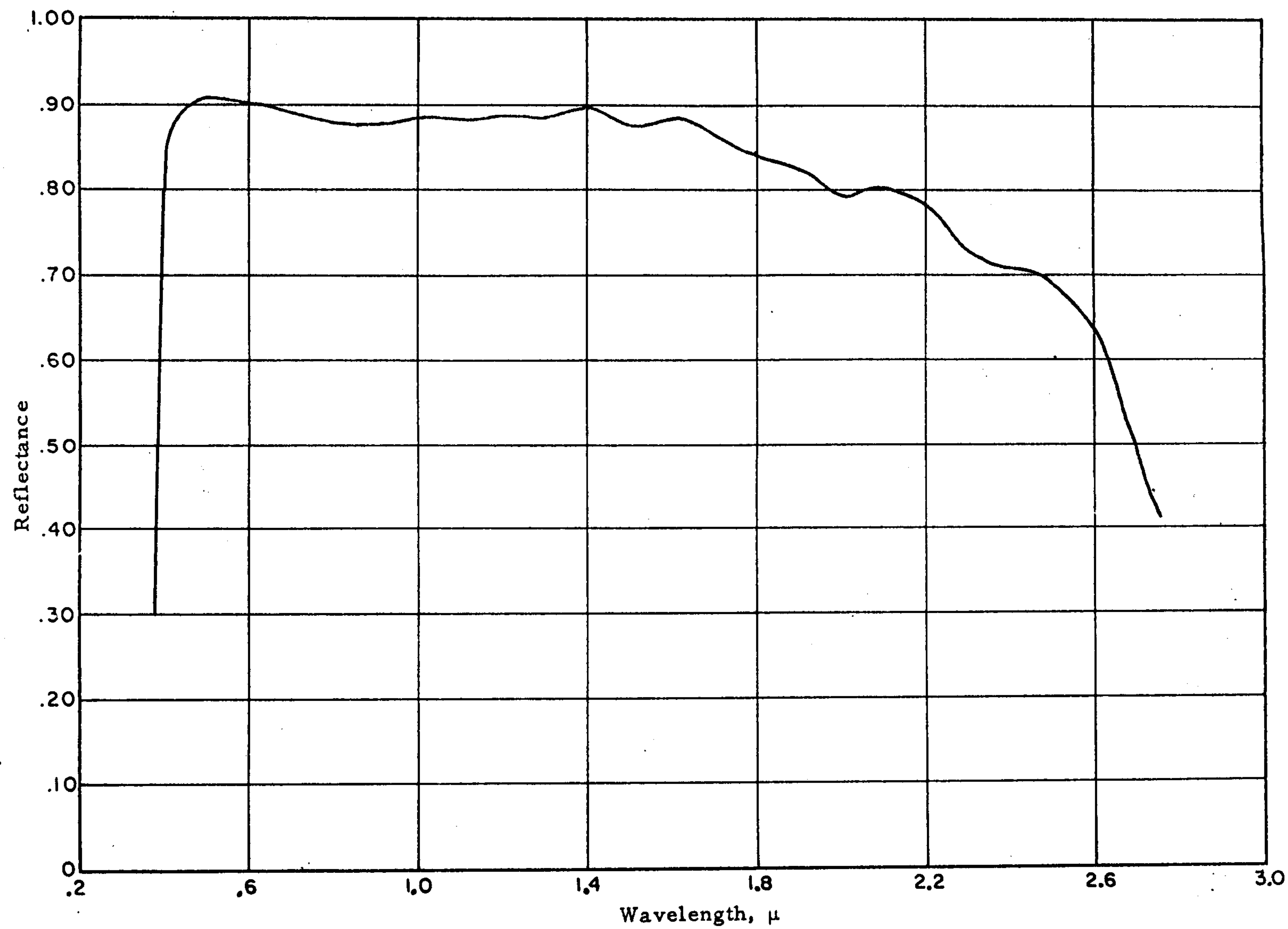

Figure 10

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 2.5 MILS THICK
(sample 3-21-5k; 0.195 absorptance)

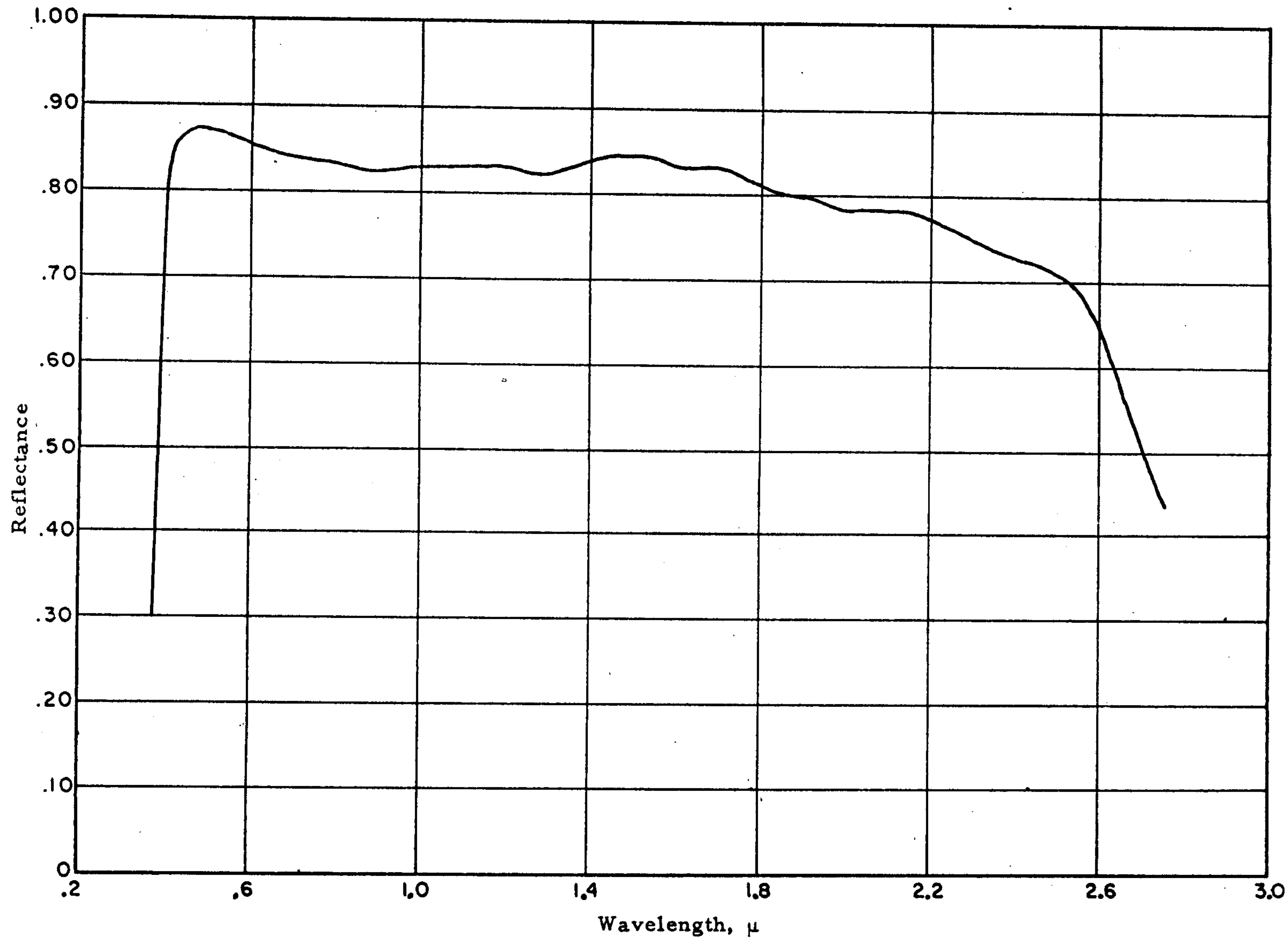

Figure 11

REFLECTANCE CURVE FOR SILICATE-BONDED SP500 ZINC OXIDE COATING 1.5 MILS THICK
(sample 3-21-51; 0.231 absorptance)

in the system, argon, and oxygen. A startling color change to a blue gray occurred in SP500 when heated in the argon-titanium sponge system. A slight graying of the 730 pellets took place.

Table 7

REFLECTANCE OF ZINC OXIDE PELLETS
FIRED IN VARIOUS ATMOSPHERES AT 500°C

Atmosphere	Reflectance of SP500		Reflectance of E-P 730	
	10,000 psi	50,000 psi	10,000 psi	50,000 psi
As pressed	99.5	95.5	81.5	76.5
Argon-titanium sponge	a	19.0	a	74.0
Argon	68.5	59.0	78.0	68.5
Oxygen	98.5	98.5	86.0	81.5

[a]These samples were not measured; they were similar in color to their 50,000 psi counterparts.

Examination of the titanium sponge, which was incorporated in the system to remove traces of oxygen in the argon, revealed considerable oxidation. Heating of the discolored pellets in air at 500°C for 1 hour restored them to their original color. Evidently the use of the sponge as an oxygen getter chemically reduced the zinc oxide. Removal of titanium from the system did not completely eliminate this reduction, as seen in the value for the argon run in Table 7. Again, the SP500 was more sensitive to oxygen removal than the 730 pigment. An oxidizing atmosphere bleached the SP500 pigment somewhat and the 730 pigment to a more marked degree.

Thus, it is obvious that the yellow color is due to interstitial zinc and/or oxygen ion deficiency. The surprising susceptibility of SP500 zinc oxide to reduction at relatively low temperature is somewhat disconcerting and suggests that other zinc oxides should be investigated more thoroughly.

E. Effect of Air Drying

A gravimetric study was conducted on zinc oxide-potassium silicate paints to determine air-drying properties. Five aluminum plates 1-3/4 x 1-3/4 x 1/4 inches were coated to varying thicknesses and were weighed at various intervals as they dried. A plot of the values (Figure 12) reveals that water was essentially completely volatilized from the coatings within 1 hour after spraying. Percent weight losses were based on coating weights 10 min after spraying. This time lag prior to the initial weighing is probably the reason for the discrepancy in values of the final percent weight losses, since evaporation of water undoubtedly occurs more rapidly in thinner coatings. A coating 2 mils thick was not included in Figure 12 because it lost its water within 10 min.

A second series of paints, ranging in thickness from 1 to 4.5 mils, was air dried for 100 hours and then heat cured at 140°C for 17 hours. The percent weight loss on heating, based on the air-dried weight, was 0.7 ± 0.1% for each of five samples 24 hours after removal from the oven. Thus, it appears that essentially all water is removed by volatilization during air drying and that heat curing can be eliminated.

F. Space-Simulation Tests

1. Test D - 300 Equivalent Sun-Hours

Extremely small reflectance losses and solar absorptance changes resulted for all zinc oxide paints in Test D (Table 8). Incorporation of an organic wetting agent, Monamine AD-100, appeared to be detrimental to optical stability. Substitution of PS7 potassium silicate with other silicate binders in SP500 coatings did not materially influence stability. However, the physical properties of PS7 paints were superior to those of compositions

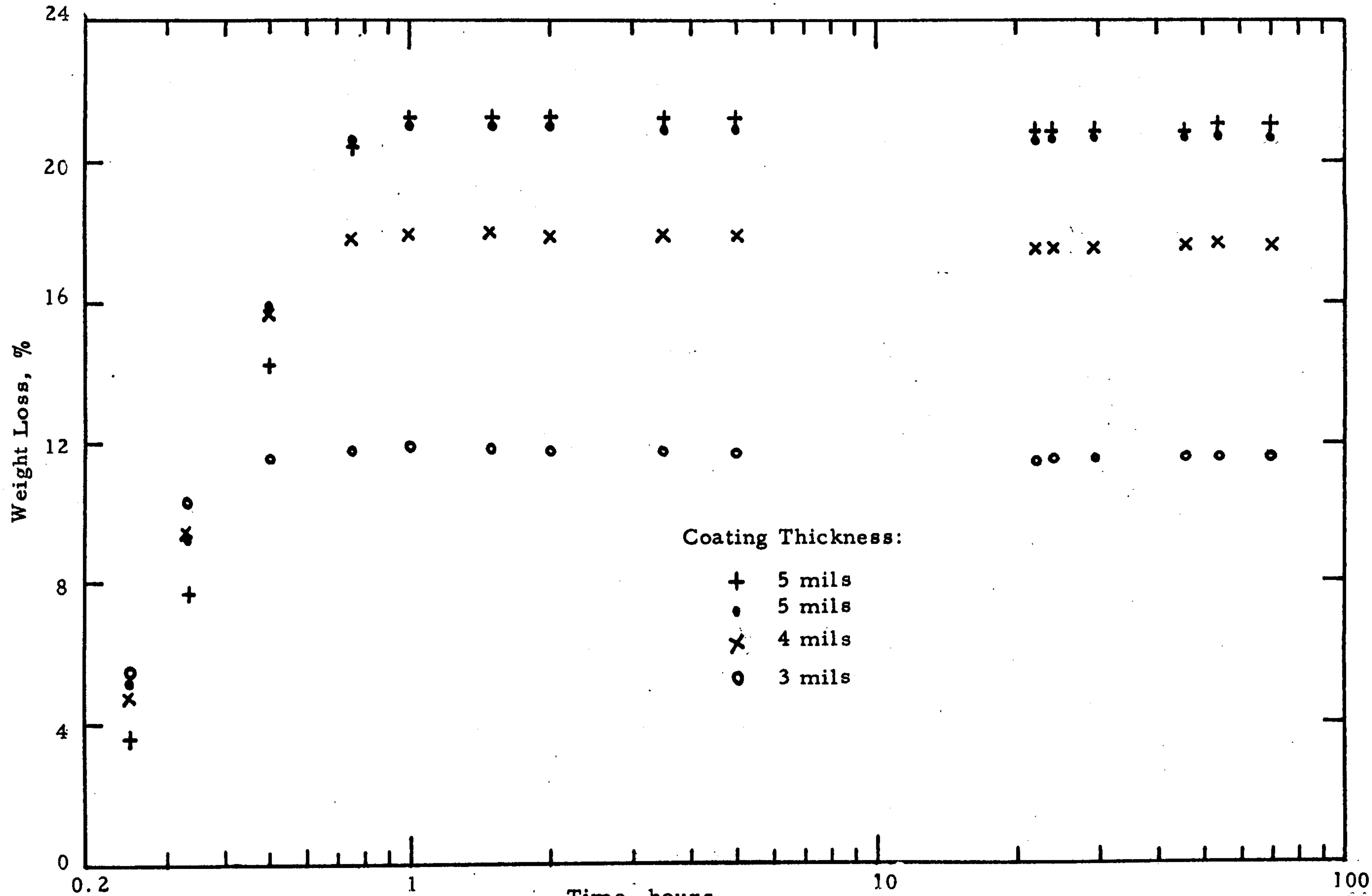

Figure 12

CURING OF SILICATE-BONDED ZINC OXIDE COATINGS DURING AIR DRYING AS A FUNCTION OF TIME

Table 8

CHANGES IN REFLECTANCE OF SILICATE-BONDED ZINC OXIDE COATINGS AND PIGMENTS - TEST D

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-16-3x	30 g SP500 15 cc PS7[a] 30 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	28.5 28.0	94.0 93.0	97.0 98.0	97.0 98.0	0.139 0.142
2-17-2a	30 g SP500 15 cc PS7 20 cc water 1 drop AD-100 Cured at 140°C for 18 hr	4.30	None 300 sun-hours	27.5 26.0	93.0 91.5	97.5 97.0	97.0 97.0	0.143 0.161
2-17-2c	30 g SP500 15 cc PS7 20 cc water 1 drop AD-100 Sprayed on Leonite-ZnO primer Cured at 140°C for 18 hr	4.30	None 300 sun-hours	26.5 26.0	93.5 92.5	97.5 97.5	97.5 97.5	0.144 0.152
2-18-0	30 g SP500 15 cc Kasil 1[a] 30 cc water Cured at 140°C for 18 hr	5.45	None 300 sun-hours	29.5 27.5	92.0 91.0	97.0 96.5	96.5 96.5	0.146 0.154

Table 8 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-18-1	30 g SP500 15 cc S-35[a] 30 cc water Cured at 140°C for 18 hr	4.72	None 300 sun-hours	27.5 27.5	91.5 91.5	96.5 96.5	96.0 96.5	0.150 0.154
2-19-6	30 g SP500 15 cc N-silicate[a] 30 cc water Cured at 140°C for 18 hr	3.83	None 300 sun-hours	28.5 27.5	89.5 90.5	96.5 96.5	96.5 96.5	0.152 0.157
2-17-6	20 g AZO 66 10 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	32.0 30.0	93.5 92.0	96.5 96.5	95.5 95.5	0.154 0.165
55LO	20 g AZO 55-LO 10 cc PS7 10 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	19.0 19.0	85.0 85.0	94.5 93.0	93.5 93.0	 0.192
2-17-7	20 g c.p. ZnO 10 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	30.5 30.0	94.5 92.0	96.0 96.0	95.5 95.5	0.161 0.170

Table 8 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-13-0b	30 g SP500 15 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	250 sun-hours 550 sun-hours	32.5 29.0	92.5 92.0	96.5 97.0	96.0 96.5	0.156[b] 0.157
1-9-5	20 g SP500 10 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	575 sun-hours 875 sun-hours	30.5 28.0	91.0 91.0	96.0 96.0	96.0 96.0	0.154 0.155
2-10-0	15 g c.p. ZnS 10 cc PS7 5 cc water Cured at 140°C for 18 hr	4.30	250 sun-hours 550 sun-hours	60.5 59.0	81.0 80.0	88.5 88.0	67.0 66.5	0.231[c] 0.238
SP8 pigment	SP500 calcined at 800°C for 16 hr		None 300 sun-hours	11.0 11.0	69.0 69.0	92.5 92.5	95.5 94.5	
USP12 pigment	New Jersey Zinc ZnO		None 300 sun-hours	31.5 30.0	93.5 92.0	98.0 97.5	98.0 97.5	
AZO33 pigment	American Zinc ZnO		None 300 sun-hours	24.5 23.5	88.0 86.5	95.0 93.5	94.5 94.0	

Reflectance based on magnesium oxide scale. Wavelengths chosen arbitrarily in visible range.

[a]Binders: PS7, potassium silicate, 35% solution (SiO_2/K_2O = 3.30). Kasil 1, potassium silicate, 29.1% solution (SiO_2/K_2O = 2.50). S-35, sodium silicate, 32.1% solution (SiO_2/Na_2O = 3.75). N-silicate, sodium silicate, 37.6% solution (SiO_2/Na_2O = 3.22).

[b]Original α = 0.149. [c]Original α = 0.220.

incorporating the other vehicles. Use of a coarser but less pure zinc oxide, AZO 55-LO, resulted in a paint of higher initial solar absorptance, although its solar stability appeared comparable with SP500 and the hardness was improved. Two previously exposed SP500 samples, 2-13-0b and 1-9-5, were unaffected by the added irradiation. Sample 2-10-0 experienced only slight degradation on reexposure.

Sample SP8 contained SP500 which was calcined at 800°C for 16 hours to reduce liquid requirements. The stability of this material suggests thermal treatment as a means of improving the physical properties of SP500 coatings.

Among the non-zinc systems, listed in Table 9, a paint pigmented with stannic oxide displayed excellent stability. Initial experiments indicated a reaction between the potassium silicate-tin oxide mixture and aluminum. Spraying of this formulation on glass slides eliminated the gas evolution which occurred on aluminum. Molochite (mullite plus amorphous silica)-silicate paints were significantly superior to coatings pigmented with Dicalite or Celite (diatomaceous earths). The most promising of the calcined china clays was Molochite No. 6, a coarser grade than superfine. Paints of high-purity fused quartz powder or crystal experienced degradation similar to that of the diatomaceous earths. Therefore these silica pigments were eliminated as possible candidates. Calcined aluminum oxide, zirconium oxide, and zircon suffered reflectance losses which were practically identical with their uncalcined counterparts. Apparently any loss of adsorbed and absorbed water and the possible strain relief gained by thermal treatment did not change the degradation characteristics of these materials.

Table 9

CHANGES IN REFLECTANCE OF INORGANIC COATINGS - TEST D

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-18-3	30 g Molochite SF 15 cc PS7 15 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	71.5 61.5	77.5 71.0	81.0 79.0	81.0 80.0	0.251 0.281
2-18-5	15 g Molochite SF 7.5 cc AP[a] 7.5 cc water Cured at 140°C for 18 hr Sprayed on Leonite organic primer	2.80	None 300 sun-hours	68.5 65.5	75.5 73.5	81.5 82.0	84.0 84.0	0.229 0.240
2-20-2	30 g Molochite 6 15 cc PS7 15 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	66.5 62.5	76.5 73.5	82.5 81.5	83.0 82.5	0.243 0.260
2-17-3	10 g Dicalite WB5 10 cc PS7 25 cc water Cured at 140°C for 18 hr	2.15	None 300 sun-hours	85.0 68.5	90.0 77.0	91.5 88.5	91.0 89.5	0.136 0.173
2-17-3 HC	10 g Dicalite WB5 10 cc PS7 25 cc water Cured at 800°F for 16 hr	4.30	None 300 sun-hours	87.5 75.5	91.5 82.0	93.0 91.5	93.5 92.5	0.117 0.152

Table 9 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-17-8	10 g Dicalite WB5 5 cc PS7 30 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	84.0 62.5	89.0 73.5	91.5 88.00	91.5 90.0	0.128 0.186
2-18-2	10 g Dicalite L-5 10 cc PS7 25 cc water Cured at 140°C for 18 hr	2.15	None 300 sun-hours	78.5 69.0	84.5 78.5	88.0 86.0	87.5 86.0	0.175 0.207
2-18-4	5 g Dicalite WB5 5 cc AP 12.5 cc water Cured at 140°C for 18 hr Sprayed on Leonite organic primer	1.40	None 300 sun-hours	77.5 68.5	83.0 75.5	86.0 83.5	86.5 84.5	0.206 0.228
2-19-0	10 g Celite SF 10 cc PS7 10 cc water Cured at 140°C for 18 hr	2.15	None 300 sun-hours	81.0 63.5	87.5 71.5	91.5 87.0	91.0 89.0	0.154 0.200
2-19-1	10 g Celite 281 10 cc PS7 25 cc water Cured at 140°C for 18 hr	2.15	None 300 sun-hours	76.5 62.5	84.5 74.0	89.0 87.0	89.0 88.5	0.165 0.204

Table 9 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
2-20-0	10 g Celite 110 10 cc PS7 25 cc water Cured at 140°C for 18 hr	2.15	None 300 sun-hours	79.5 67.5	86.0 77.5	85.5 83.5	85.0 84.0	0.200 0.230
2-20-5	20 g fused quartz powder 10 cc PS7 6 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	83.5 67.0	87.0 76.0	87.5 85.0	87.5 86.5	0.177 0.221
2-20-6	20 g fused quartz crystal 10 cc PS7 6 cc water Cured at 140°C for 18 hr	4.30	None 70 sun-hours	65.5 59.0	67.5 64.0	70.0 68.0	70.0 69.0	0.346 0.376
2-20-4	30 g c.p. SnO_2 15 cc PS7 10 cc water Cured at 140°C for 18 hr	4.30	None 300 sun-hours	69.5 68.5	77.0 76.5	82.5 82.0	82.5 82.5	0.264 0.278
2-13-3	15 g zircon, Superpax 7.5 cc PS7 7.5 cc water Cured at 140°C for 18 hr	4.30	250 sun-hours 550 sun-hours	52.5 42.5	63.0 55.0	81.5 78.5	86.0 85.0	0.249 0.266[b]

Table 9 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
1-9-4	30 g zircon, milled 15 cc PS7 5 cc water Cured at 140°C for 18 hr	4.30	75 sun-hours 375 sun-hours	60.0 54.5	71.5 66.0	80.5 79.0	80.5 81.0	0.280 0.293
1-16-6	30 g c.p. ZrO_2 15 cc PS7 5 cc water Cured at 140°C for 18 hr	4.30	75 sun-hours 375 sun-hours	75.0 65.5	85.0 76.0	90.5 88.5	91.5 90.5	0.165 0.191
659 AR, from JPL	ZnO-60		None 300 sun-hours	27.5 26.5	89.5 84.0	93.0 92.5	92.0 92.0	0.190 0.195
662 AR, from JPL	ZnO-40		None 300 sun-hours	24.5 23.0	89.5 82.0	94.5 93.0	93.0 93.0	0.197 0.204
663 AR, from JPL	ZW-60		None 300 sun-hours	62.5 57.5	87.0 80.0	91.5 90.0	64.0 64.0	0.225 0.242

[a]Binder AP: monoaluminum dihydrogen phosphate, 50% solution.

[b]Original α = 0.180.

2. Test E - 250 Equivalent Sun-Hours

Test E represented an increased emphasis on zinc oxide-potassium silicate systems and a narrowing of the choice of other materials (Table 10). Included in this series were paints which were soiled with vacuum oil and cleaned with acetone or with water and detergent. The preliminary results were encouraging; good stability was exhibited by SP30, AZO30, and XX30. Also included was an SP500 sample which received a top layer of silicate vehicle intended as a protective coating. This sample also showed good stability, but inspection of this composite coating under 10x magnification revealed the presence of microcracks in the silicate film. Subsequent soiling and cleaning of the sample destroyed the overlayer. The problem of crazing was not overcome by additional attempts to achieve this composite paint.

The zinc sulfide paints were formulated with pigment-grade material of slightly higher purity than zinc sulfide. These coatings,XXXN and XXXHD, had slightly improved stability. Molochite No. 6 displayed good stability, and leaching with hot hydrochloric acid appeared to improve its stability. Use of a phosphate binder produced a paint of lower initial a and increased degradation. Similar property losses were exhibited by phosphate-bonded tin oxide. Silicate-bonded tin oxide also showed potential as a possible paint. Use of a Prime Metal tin oxide of 99.9% purity resulted in reflectance losses not exhibited by c.p. tin oxide (samples 3-4-3c and 2-24-5).

3. Test F - 315 to 360 Equivalent Sun-Hours

A number of silicate-bonded zinc oxide coatings were deliberately soiled by immersion in Duo Seal vacuum-pump oil. This simulates one of the soiling problems which can be expected to occur in satellite evaluation tests. After

Table 10

CHANGES IN REFLECTANCE OF INORGANIC COATINGS - TEST E

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
2-22-7	30 g AZO 55-LO 15 cc PS7 15 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	18.5 18.5	81.5 80.0	92.0 91.5	91.5 91.5
2-24-1	30 g XX 504 15 cc PS7 10 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	18.5 18.0	78.5 76.0	88.5 87.5	88.5 87.5
2-23-0	40 g SP500 30 cc PS7 30 cc water Cured at 140°C for 18 hr	2.87	None 250 sun-hours	22.5 22.5	84.0 82.0	88.0 87.5	86.5 86.5
2-25-3	15 g Molochite 6 15 g SP500 15 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	29.5 29.5	88.5 86.5	92.5 92.0	92.5 92.0
2-25-4	7.5 g Molochite 6 22.5 g SP500 15 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	27.5 27.5	91.5 90.0	95.5 94.5	94.5 94.5
SP30	30 g SP500 15 cc PS7 30 cc water Cured at 140°C for 18 hr Soiled and cleaned	4.30	None 250 sun-hours	23.5 25.0	90.5 90.0	92.5 94.0	89.5 93.0

Table 10 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
AZO 30	40 g AZO 55-LO 20 cc PS7 20 cc water Cured at 140°C for 18 hr Soiled and cleaned	4.30	None 250 sun-hours	18.5 17.5	82.5 81.0	92.0 93.0	91.5 92.5
XX30	40 g XX 504 20 cc PS7 15 cc water Cured at 140°C for 18 hr Soiled and cleaned	4.30	None 250 sun-hours	17.5 16.5	77.5 75.5	88.0 88.5	87.5 88.5
PS7	30 g SP500 15 cc PS7 30 cc water Cured at 140°C for 18 hr Sprayed with an overlayer of PS7	4.30	None 250 sun-hours	22.5 20.5	88.5 87.0	95.0 95.0	94.5 94.5
2-23-3	30 g XXXN ZnS 15 cc PS7 15 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	67.5 64.5	88.5 86.5	88.0 87.5	59.5 59.5
2-25-2c	30 g XXXN ZnS 20 cc PS7 10 cc water Cured at 140°C for 18 hr	3.22	None 250 sun-hour	63.5 62.5	88.5 86.5	89.0 88.5	55.5 54.0
3-4-5a	30 g XXXHD ZnS 15 cc PS7 15 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	67.5 65.5	88.5 86.0	90.0 90.5	66.0 65.0

Table 10 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
2-24-2	30 g petalite 15 cc PS7 7.5 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	55.5 46.5	59.0 52.0	64.5 62.5	65.5 65.0
3-5-0	30 g $LiAlSiO_4$ 15 cc PS7 7.5 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	82.5 77.5	86.5 81.5	85.5 84.5	83.5 83.5
2-24-0	30 g Molochite 6, leached 15 cc PS7 10 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	65.5 63.5	74.5 74.5	83.5 83.5	84.5 84.5
2-24-6	30 g Molochite 6 10 cc AP 10 cc water Cured at 140°C for 18 hr On glass	4.20	None 250 sun-hours	57.5 52.5	65.0 61.5	76.5 75.5	80.5 79.0
2-24-7	6 g Molochite 6, leached 2 cc AP 2 cc water Cured at 140°C for 18 hr Brush-painted on glass	4.20	None 250 sun-hours	56.5 52.5	64.5 61.5	76.5 75.5	81.0 79.5
2-24-4	30 g c.p. SnO_2 15 cc PS7 7.5 cc water Cured at 140°C for 18 hr On glass	4.30	None 250 sun-hours	71.0 70.0	80.5 80.5	87.5 88.5	87.5 88.5

Table 10 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
2-24-5	30 g c.p. SnO_2 10 cc AP 20 cc water Cured at 140°C for 18 hr On glass	4.20	None 250 sun-hours	63.5 58.5	69.5 65.5	76.5 75.0	78.0 76.5
3-2-3c	30 g Prime Metal SnO_2 15 cc PS7 20 cc water Cured at 140°C for 18 hr	4.30	None 250 sun-hours	71.5 68.5	77.5 74.5	82.0 81.0	82.5 81.5

removal from the oil, the samples were exposed to ambient conditions for 5 hours. The excess oil was then removed with paper towelling. Two cleaning operations followed, the first utilizing acetone-soaked paper towels and the second utilizing Alconox-tap water scouring with a nylon brush. Final rinsing with distilled water preceded drying under an airblast and complete drying at 130°C. Application of moderate care in all operations prevented any apparent damage to the coatings. The samples were exposed in a range of 315 to 360 equivalent sun-hours, depending upon their position in the chamber.

As shown in Table 11, a slight decrease in reflectance resulted in most of the soiled and cleaned samples. Exceptions to this were some samples of lower initial reflectance (lower than 80% at 440 mμ); these coatings exhibited a slight increase in reflectance. Upon exposure to the simulated space environment many of the samples which suffered losses on washing bleached slightly. On the other hand, coatings which showed an increased reflectance on washing revealed slight losses after exposure to simulated space. In all cases the washing appears to have been adequate in removing any degradable residual oil.

4. Long-Term Tests

Some longer-term space-simulation tests were conducted with the VacIon ion-pumping system. Coatings were exposed to approximately 10 suns for varying times. The data are tabulated in Table 12.

The SP500 coatings exhibited no degradation in the 45-hour test. The zirconia coatings showed reflectance losses similar to those observed in earlier experiments of lesser intensity.

Table 11

CHANGES IN REFLECTANCE OF INORGANIC PAINTS - TEST F

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
3-10-3a3	SP500	4.30	None	13.0	91.0	94.5	94.5
	PS7		Soiled and washed	28.0	90.5	92.5	92.0
	46.3% solids		Then 315 sun-hours	27.5	90.5	94.0	93.5
	Cured at 140°C for 18 hr						
3-10-4b[a]	SP500	4.30	None	31.5	93.5	98.5	98.5
	PS7		Soiled and cleaned	28.0	90.5	94.5	94.5
	51.1% solids		Then 315 sun-hours	28.5	91.0	96.0	96.0
	Cured at 140°C for 18 hr						
3-14-0f	SP500	3.22	None	28.0	89.5	92.5	92.0
	PS7		Soiled and washed	25.0	86.0	88.5	87.5
	51.3% solids		Then 315 sun-hours	24.0	86.5	91.0	90.5
	Cured at 140°C for 18 hr						
3-14-4c	SP500	3.58	None	28.0	89.0	93.5	93.0
	PS7		Soiled and cleaned	25.0	88.5	90.5	89.5
	49.3% solids		Then 360 sun-hours	25.0	87.0	92.0	92.0
	Cured at 140°C for 18 hr						
3-12-1b	SP500	4.30	None	31.5	93.0	97.5	98.0
	PS7		Soiled and cleaned	28.5	91.5	95.5	95.5
	52.9% solids		Then 315 sun-hours	28.5	91.0	96.0	96.0
	Calcined at 500°C for 66 hr						
	Cured at 140°C for 18 hr						
3-13-6c	SP500	4.30	None	29.0	94.0	97.0	97.0
	PS7		Soiled and cleaned	25.0	90.5	94.5	95.0
	56.9% solids		Then 360 sun-hours	25.5	89.0	95.0	95.5
	Calcined at 650°C for 18 hr						
	Cured at 140°C for 18 hr						

Table 11 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	420 mμ	600 mμ	700 mμ
3-12-46	SP500 PS7 52.9% solids Calcined at 700°C for 2 hr Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 315 sun-hours	26.5 24.0 25.0	91.0 88.5 89.0	94.5 91.0 93.0	94.5 90.5 93.0
3-14-2b	SP500 PS7 56.9% solids Calcined at 700°C for 16 hr Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 315 sun-hours	27.0 24.0 24.5	93.5 90.5 90.5	97.5 95.0 95.5	97.5 94.5 96.0
3-13-5c	SP500 PS7 56.9% solids Calcined at 750°C for 2 hrs Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 360 sun-hours	24.0 21.0 23.5	89.0 87.0 85.5	95.5 93.5 94.0	94.5 93.0 94.5
3-10-6a	SP500 PS7 64.4% solids Calcined at 800°C for 12 hrs Cured at 140°C for 18 hrs	4.30	None Soiled and cleaned Then 315 sun-hours	9.0 8.5 8.0	54.0 57.5 56.0	75.0 77.0 76.5	75.0 77.0 77.0
3-12-2a	SP500 PS7 64.4% solids Calcined at 1000°C for 1 hr Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 315 sun-hours	15.0 14.0 13.5	76.0 75.5 75.0	83.0 80.5 83.0	83.0 80.0 82.5
14-1c	AZO 55-LO PS7 59.0% solids Cured at 140°C for 18 hr	3.22	None Soiled and cleaned Then 315 sun-hours	19.0 19.0 18.5	77.0 77.5 75.0	87.0 86.5 85.5	86.5 86.5 85.5

Table 11 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
3-14-3b	AZO 55-LO PS7 61.7% solids Calcined at 700°C for 16 hr Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 315 sun-hours	19.0 21.0 20.5	87.5 87.5 86.5	94.5 93.5 93.0	94.5 93.0 93.0
3-15-02	E-P 730 PS7 73.0% solids Cured at 140°C for 16 hr	4.30	None Soiled and cleaned Then 360 sun-hours	13.5 10.5 10.5	52.5 56.5 55.0	75.0 76.5 76.5	77.5 78.5 79.5
3-15-1a	E-P 414 PS7 56.9% solids Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 360 sun-hours	20.0 17.0 17.5	79.0 80.0 76.5	91.5 88.5 88.5	92.0 88.5 90.0
3-15-2d	XX254 PS7 61.7% solids Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 360 sun-hours	20.0 19.0 17.5	78.5 78.5 76.0	89.5 87.5 87.0	89.5 87.5 87.5
3-15-3c	XX254 PS7 73.0% solids Cured at 140°C for 18 hr	4.30	None Soiled and cleaned Then 360 sun-hours	18.0 16.0 15.5	75.5 78.0 75.0	89.0 88.5 87.0	89.0 88.5 87.5
3-21-6c2	TAM c.p. ZrO_2 PS7 64.4% solids Cured at 140°C for 18 hr	4.30	None 360 sun-hours	85.0 76.0	91.0 83.5	92.0 86.5	91.5 88.0

Table 11 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
24-7a	E-P 730 SP500 61.7% solids Cured at 140°C for 18 hr	4.30	None 360 sun-hours	19.0 18.5	73.5 72.5	86.5 86.5	88.5 88.5
3-21-5d	SP500 PS7 46.3% solids Air dried only	4.30	None 315 sun-hours	32.0 28.5	94.0 93.0	96.5 96.0	95.5 96.0

[a] Two drops Monoamine AD-100 added.

Table 12

CHANGES IN REFLECTANCE OF INORGANIC COATINGS - LONG-TERM TESTS

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
3-19-6	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 450 sun-hours	31.0 31.0	89.0 92.5	95.5 95.5	95.0 95.5	
3-13-5c	SP500 PS7 56.9% solids Calcined at 750°C for 2 hr Cured at 140°C for 18 hr	4.30	None 450 sun-hours	23.0 24.5	87.0 87.0	95.5 95.5	95.5 95.5	
3-21-6	TAM c.p. ZrO_2 PS7 64.4% solids Cured at 140°C for 18 hr	4.30	None 450 sun-hours	83.5 77.5	90.0 82.5	92.5 89.0	92.0 91.0	
3-10-1b4	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 2100 sun-hours	32.0 30.0	93.5 87.5	97.5 94.5	97.5 95.0	
3-14-2e	SP500 PS7 56.9% solids Calcined at 700°C for 16 hr Cured at 140°C for 18 hr	4.30	None 2100 sun-hours	27.0 25.0	93.5 87.0	96.0 93.0	96.0 93.5	

Table 12 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
3-14-0g	SP500 PS7 51.3% solids Cured at 140°C for 18 hr	3.22	None 2100 sun-hours	28.0 24.5	89.0 80.5	93.5 87.5	93.0 88.0	
2-20-4	C.p. SnO_2 PS7 61.7% solids Cured at 140°C for 18 hr	4.30	None 2100 sun-hours	69.0 59.5	76.5 67.0	83.0 78.5	84.0 80.5	
2-24-0	Molochite 6, leached PS7 61.7% solids Cured at 140°C for 18 hr	4.30	None 2100 sun-hours	64.5 52.5	75.0 63.5	84.5 76.5	86.5 81.5	
3-15-4	Lithafrax[a] PS7 64.4% solids Cured at 140°C for 18 hr	4.30	None 2100 sun-hours	81.5 37.5	85.0 43.5	86.0 60.5	86.0 68.5	
441-1b	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	30.0 29.5	93.5 85.0	95.5 91.5	95.0 93.5	0.173 0.195

Table 12 (cont.)

Sample	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, %				Solar Absorptance
				380 mμ	440 mμ	600 mμ	700 mμ	
3-19-6f	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	33.5 28.5	92.5 85.0	95.0 91.5	94.5 92.5	0.172 0.197
24-6b	AZO 55-LO PS7 56.9% solids Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	22.5 21.5	84.5 79.0	93.0 90.0	93.0 91.5	0.202 0.217
441-2b	AZO 55-LO PS7 56.9% solids Calcined at 700°C for 16 hr Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	22.5 21.5	88.5 78.5	94.0 89.0	94.0 91.0	0.180 0.205
24-4a	E-P 414 PS7 56.9% solids Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	19.5 18.0	83.5 73.5	91.5 85.5	92.0 88.0	0.210 0.240
24-5b	XX254 PS7 61.7% solids Cured at 140°C for 18 hr	4.30	None 1700 sun-hours	20.5 18.5	82.5 70.5	90.5 84.5	90.5 87.0	0.217 0.249

Table 12 (cont.)

Sample -	Composition	Pigment-to-Binder Ratio	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance
3-21-5gB	SP500 PS7 46.3% solids Air dried only	4.30	None 1200 sun-hours	31.5 23.5	91.5 63.5	96.5 81.0	96.5 87.5	
3-19-6a2	SP500 PS7 46.3% solids Air dried only	4.30	None 1200 sun-hours	31.0 27.0	88.0 86.0	94.5 90.5	93.5 91.5	
4-11-42	E-P 414 PS7 Calcined at 700°C for 16 hr Cured at 140°C for 18 hr		None 1200 sun-hours	20.0 18.5	85.5 81.5	93.0 89.5	93.5 91.0	
WD	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 3100 sun-hours	27.5 24.5	93.5 84.5	95.0 91.0	94.5 92.0	0.187 0.207
W_1	SP500 PS7 46.3% solids Cured at 140°C for 18 hr	4.30	None 3100 sun-hours	28.5 27.5	94.0 86.0	97.0 93.0	97.0 94.0	0.172 0.184

[a] Commercial lithium aluminum silicate, supplied by Carborundum.

In the 2100 equivalent sun-hour run, comparable losses in reflectance were demonstrated by the calcined and uncalcined SP500 zinc oxide samples. The coating with a lower pigment-to-binder ratio, sample 3-14-0g, was visibly more degraded at the edges -- a fact not fully shown by reflectance measurements. This edge effect may have beed due to segregation of the pigment at degradable, binder-rich areas. Slightly stronger discoloration occurred in the tin oxide and Molochite No. 6 (calcined china clay) samples. A Lithafrax composition underwent considerable degradation.

In the 1700 equivalent sun-hour series, there was no significant reflectance loss difference between the heat-cured and the air-dried SP500 zinc oxide samples. The calcined AZO 55-LO coating degraded more than its calcined counterpart, which, surprisingly, showed the best stability of all the coatings in this test. Moderate losses were exhibited by paints containing the less pure forms of zinc oxide, namely, E-P 414 and XX254. Representative reflectance curves for α determinations appear in Figures 13, 14, and 15.

The 1200 equivalent sun-hour run included a sample which had been soiled with dirt and repainted with a second coat of silicate-bonded SP500 zinc oxide 3.5 mils thick. Severe degradation of this coating, sample 3-21-5gB, occurred. Obviously application of a topcoat over a soiled area is not sufficient to retain solar stability. It is possible that a cleaning operation might adequately remove any soluble degradable materials which may be dissolving in the second coat during respraying.

The longest test lasted for 313 hours, or over 3100 equivalent sun-hours. The two samples tested were both SP500 zinc oxide coatings, each sprayed with a different technique. W_1 was a "wet" application and WD a "dry" one. The dry application consisted of spraying at a distance of about 12 inches

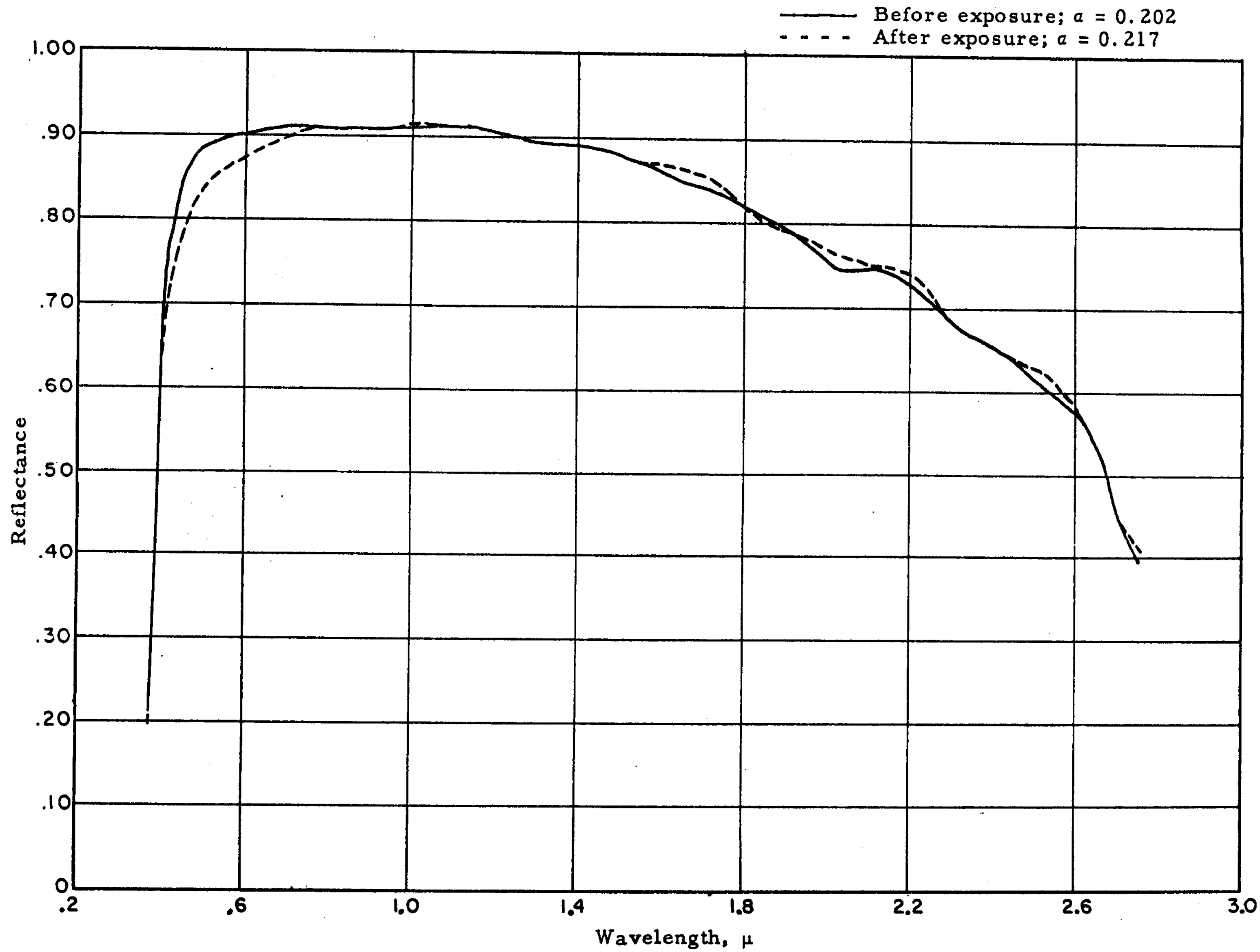

Figure 13

REFLECTANCE OF AZO 55-LO ZINC OXIDE-PS7 POTASSIUM SILICATE COATING (SAMPLE 24-6b) BEFORE AND AFTER EXPOSURE TO 1700 EQUIVALENT SUN-HOURS

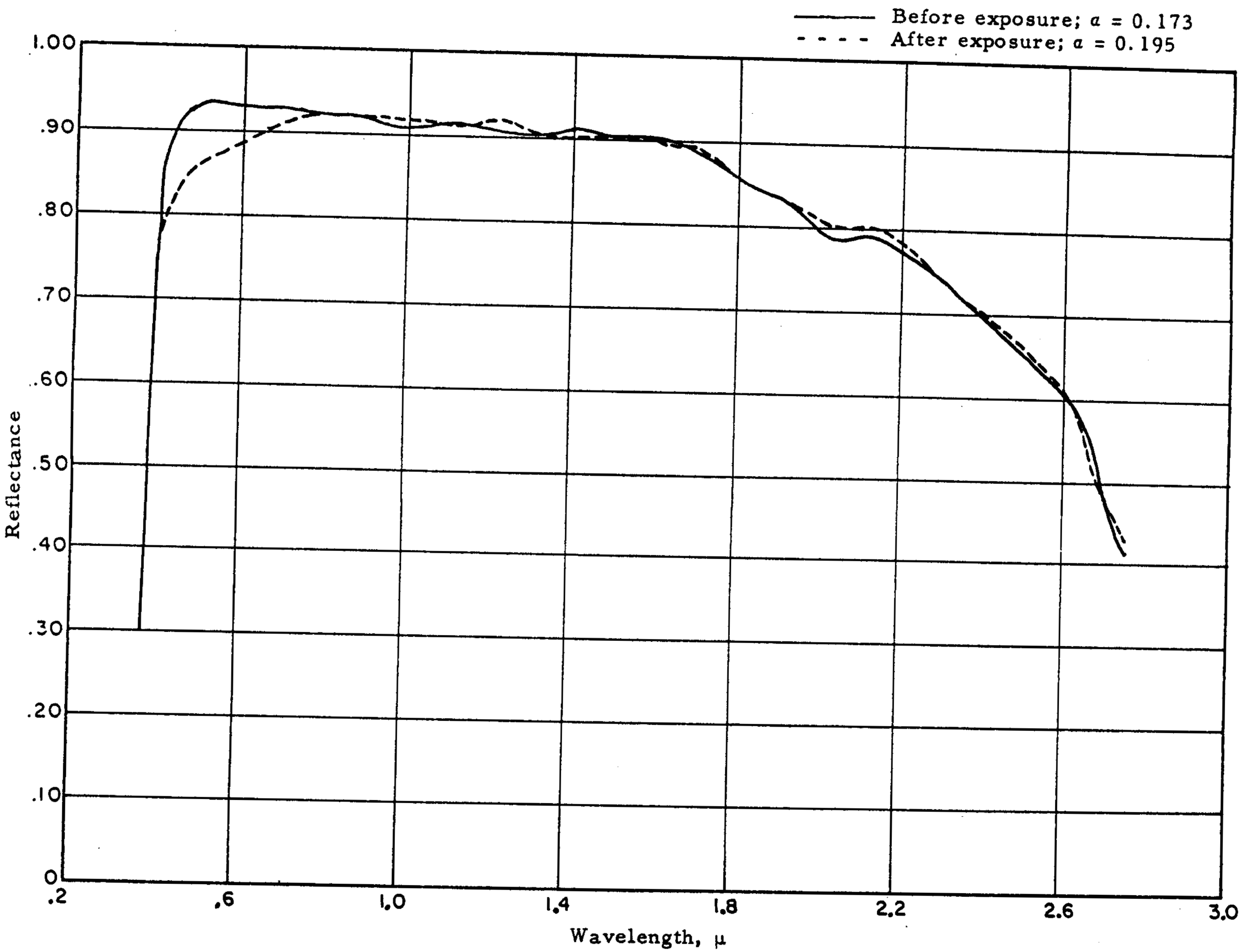

Figure 14

REFLECTANCE OF SP500 ZINC OXIDE-PS7 POTASSIUM SILICATE COATING (SAMPLE 441-1b) BEFORE AND AFTER EXPOSURE TO 1700 EQUIVALENT SUN-HOURS

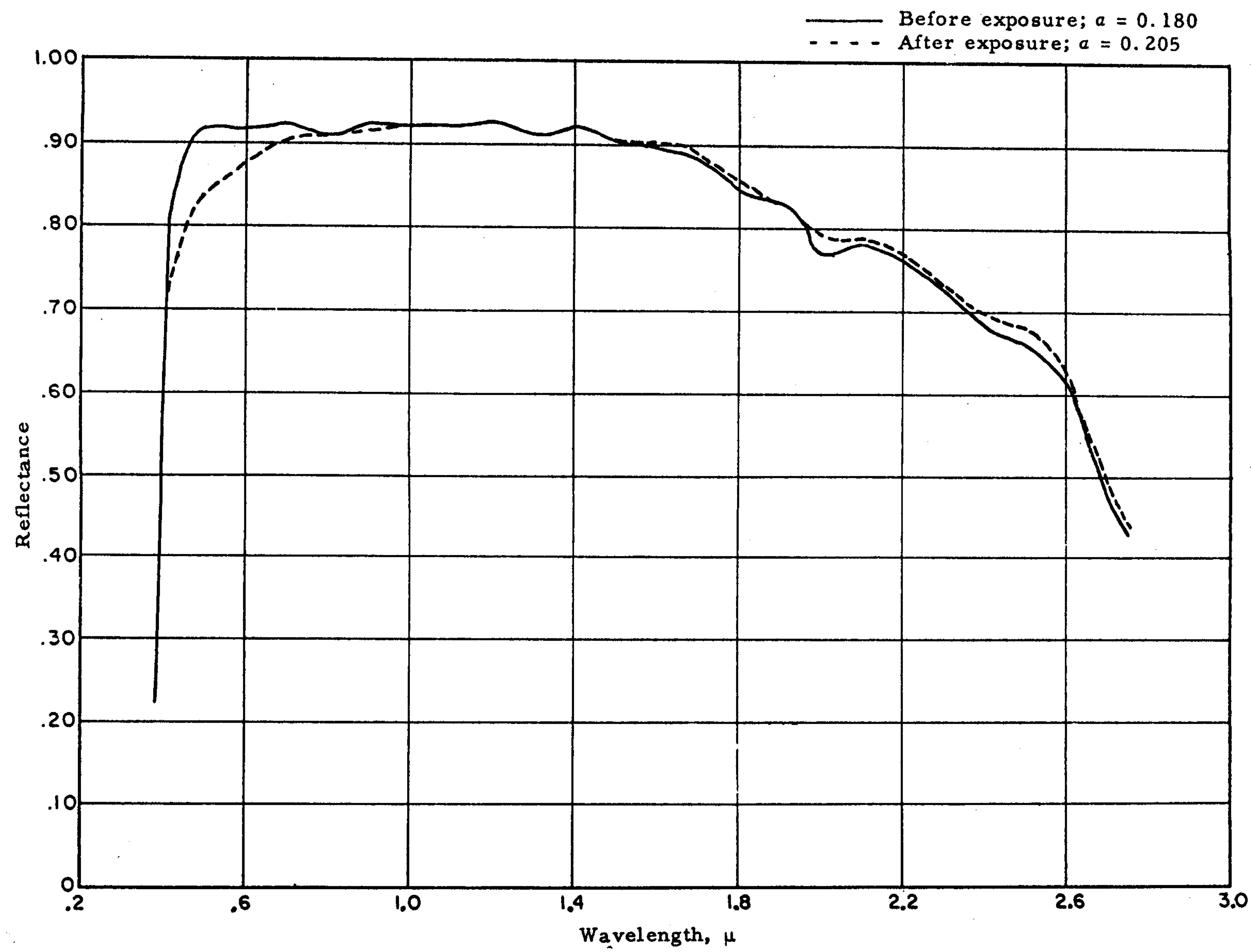

Figure 15

REFLECTANCE OF AZO 55-LO ZINC OXIDE-PS7 POTASSIUM SILICATE COATING (SAMPLE 441-2b) BEFORE AND AFTER EXPOSURE TO 1700 EQUIVALENT SUN-HOURS until the coating appeared wet and stopping until it again looked dry, at which time the cycle was repeated. Five cycles were used. In the wet method a distance of 6 to 12 inches was used. After the wetness was apparent, the spraying was repeated just before the coating appeared completely dry. It was anticipated that wet spraying would permit more settling of the pigment than the dry method and would therefore result in a more degradable, vehicle-rich surface. However, the results in Table 12 and Figure 16 show that WD degraded more than W_1. Furthermore, the increase in solar absorptance was less for both samples than for an identical composition after 1700 equivalent sun-hours (sample 441-lb). A close look at the data reveals that the degradation in the visible for W_1 is comparable with that of sample 441-lb. The lower increase in α for W_1 is accounted for by increased reflectance in the infrared (Figure 17) -- also shown to a much more limited degree by sample 441-lb (Figure 14).

The longer-term tests disclosed degradation of zinc oxide coatings not revealed in the shorter-term tests. Furthermore, some inconsistencies were found in the degradation characteristics of zinc oxide. A variable which was not closely controlled previously is the spraying technique. These anomalies, the degradation at the edges, and the absence of a suspending agent suggest that the zinc oxide pigment may be segregating from the more degradable vehicle. Further experiments on spraying techniques may answer some of the questions raised by the long-term expsoures.

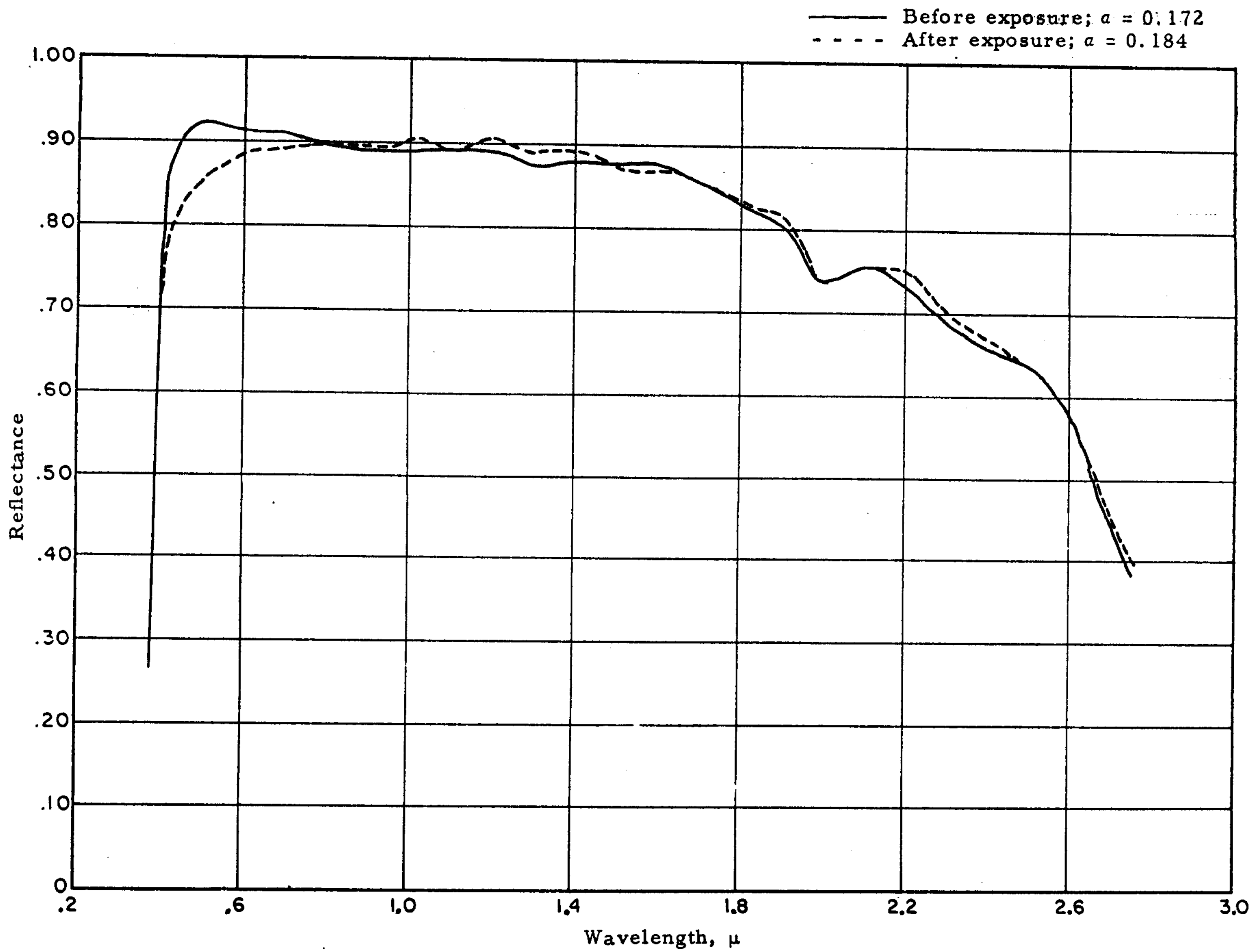

Figure 16

REFLECTANCE OF SP500 ZINC OXIDE-PS7 POTASSIUM SILICATE "DRY" COATING (SAMPLE WD) BEFORE AND AFTER EXPOSURE TO 3100 EQUIVALENT SUN-HOURS

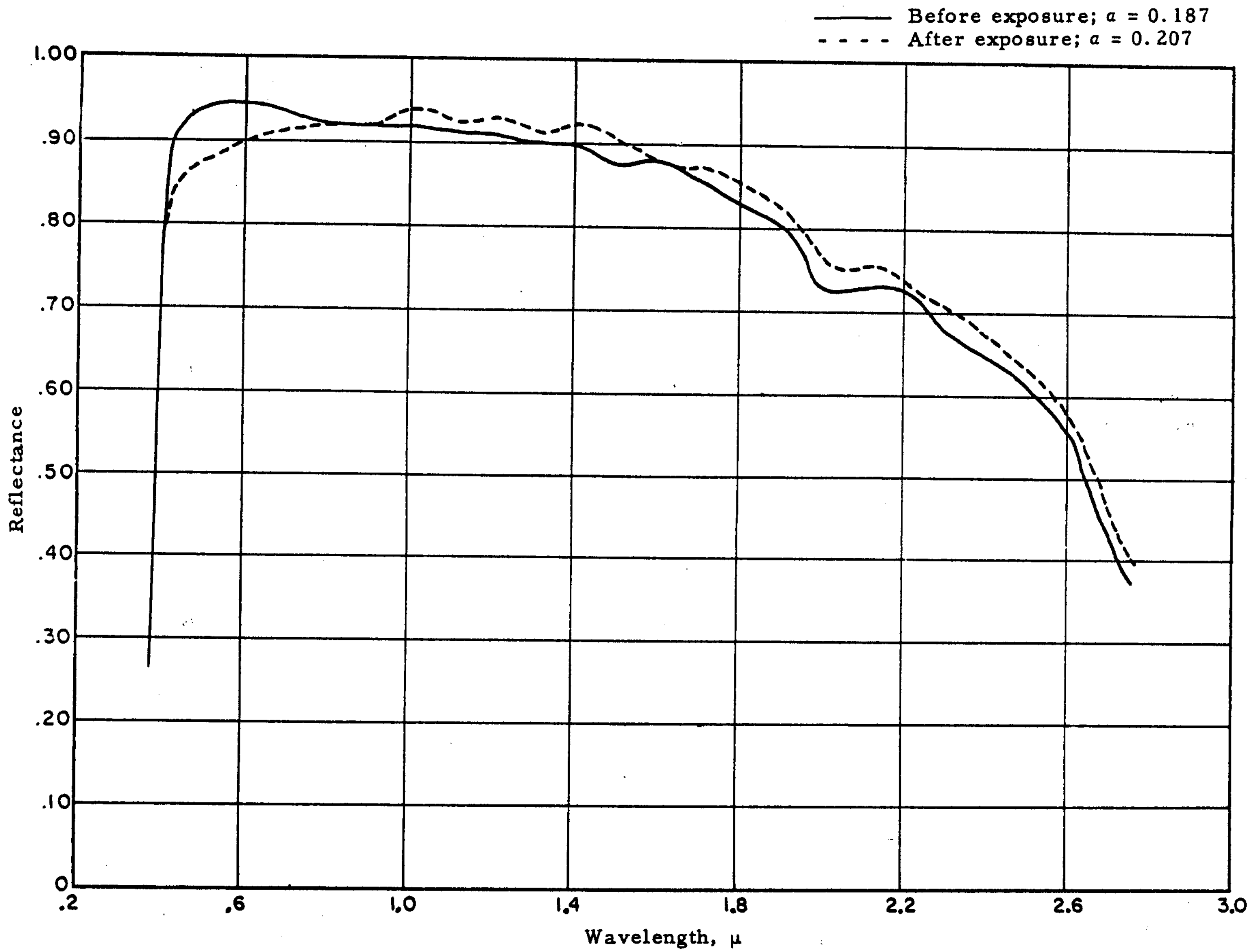

Figure 17

REFLECTANCE OF SP500 ZINC OXIDE-PS7 POTASSIUM SILICATE "WET" COATING (SAMPLE W_1) BEFORE AND AFTER EXPOSURE TO 3100 EQUIVALENT SUN-HOURS

III. EVALUATION OF ORGANIC PAINTS

A. Preparation of Materials

Except as noted, all the paints were ground in porcelain jar mills for about 16 hours at approximately two-thirds critical speed. The critical speed (rpm) is given by[2]

$$W_{Cs} = \frac{54.2}{\sqrt{R}}$$

where R is the radius of the mill (feet). The ingredients used were pigment, vehicle, and solvent. Thus, the possibilities of volatilization as well as photo-oxidation of additives at reduced pressure were eliminated.

The paints were made by charging a sufficient amount of the premixed paint to the mill to just fill the void space when the mill was one-half full of grinding stones. The premixed paint contained enough solvent to make a thin paste on grinding. The paint was then reduced to a total solids content of 40% by volume. The coating was applied with a Paasche type V-1 airbrush at about 30 psi. The formulation data for all the silicone paints are given in Table 13.

Synthesis of Experimental Silicone Resin ARF S-83-10: Two-tenths moles (25.8 grams) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 grams) of methyltrichlorosilane (95%) were mixed in 300 grams of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 30 min, to 1000 grams of ice. The resultant water/ether phases were separated and the ether solution dried over anhydrous magnesium sulfate. The ether was evaporated, leaving the silicone resin in the form of an extremely hydrophobic viscous liquid. The oil was taken up with sufficient xylene to make a 30% by weight solution of the resin. The specific gravity of the resin solution was 0.99. The Me/Si (methyl groups/silicon atoms) ratio was calculated to be 1.29.

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[2]DallaValle, J. M., Micromeritics, Pitman Publishing Corp., 1943.

Table 13

FORMULATION DATA FOR SILICONE PAINTS

Paint No.	Ingredients,	parts by wt.	Pigment Vol. Conc., %	Solids, % by vol.	Pigment-to Binder Ratio (wt.)
TC-83-5	Zinc sulfide	107.5	40	40	2.15
	Dow Corning 806A resin	100.0			
	Toluene	37.0			
TC-83-7	New Jersey SP500 zinc oxide	156.0	40	40	3.1
	Union Carbide R-621 resin	100.0			
	Xylene	40.0			
TC-83-8	New Jersey SP500 zinc oxide	141.0	20	40	1.19
	Dow Corning XR-6-1057 resin	173.0			
	Tetrabutoxy titanium	3.0			
	Toluene	108.0			
TC-83-11	New Jersey SP500 zinc oxide	45.0	25	26	1.35
	ARF S-83-10 resin solution	111.0			
TC-83-12	New Jersey SP500 zinc oxide	93.4	25	40	1.8
	Dow Corning XR-6-0049 resin	100.0			
	Xylene	38.0			
TC-83-13	New Jersey SP500 zinc oxide	186.8	25	40	1.87
	General Electric LTV-602 resin	100.0			
	General Electric SC-04 catalyst	1.0			
	Toluene	171.0			
TC-83-16	New Jersey SP500 zinc oxide	140.1	20	40	1.40
	General Electric LTV-602 resin	100.0			
	General Electric catalyst SC-05	0.5			
	Toluene	160.0			
TC-83-18	New Jersey SP500 zinc oxide	112.0	25	40	1.70
	ARF S-83-14 resin solution	100.0			
	Toluene	67.0			
TC-83-19	New Jersey SP500 zinc oxide	94.8	25	40	1.70
	ARF S-83-17 resin solution	100.0			
	Toluene	43.6			
TC-83-21	New Jersey SP500 zinc oxide	77.5	25	40	1.78
	ARF S-83-20 resin solution	100.0			
	Xylene	17.7			
TC-50-8	New Jersey SP500 zinc oxide	123.6	25	40	1.63
	ARF S-50-3 resin solution	104.0			
	Toluene	86.0			
TC-50-10[a]	New Jersey SP500 zinc oxide	186.8	25	40	1.87
	General Electric LTV-602 resin	100.0			
	General Electric catalyst SC-05	0.5			
	Toluene	170.0			
TC-50-11[a]	New Jersey SP500 zinc oxide	240.0	30	40	2.40
	General Electric LTV-602 resin	100.0			
	General Electric catalyst SC-05	0.5			
	Toluene	183.8			

[a]Milled 32 hours.

Synthesis of Experimental Silicone Resin ARF S-83-14: Four-tenths moles (51.6 grams) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 grams) of methyltrichlorosilane (95%) were mixed in 300 grams of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 40 min, to 1000 grams of ice. The ether layer was separated and washed with distilled water until a water layer neutral to litmus was obtained. The ether solution was dried over anhydrous magnesium sulfate and allowed to evaporate in the hood for 4 days. The Me/Si ratio was calculated to be 1.46. A 60% solution by volume in toluene was prepared. The specific gravity of the resin solution was 1.015.

Synthesis of Experimental Silicone Resin ARF S-83-17: Four-tenths moles (59.2 grams) of dimethyldiethoxysilane (90%) and 0.48 moles (85.5 grams) methyltriethoxysilane (90%) were mixed and added to 200 grams of anhydrous ethyl alcohol. The mixture of silanes and alcohol was added to about 400 grams of distilled water containing 10 grams of 37% hydrochloric acid. The mixture was refluxed 3-1/2 hours. The resinous mass was separated by decantation, washed, and allowed to stand in a separatory funnel for 72 hours. The resin was again separated and diluted to 50% by volume with toluene. The resin solution was then dried over Drierite. The specific gravity of the solution was 0.984. The Me/Si ratio was calculated to be 1.96.

Synthesis of Experimental Silicone Resin ARF S-83-20: Four-tenths moles (59.2 grams) of dimethyldiethoxysilane (90%) and 0.48 moles (85.5 grams) of methyltriethoxysilane (90%) were mixed with 150 grams of 95% ethyl alcohol and added to 400 grams of distilled water. To this mixture was added 22 ml of 37% hydrochloric acid, and the mixture was refluxed vigorously for 19 hours. A syrupy, viscous, colorless fluid of density greater than water resulted. The polymer was washed by decantation until a neutral test to litmus was obtained. Seventy grams of xylene was added, effecting separation of a water/organic phase. The organic layer was washed with distilled water twice, and was dried over Drierite after weighing. The resultant solution contained 40% resin by vol (47% by weight) and the polymer possessed a calculated Me/Si ratio of 1.46. The specific gravity of the resin solution was 0.965.

Synthesis of Experimental Silicone Resin ARF S-50-3: Three-tenths moles (38.7 grams) of dimethyldichlorosilane (99.4%) and 0.48 moles (72.0 grams) of methyltrichlorosilane (95.0%) were mixed in 300 grams of anhydrous diethyl ether. The resultant mixture was added dropwise with agitation, over a period of 40 min, to 1000 grams of ice. The ether layer was separated and washed with distilled water until a water layer neutral to litmus was obtained. The ether solution was dried over Drierite and evaporated at reduced pressure, leaving a viscous, colorless resin. A resin solution in toluene was made at 67.4% solids by volume. The specific gravity of the resin solution was 1.040. The Me/Si ratio was calculated to be 1.38.

Synthesis of Experimental Silicone Resin ARF S-50-4: Four-tenths moles (59.2 grams) of dimethyldiethoxysilane (90%) and 0.96 moles (171 grams) of methyltriethoxysilane (90%) were mixed in 200 grams of ethyl alcohol and added to 600 grams of distilled water. To this mixture was added 33 ml of 37% hydrochloric acid, and the mixture was refluxed vigorously for 19 hours.

A waxy, colorless gum residue (solid) resulted in large yield. On drying the solid at reduced pressure, it was found to be insoluble in all common laboratory solvents. The Me/Si ratio was calculated to be 1.30.

The general reaction scheme for methyl silicone resins is given by Rochow and Gilliam[3] as:

$$(CH_3)_2SiCl_2 + 2H_2O \longrightarrow (CH_3)_2Si(OH)_2 + 2HCl$$

$$CH_3SiCl_3 + 3H_2O \longrightarrow CH_3Si(OH)_3 + 3HCl$$

$$2n(CH_3)_2Si(OH)_2 + nCH_3Si(OH)_3 \longrightarrow \left[\begin{array}{c} CH_3 \quad CH_3 \quad CH_3 \\ | \qquad\; | \qquad\; | \\ -Si-O-Si-O-Si-O- \\ | \qquad\; | \qquad\; | \\ CH_3 \quad O \qquad CH_3 \\ \quad | \end{array}\right]_n + \frac{7}{2}nH_2O$$

In these reactions a mixture of mono- and disubstituted silicon halides (or ethoxy esters) is hydrolyzed, and the resultant silanetriols and silanediols are condensed to the resinous product. The composition of the resin is controlled by the choice of Me/Si mol ratio, which is essentially the same for both the reactant mixture and the product. Methyl silicone polymers prepared in this way with a Me/Si ratio of less than 1.2 are sticky syrups which cure at room temperature to hard, brittle solids. Resins with a Me/Si ratio greater than 1.5, and especially greater than 1.7, are oily, somewhat volatile liquids which cure to soft gels only after prolonged heating at 200°C.[3] The relevant data on the various experimental silicones are tabulated in Table 14.

B. Determination of Physical Properties

1. General

Paints TC-83-5 and TC-83-7 were formulated for purposes of comparison with the methyl silicones (See Table 13). They both are phenyl-methyl silicones and therefore require curing at 400°F. The film properties and curing conditions of all the silicone paints are presented in Table 15.

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[3]Rochow, E. G., and Gilliam. W. F., J. Am. Chem. Soc. 63, 798 (1941).

Table 14

DATA ON EXPERIMENTAL METHYL SILICONE RESINS

ARF Experimental Silicone No.	Corresponding Paint No.	Silane Derivative (X)	Mol Ratio $MeSiX_3/Me_2SiX_2$	Mol Ratio Me/Si
S-83-10	TC-83-11	Chloro	2.4	1.29
S-83-14	TC-83-18	Chloro	1.2	1.46
S-83-17	TC-83-19	Ethoxy	1.2	1.46
S-83-20	TC-83-21	Ethoxy	1.2	1.46
S-50-3	TC-50-8	Chloro	1.6	1.38
S-50-4		Ethoxy	2.4	1.30

Three commercial and six experimental methyl silicone polymers were evaluated. The commercial polymers were Dow Corning resins XR-6-0049 and XR-6-1057 and General Electric LTV-602, a methyl silicone potting compound. The first batch of XR-6-0049 formed an irreversible gel before it could be used, and paint TC-83-12 (Table 13) was formulated from a second batch (with a shelf life of over 6 months). XR-6-1057 was pigmented with SP500 zinc oxide at pigment volume concentrations of 30, 25, and 20%. All three coatings as well as a clear varnish of XR-6-1057 underwent catastrophic "checking" on incipient curing at 360°F.

An air-drying modification of XR-6-1057 was prepared by careful addition of 1% tetrabutoxy titanium in n-butanol. This resin solution was subsequently pigmented with SP500 zinc oxide at 20% pigment volume concentration and applied to aluminum substrates. The coating air dried to the touch in 1 hour and formed a film capable of being evaluated in the ultraviolet chamber for resistance to yellowing. The coating was designated TC-83-8.

Table 15

GENERAL CURING CONDITIONS AND FILM PROPERTIES OF THE SILICONE PAINTS

Paint No.	Cure	Film Properties
TC-83-5	4 hr at room temp. + 1 hr at 400°F	Film integrity, appearance, and adhesion excellent. Good gloss.
TC-83-7	4 hr at room temp. + 1 hr at 400°F	Film integrity, appearance, and adhesion excellent. Good gloss.
TC-83-8	16 hr at room temp.	Film hard and brittle. Appearance and gloss good. Cracked off on heating to 300°F.
TC-83-11	4 hr at room temp. + 1 hr at 330°F	Film integrity and adhesion good. Checked on heating to 360°F for 1 hr. Semiglossy.
TC-83-12	4 hr at room temp. + 1 hr at 330°F	Film integrity and adhesion good. Checked severely on heating to 360°F.
TC-83-13	12 hr at room temp. + 2 wk at 360°F	Adhesion poor. Not thoroughly cured. Good gloss.
TC-83-16	16 hr at room temp.	Very slight tackiness. Cured on heating to 150°F; 48 hr at room temp. cured film. Resilient, excellent gloss. Required primer.
TC-83-18	4 hr at room temp. + 16 hr at 300°F	Film integrity and adhesion good. Flat.
TC-83-19	4 hr at room temp. + 18 hr at 300°F	Did not cure until baked 2 hr at 400°F (in addition to 18 hr at 300°F). Checked severely.
TC-83-21	4 hr at room temp. + 2 hr at 450°F	Film integrity and adhesion good. Flat.
TC-50-8	4 hr at room temp. + <24 hr at 260°F	Film integrity and adhesion good to excellent. Flat. Vitreous-like.
TC-50-10	18 hr at room temp.	Resilient, high-gloss film with good adhesion when primed.
TC-50-11	18 hr at room temp.	Resilient, high-gloss film with good adhesion when primed.

Paint TC-83-13 is a zinc oxide-pigmented methyl silicone elastomer made from LTV-602 and General Electric SC-04 catalyst. The paint required over 2 weeks at 360°F to cure tack-free. Subsequent coatings based on LTV-602 utilized GE's SC-05 catalyst and their proprietary primer SS-4004; these coatings all cured within 48 hours at room temperature. Paints formulated at higher pigment volume concentrations cured at room temperature in 18 hours or less. This is possibly due to greater porosity in the more highly pigmented systems, permitting faster solvent evaporation. Adhesion of LTV-602 paints was quite poor when the SS-4004 primer was not used. In fact, unprimed coatings were easily stripped intact from surfaces as large or larger than 1 square foot. The adhesion of the primed material was adequate, as determined by subsequent tests. Another problem with the elastomeric coatings was their affinity for dirt, dust, and debris. Although it was virtually impossible to keep their surfaces clean, the collected dirt was easily removed by wiping with a soft, damp cloth.

The curing properties of the paints containing the experimental silicones derived from silicon halides were essentially as expected. The coating containing the lowest Me/Si ratio, 1.29 (Table 14), cured in only 1 hour at 330°F; some checking occurred on heating to a slightly higher temperature. The coating with the highest Me/Si ratio, 1.46, required 16 hours at 300°F, while the coating with an intermediate Me/Si ratio, 1.38, cured in about 16 hours at 260°F.

The methyl silicones derived from silicon esters required higher baking temperatures to cure compared with those derived from silicon halides at the same Me/Si ratio.

With the exception of TC-83-8, which was catalyzed with tetrabutoxy titanium, all the silicone paints studied had adequate shelf lives. The main problem encountered was pigment settling, which occurred rapidly in the methyl resin coatings. No difficulties were experienced in redispersing the pigment in these coatings, however.

2. Thermal Shock

The thermal shock test was the same as that described for the inorganic coatings. All coatings listed in Table 15 except TC-83-12, TC-83-13, and TC-83-19 were tested. The phenyl-methyl paints, TC-83-5 and TC-83-7, flaked and cracked on the first cycle. The remainder of the coatings, all methyl silicone paints, withstood 10 cycles of 200 to -320 to 200°F.

3. Torsion

The results of torsion tests on six silicone paints are presented in Table 16. The zinc sulfide-DC 806A phenyl silicone paint (TC-83-5) failed the 90° torsion tests, while the zinc oxide-UC R-621 phenyl silicone paint (TC-83-7) was stressed 90° without failure. Of significance is the fact that TC-83-11 exhibited poorer twist resistance than TC-83-18. TC-83-11 contained a polymer with a Me/Si ratio of 1.29, whereas TC-83-18 was formulated from a polymer with a Me/Si ratio of 1.46. The pigment volume concentration of both paints was 25%, and the resins were both synthesized from appropriate mixtures of chlorosilanes.

The torsional stress resistance of several other organic coatings is presented in Table 17 for comparison purposes.

Table 16

TORSIONAL STRESS RESISTANCE OF SEVERAL SILICONE PAINTS

Paint No.	Cure	Thickness, mils	Results of 90° Stress
TC-83-5	Air dried for 24 hr	4	Subsurface cracked at 82°.
	+ 16 hr at 300°F	5	Cracked at 18°.
	+ 2 hr at 400°F	3	Cracked at 75°.
TC-83-7	Air dried for 24 hr	4	No failure.
	+ 16 hr at 300°F	4	No failure.
	+ 2 hr at 400°F	4	No failure.
TC-83-11	Air dried for 24 hr	3	Cracked at grip at 52°.
	+ 16 hr at 300°F	3	Cracked at grip at 47°, cracked at 85°.
		3	Cracked at grip at 65°.
TC-83-16	Air dried for 72 hr	4.5	No failure.
		4.5	No failure.
		4.5	No failure.
TC-83-18	Air dried for 4 hr	4	No failure.
	+ 16 hr at 300°F	4	No failure.
		4	No failure.
TC-83-21	Air dried for 4 hr	3+	No failure.
	+ 2 hr at 450°F	3+	No failure.
		3+	No failure.
		3+	No failure.

Table 17

TORSIONAL STRESS RESISTANCE OF MISCELLANEOUS ORGANIC COATINGS

Composition	Thickness, mils	Results of 90° Stress
B-V A29550 acrylic-phenolic	2	No failure after 120°.
Leonite 201s	4	Subsurface cracked at 42°. No separation from aluminum substrate after 90°.
Leonite 201s and SP500	5	Subsurface cracked at 75°. No separation from aluminum substrate after 90°.
Butylated urea-formaldehyde and Epon 1007	7	Subsurface cracked at 70°. No separation from aluminum substrate after 90°.
Marietta 6301 epoxy enamel	3	Subsurface cracked at 62°. No separation from aluminum substrate after 90°.
Silicone 806A and SP500	4	Subsurface cracked at 24°. Surface cracked at 42°. Separation from aluminum substrate at 52°.

4. Abrasion

Three methyl silicone paints were applied to 4 x 4-inch panels for abrasion resistance tests with the Taber Abraser (Figure 4). Each sample received 1000 revolutions at forces of either 125 or 150 g (see Section IIB2). As expected, the abrasion resistance of zinc oxide-pigmented methyl silicones (Table 18) was not as good as that of the inorganic paints. Although the loss in weight of the elastomeric silicone paint was of the same order of magnitude as that of the inorganic paints, the low weight loss was due less to film hardness than to coating resiliency.

Table 18

ABRASION RESISTANCE
OF ZINC OXIDE-PIGMENTED METHYL SILICONE PAINTS

Paint No.	Weight Loss, grams At 125 g	Weight Loss, grams At 500 g
TC-83-16	0.0098	0.0915
		0.0532
TC-83-18	0.0929	
		0.2224
TC-83-21	0.0790	
	0.0661	

C. Determination of Optical Properties

The effect of film thickness on the solar absorptance of the elastomeric silicone paint formulated from General Electric's LTV-602 silicone is shown in Figure 18. The total normal emittance at 200°F for six specimens is presented in close proximity to the points on the graph. The higher values for both solar absorptance and total normal emittance in Run 2 cannot be explained at this time.

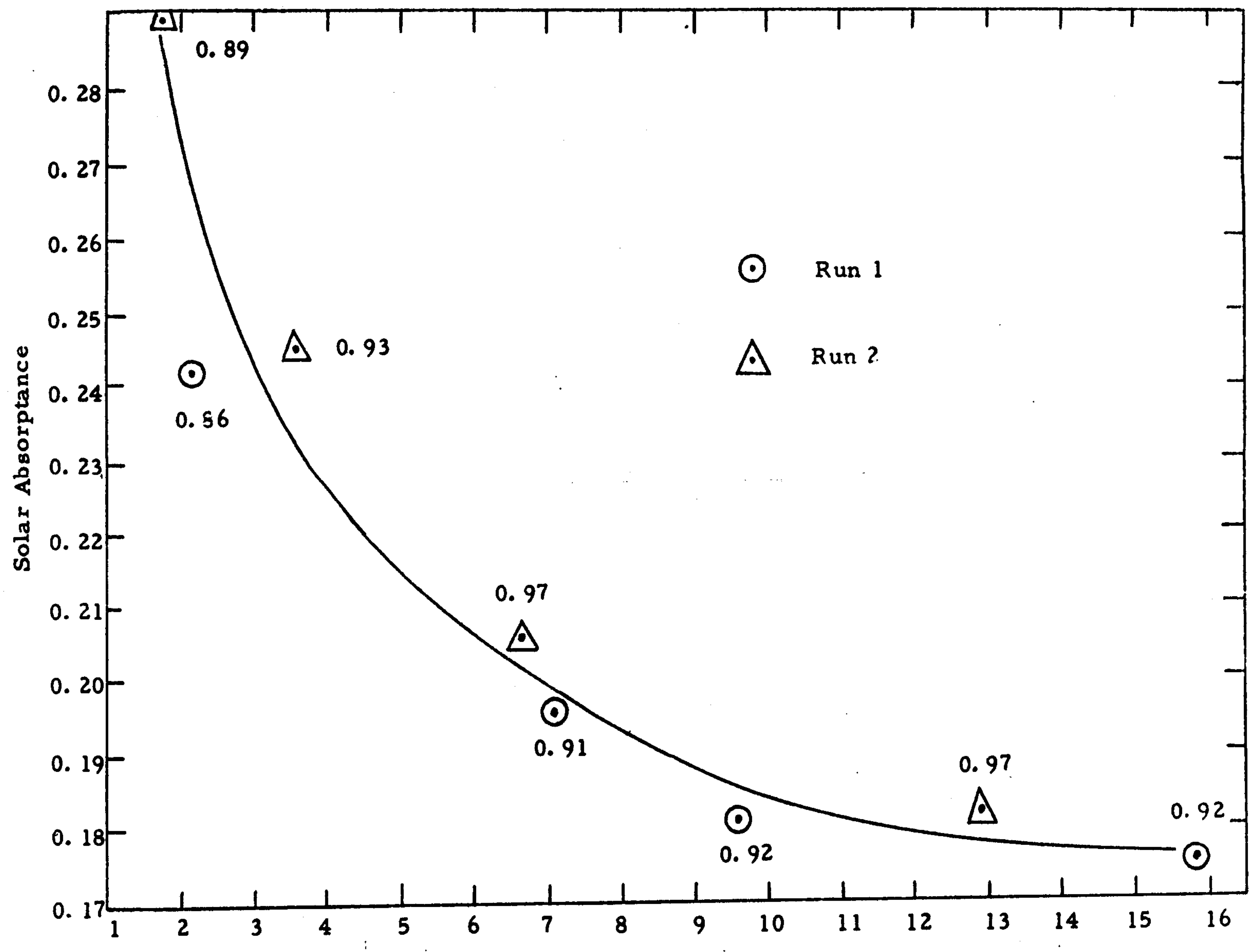

Figure 18

SOLAR ABSORPTANCE VERSUS THICKNESS OF SILICONE PAINT NO. TC-83-16

The data confirm the necessity for thick coatings of approximately 10 mils in order to optimize reflectance and avoid the necessity for precise film thickness control. On the other hand, considerably thinner coatings appeared to optimize the emittance characteristics of the paint. In the infrared (emitting) region the paint is essentially an absorber, whereas in the region of the solar spectrum the paint is a mixture of two nonabsorbing, transparent materials, the silicone vehicle and the zinc oxide. Except for the ultraviolet region, where zinc oxide is a strong absorber, opacity and reflectance are achieved by a scattering mechanism. The strong dependency of solar absorptance on thickness, even for relatively thick films, is emphasized by the facts that (1) zinc oxide possesses a low refractive index compared with rutile titanium dioxide and zinc sulfide and (2) its concentration in the paint is low (the pigment volume concentration is only 20%).

D. Space-Simulation Tests

1. Test D - 300 Equivalent Sun-Hours

Table 19 presents the changes in reflectance of several silicone paints after 300 equivalent sun-hours of ultraviolet irradiation. The four aliphatic silicone paints, TC-83-8, TC-83-11, TC-83-12, and TC-83-13, exhibited little change on irradiation. The maximum change recorded was only 1.0%, and for TC-83-8 and TC-83-12 these changes were increases. These increases are considered to be a result of experimental errors such as changes in the measuring position on the sample before and after exposure.

2. Test F - 315 to 360 Equivalent Sun-Hours

An analytical understanding of the nature of the ultraviolet degradation of paints, as manifested by yellowing, is of considerable interest. The protective effect of increasing pigment volume concentration on ultraviolet stability has been reported previously;[4] curves were presented which illustrated the inverse dependence of yellowing on pigment volume concentration for ultraviolet-absorbing pigments. Since ultraviolet damage occurs in the outermost layers (approximately 10^{-7} cm) of these paints and since some pigment probably settles before the vehicle "sets", an unprotected (pigment-deficient) glossy layer might contribute to the observed degradation.

Table 19

CHANGES IN REFLECTANCE OF SILICONE PAINT - TEST D

Paint No.	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
TC-83-5	None	62.5	84.4	89.0	59.5
	300 sun-hours	38.6	63.0	87.3	60.0
TC-83-7[a]	None	25.5	85.2	83.3	81.5
	300 sun-hours	24.0	77.8	81.5	79.5
TC-83-8[b]	None	23.0	82.0	90.0	89.5
	300 sun-hours	23.5	83.2	91.0	91.0
TC-83-11[b]	None	23.0	82.0	90.0	89.5
	300 sun-hours	26.5	79.5	80.5	78.5
TC-83-12[b]	None	22.5	80.5	83.5	82.5
	300 sun-hours	22.5	81.0	84.5	83.5
TC-83-13[b]	None	No visible change			
	300 sun-hours				

[a]Contains phenyl silicone resin.

[b]Contains methyl silicone resin.

Accordingly, an experiment was constructed to determine the extent of the contribution to degradation of a pigment-poor layer, if present. For the

[4]Zerlaut, G. A, ,Pigment-Binder Relationships in Ultraviolet Irradiated Paints in Vacuum, Preprints, Division of Organic Coatings and Plastics Chemistry, 40th National Meeting Americal Chemical Society, Chicago, Sept. 1961.

purposes of defining the problem, a moderately degradable paint was chosen rather than one of the more stable coatings. Four 1 x 3-inch aluminum panels were abraded and coated with paint TC-83-5, a zinc sulfide-pigmented phenyl-methyl silicone with a pigment volume concentration of 40%. The coatings were applied at thicknesses in excess of 3 mils, allowed to air dry for 24 hours, and then baked at 300°F for 16 hours and at 400°F for 2 hours. Two of the coatings were gently scraped with a razor blade in order to remove the top layer; approximately 1/2 mil was removed. The results after exposure to a simulated space environment are presented in Table 20. The data indicate that a pigment-deficient glossy layer was originally present and that it contributed significantly to the degradation of the untreated samples. The higher reflectance of the scraped samples than that of the untreated samples before exposure to space simulation is further indication of the existence of a binder-rich layer. While the existence of a binder-rich layer is not serious in the more stable zinc oxide-pigmented methyl silicones (e.g., LTV-602), it will be significant when such paints are exposed to 2000 or more equivalent sun-hours.

The effects of various treatments on the ultraviolet stability of three zinc oxide-pigmented methyl silicone paints are presented in Table 21. Soiling and cleaning had little effect on either reflectance or ultraviolet stability. The only exception was TC-83-16, which showed a 6.0% loss in reflectance at 440 mμ. This loss might be attributed in part to the affinity of elastomric methyl silicone for dirt. It was necessary to clean all the elastomeric samples (TC-83-16) with acetone before reflectance was measured. Coatings TC-83-11 and TC-83-18, which contain methyl silicone resins (as opposed to elastomer), did not require cleaning. The effect of thermal shocking cannot be inferred from the data. However, the slight difference in reflectance loss of the two thermally shocked specimens suggests that the effects of thermal cycling should be further investigated. The decrease in both reflectance and stability of the three heated samples was unexpected and cannot be fully explained without further studies.

Table 20

EFFECT OF REMOVAL OF GLOSSY LAYER ON REFLECTANCE OF SILICONE PAINT NO. TC-83-5 - TEST F

Glossy Layer	Treatment	Reflectance, % 400 mμ	440 mμ	500 mμ	600 mμ	700 mμ
Present	None	72.0	83.9	88.0	87.6	59.0
	315 sun-hours	35.5	50.8	68.6	81.5	59.2
Present	None	72.0	82.5	85.0	83.5	58.8
	315 sun-hours	39.0	53.2	68.5	78.2	58.0
Scraped off	None	75.0	86.4	89.3	88.7	60.0
	315 sun-hours	51.2	66.2	78.6	85.4	60.0
Scraped off	None	73.0	84.1	86.3	84.7	59.5
	315 sun-hours	44.5	59.0	73.0	80.5	58.5

3. Long-Term Tests

Table 22 presents the results of a 450 equivalent sun-hour exposure using the VacIon ion-pumping system. Reflectance was measured immediately after the coatings were removed from the space-simulation chamber and again after they had been stored for about 30 days at ambient laboratory conditions. The data show that the reflectance of TC-83-16 and TC-83-18 increased to approximately the original value before the exposure to 450 equivalent sun-hours. Paint TC-83-21 showed little change in reflectance, possibly because a curing temperature of 450°F was required. Some thermal degradation

Table 21

EFFECT OF SOILING AND CLEANING ON REFLECTANCE OF SILICONE PAINTS - TEST F

Paint No.	Soiling and Cleaning[a]	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ
TC-83-11, Cured at room temp. for 24 hr + 300°F for 16 hr	P + L	None	23.5	82.6	87.6	86.3
		360 sun-hours	24.0	80.7	87.6	87.1
	P + Ac	None	24.8	81.8	84.6	83.1
		360 sun-hours	25.0	80.0	85.0	83.3
	None	None	25.0	82.6	88.6	88.0
		315 sun-hours	25.0	80.0	88.6	88.4
	None	None	24.0	81.8	83.5	81.5
		315 sun-hours	25.0	80.5	84.2	82.3
TC-83-16, Cured at room temp. for 72 hr	H + T + Ac	None	25.0	78.9	91.0	90.3
		315 sun-hours	24.0	74.5	89.0	89.3
	H + Ac	None	25.0	79.4	90.3	89.4
		315 sun-hours	24.0	75.6	89.0	89.0
	H + P + L + Ac	None	26.0	79.5	90.3	89.5
		315 sun-hours	24.5	73.5	88.1	88.1
	Ac	None	28.0	88.5	93.4	92.3
		360 sun-hours	28.0	86.3	93.0	92.3
	Ac	None	28.0	88.9	92.5	91.4
		360 sun-hours	28.0	87.2	92.2	91.4
TC-83-18, Cured at room temp. for 4 hr + 300°F for 16 hr	T	None	26.0	83.5	90.5	89.5
		360 sun-hours	26.5	82.0	90.4	90.1
	None	None	26.0	83.6	89.5	88.5
		360 sun-hours	26.0	83.4	89.4	88.4
	None	None	26.5	84.0	89.3	88.0
		315 sun-hours	26.5	83.5	89.3	88.3
	P + Ac	None	25.0	84.0	88.6	87.2
		315 sun-hours	25.0	83.0	89.0	88.0
	P + L	None	25.5	83.5	89.5	88.3
		315 sun-hours	25.5	81.5	90.0	89.0

[a] P = Soiled with Duo Seal vacuum-pump oil for 1 hr. L = Cleaned with lathered Lava soap, rinsed with tap water, wiped with paper towel, dried at room temp. for 72 hr. Ac = Cleaned with acetone-moistened facial tissue. H = Heated in forced-air oven for 3 hr at 400°F. T = Thermal shocked for 10 cycles at 200 to -200°F in about 3 min.

probably took place at this temperature, resulting in a decrease in the Me/Si ratio, and, to conjecture, a matrix which was more transparent (resistant) to ultraviolet resulted. In addition, all the methyl silicone paints are glossy coatings after the solvent evaporates, and those containing a Me/Si ratio greater than 1.3 became flat coatings upon incipient curing. The recovery, or bleaching reaction, of discolored paints is demonstrated in Table 22.

Table 22

CHANGES IN REFLECTANCE OF SILICONE PAINTS AFTER EXPOSURE TO 450 EQUIVALENT SUN-HOURS - LONG-TERM TEST

Paint No.	Treatment	Reflectance, %			
		380 mμ	440 mμ	600 mμ	700 mμ
TC-83-16	None	26.0	87.5	92.5	91.0
	450 sun-hours	27.5	82.5	90.5	90.5
	30 days in lab	28.0	86.5	92.0	90.5
TC-83-18	None	26.0	80.5	92.0	91.5
	450 sun-hours	25.0	76.0	91.5	90.5
	30 days in lab	25.0	84.0	92.0	91.0
TC-83-21	None	22.0	77.0	87.5	86.0
	450 sun-hours	24.0	77.0	87.0	87.0
	30 days in lab	23.0	78.0	87.5	86.0

The results of a longer-term space-simulation test are presented in Table 23. Three specimens were prepared at different times and were irradiated together in order to determine the degree of precision which might be expected from their preparation and from reflectance measurements. Comparision of the loss in reflectance of TC-83-16 after 450 equivalent sun-hours (Table 22) and after 1200 equivalent sun-hours (Table 23) shows that a greater effect occurred at the longer wavelengths during the longer exposure. At 440 mμ a 5.0% loss occurred after 450 sun-hours, while a total loss of only 6.0% occurred after 1200 sun-hours.

Table 23

CHANGES IN REFLECTANCE OF SILICONE PAINT NO. TC-83-16 AFTER EXPOSURE TO 1200 EQUIVALENT SUN-HOURS - LONG-TERM TEST

Treatment	Reflectance, %				
	380 mμ	440 mμ	500 mμ	600 mμ	700 mμ
None	28.5	89.5	94.3	95.3	94.4
1200 sun-hours	28.0	83.5	88.3	91.3	92.2
None	28.5	89.2	94.4	95.4	95.0
1200 sun-hours	28.0	83.5	88.6	91.8	92.7
None	27.5	89.0	93.2	92.5	91.4
1200 sun-hours	27.5	84.5	88.3	90.0	90.2

The results of exposure to 3100 equivalent sun-hours in the ion-pumping system are given in Table 24. Examination of the reflectance losses of TC-50-8 at 440 and 600 mμ shows that the loss compares favorably with the inorganic zinc oxide-potassium silicate paints WD and W_1 (Table 12).

Table 24

CHANGES IN REFLECTANCE OF SILICONE PAINTS AFTER EXPOSURE TO 3100 EQUIVALENT SUN-HOURS - LONG-TERM TEST

Paint No.	Treatment	Reflectance, %				Solar Absorptance
		380 mμ	440 mμ	600 mμ	700 mμ	
TC-50-8	None	26.0	87.5	90.0	88.5	
	3100 sun-hours	25.0	83.0	88.5	87.5	0.25
TC-50-8	None	26.0	87.5	88.2	86.3	
	3100 sun-hours	25.0	[illegible].4	86.0	85.1	0.27
TC-83-16	None	29.0	88.0	85.7	84.0	
	3100 sun-hours	26.0	75.0	82.2	82.0	0.29

Table 25 presents changes in reflectance and solar absorptance of three elastomeric silicone paints and three experimental silicone paints after about 1600 equivalent sun-hours. The corresponding spectral reflectance curves from 0.3 to 2.8 μ wavelength are given in Figure 19 through 24. The solid line is the reflectance before exposure and the broken line is the reflectance after exposure to 1600 equivalent sun-hours of ultraviolet. The thicknesses of the six paints varied from 1.5 mils to over 4 mils.

Table 25

CHANGES IN REFLECTANCE OF SILICONE PAINTS AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS - LONG-TERM TEST

Paint No.	Treatment	Reflectance, % 380 mμ	440 mμ	600 mμ	700 mμ	Solar Absorptance α	$\Delta\alpha$
TC-83-11	None	24.0	83.0	85.5	83.7	0.26	
	1600 sun-hours	23.5	71.0	81.5	82.0	0.27	0.01
TC-50-8	None	24.0	86.5	91.3	90.0	0.23	
	1600 sun-hours	25.0	82.5	88.5	88.2	0.25	0.02
TC-83-18	None	24.0	85.5	94.0	93.5	0.20	
	1600 sun-hours	25.0	82.0	91.0	91.5	0.23	0.03
TC-83-16	None	27.0	87.1	91.8	90.4	0.22	
	1600 sun-hours	27.0	80.1	88.0	88.0	0.26	0.04
TC-50-10	None	24.0	83.0	92.4	91.4	0.23	
	1600 sun-hours	25.0	77.0	87.0	88.0	0.26	0.03
TC-50-11	None	25.0	83.9	92.3	91.2	0.23	
	1600 sun-hours	26.0	79.3	88.0	88.0	0.26	0.03

It was hoped that the effect of varying Me/Si ratio on change in solar absorptance ($\Delta\alpha$) would be reflected in the data. However, examination of the reflectance losses in the visible region in Table 25 and Figure 19 shows that the

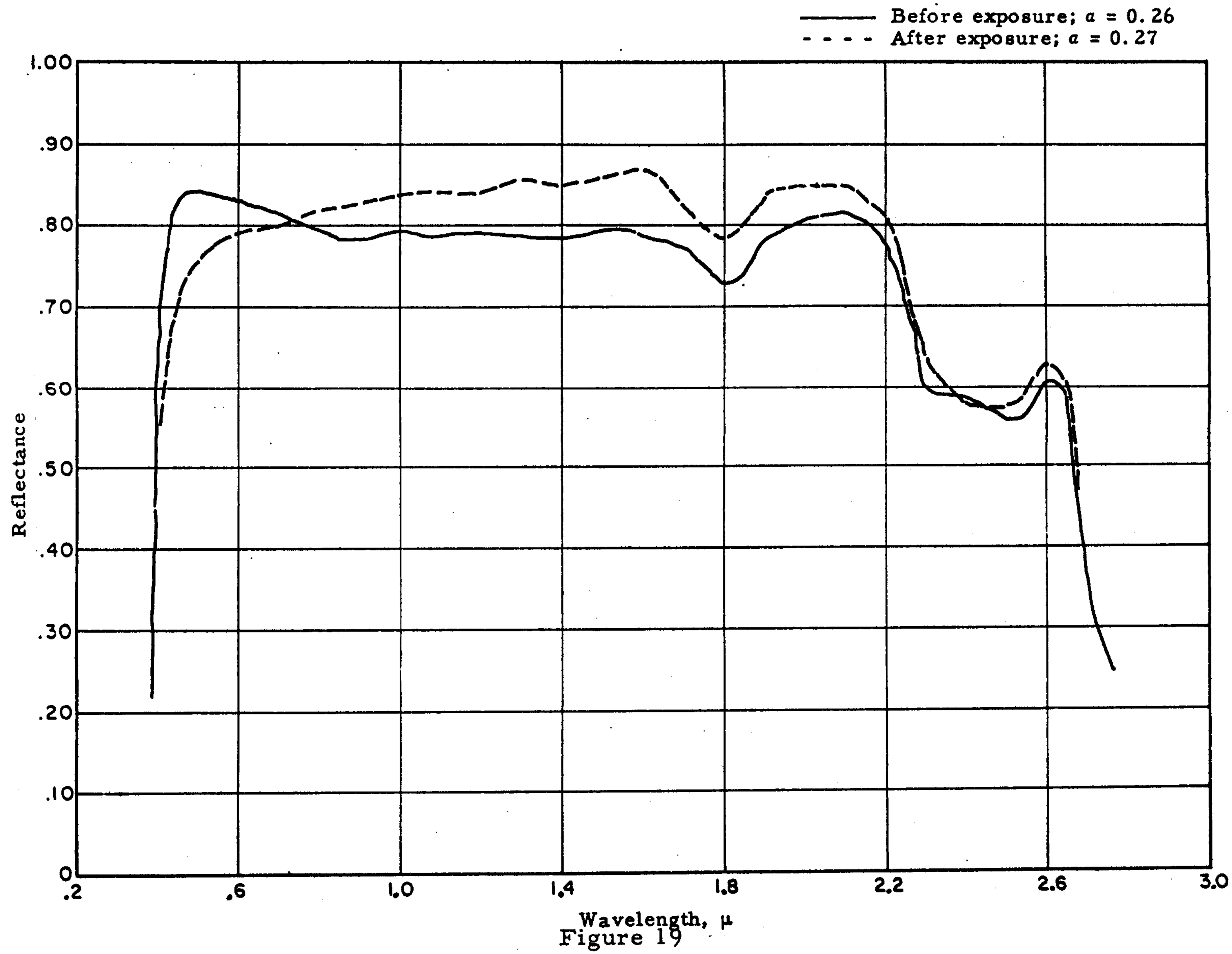

Figure 19

REFLECTANCE OF SILICONE PAINT NO. TC-83-11 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

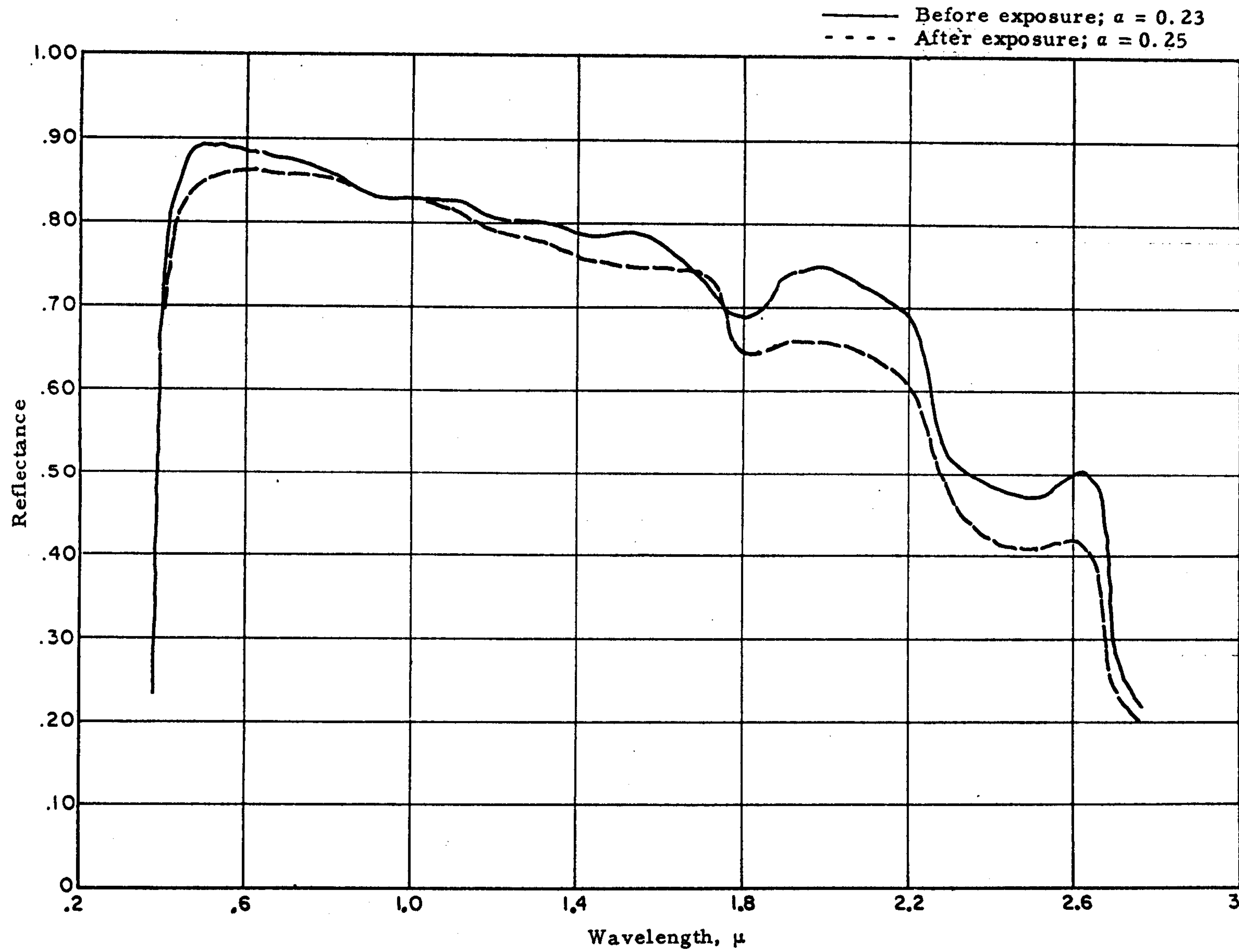

Figure 20

REFLECTANCE OF SILICONE PAINT NO. TC-50-8 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

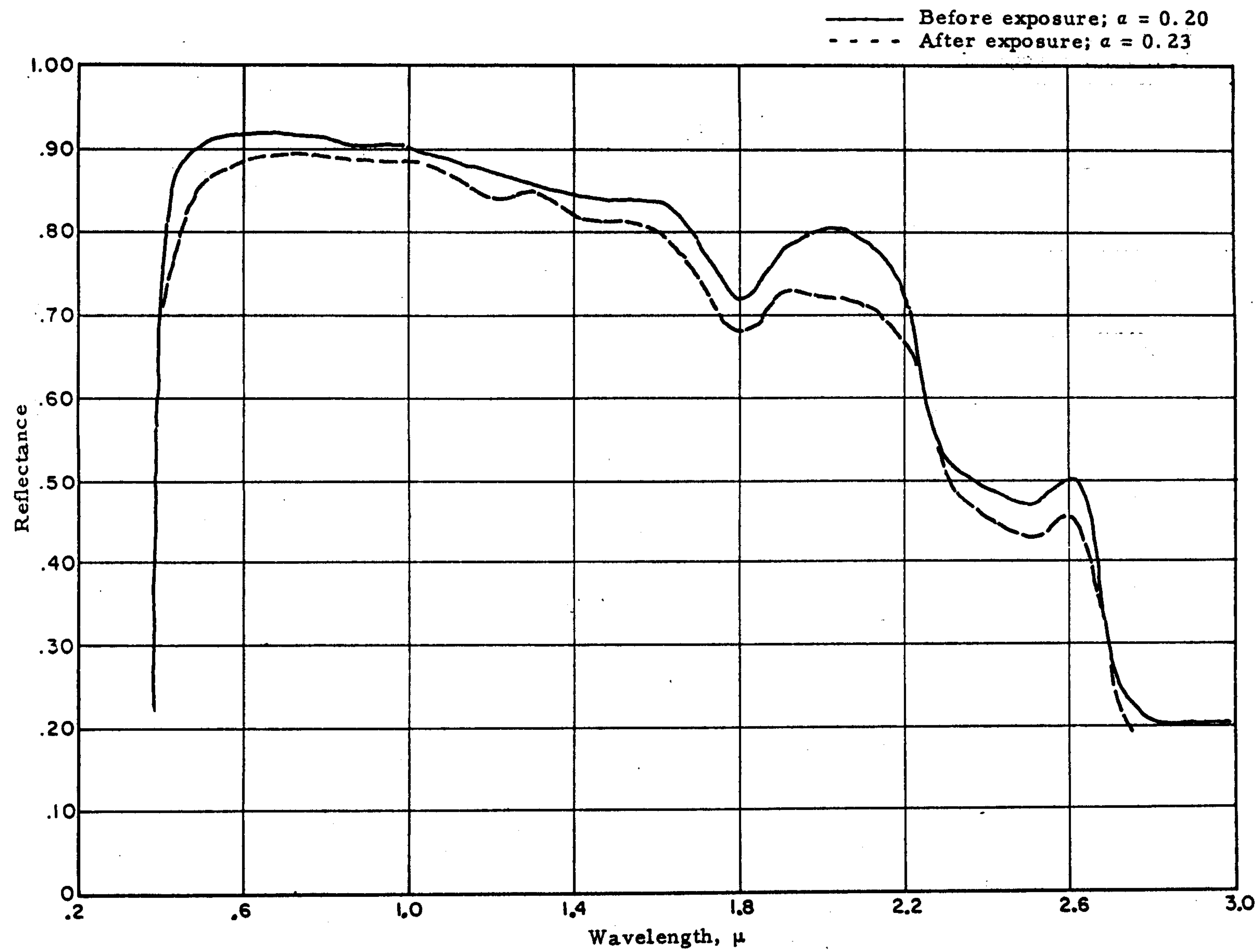

Figure 21

REFLECTANCE OF SILICONE PAINT NO. TC-83-18 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

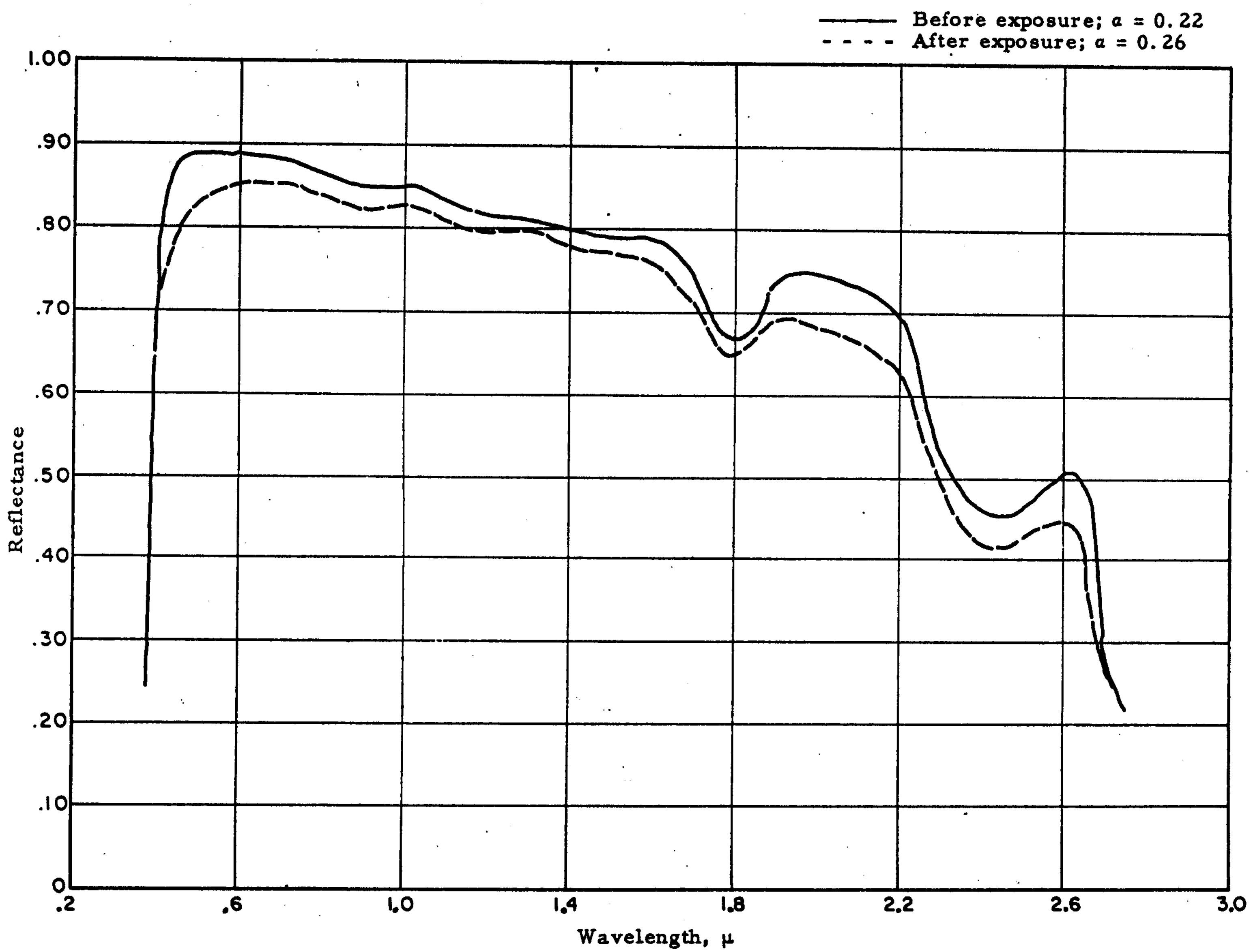

Figure 22

REFLECTANCE OF SILICONE PAINT NO. TC-83-16 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

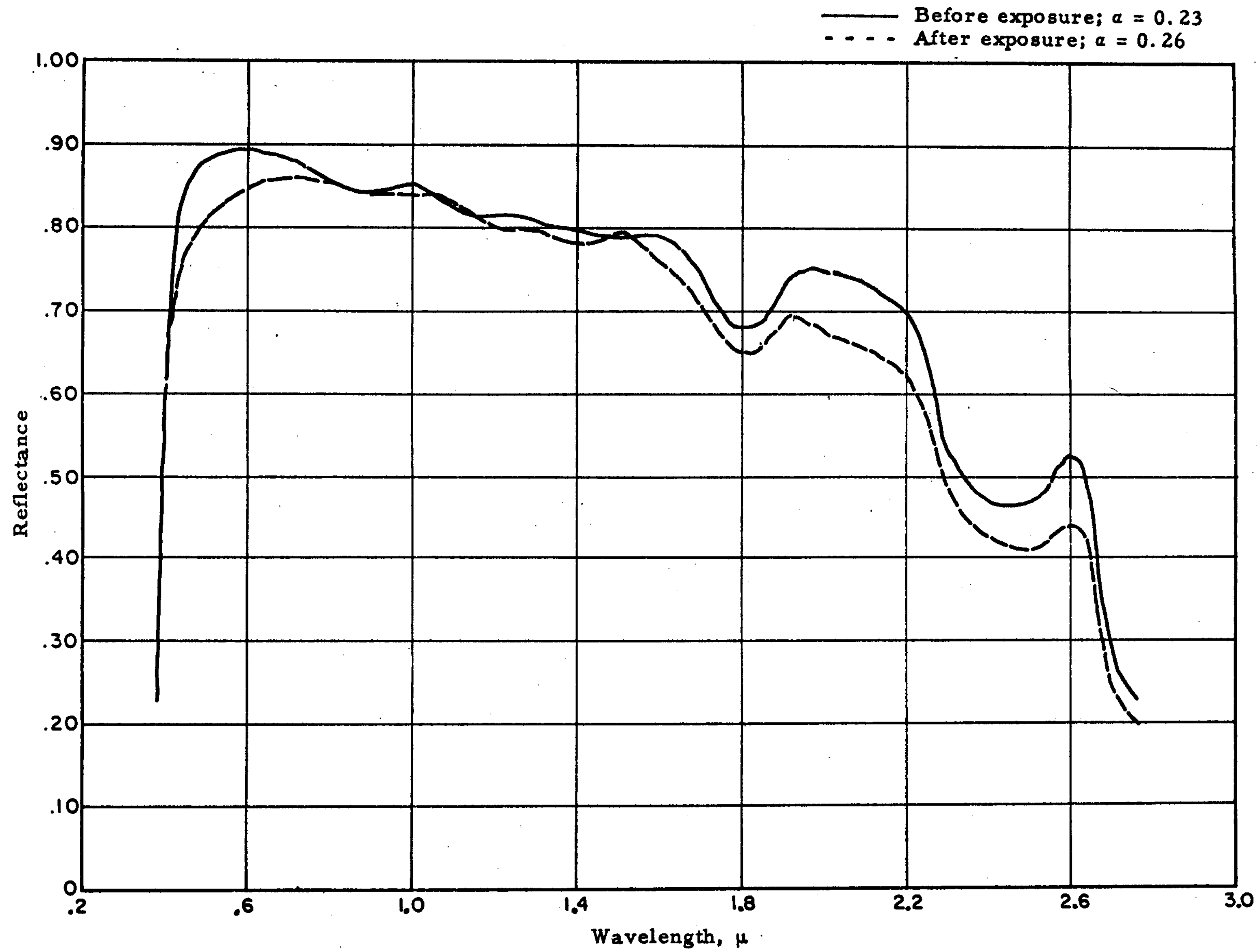

Figure 23

REFLECTANCE OF SILICONE PAINT NO. TC-50-10 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

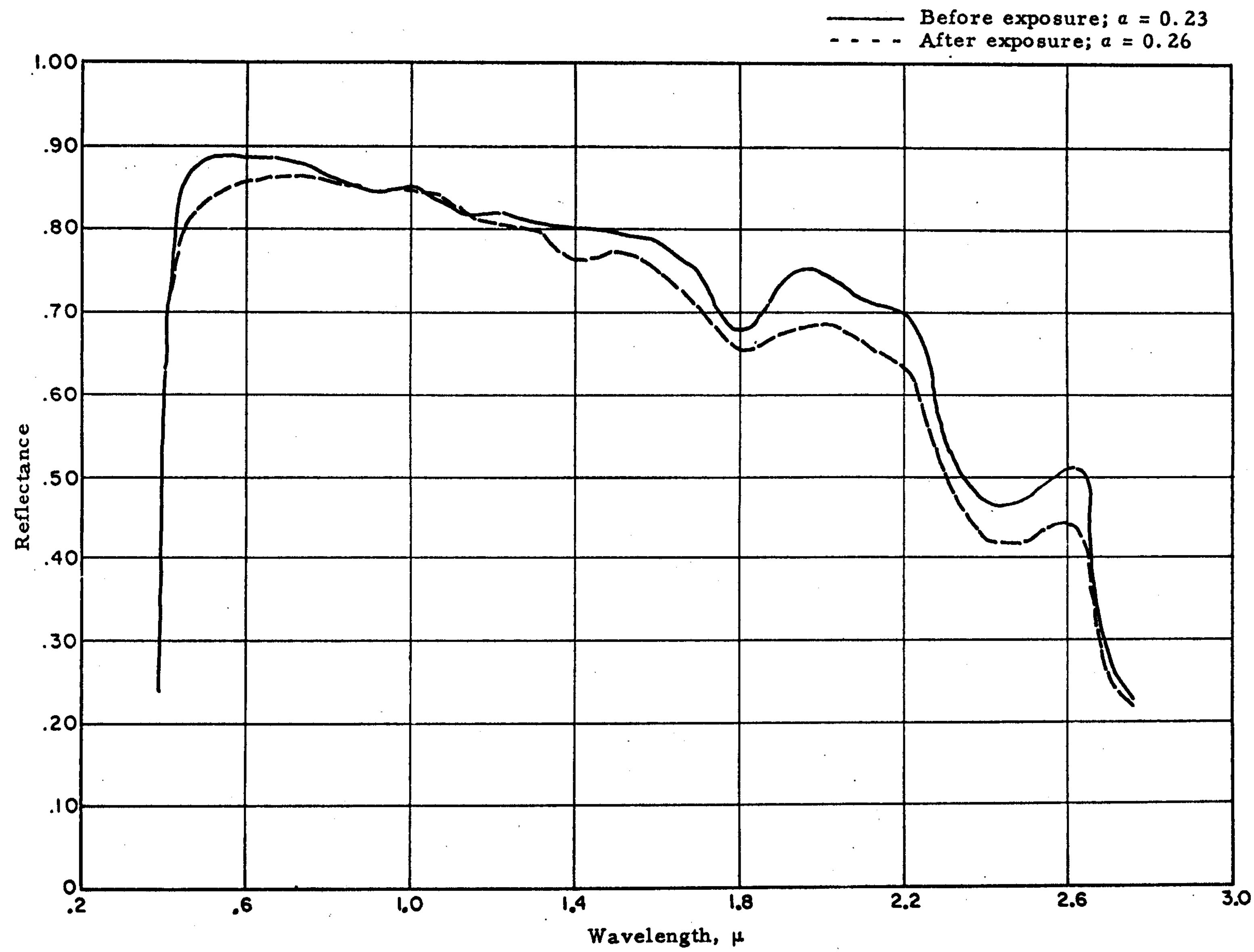

Figure 24

REFLECTANCE OF SILICONE PAINT NO. TC-50-11 BEFORE AND AFTER EXPOSURE TO 1600 EQUIVALENT SUN-HOURS

apparent decrease in $\Delta\alpha$ for decreasing Me/Si is due more to the anomalous reflectance increase in the infrared than to resistance to yellowing. This anomaly cannot be explained at this time. TC-83-11 originally possessed the highest infrared reflectance of the silicone paints and is comparable to the inorganic paints in the 1.8- to 2.2-μ wavelength region (see Figures 13 through 17).

The three LTV-602 paints, TC-50-10, TC-50-11, and TC-50-16, were tested in an attempt to establish the effect of a higher pigment volume concentration on the stability of LTV-602. A slight increase in resistance to yellowing was found, and work presently in progress indicates that a coating with a higher pigment volume concentration possesses better film properties than a coating such as TC-83-16, with a pigment volume concentration of 20%.

IV. PREPARATION OF OTHER COATINGS

Because zinc sulfide- and zinc oxide-pigmented urea-formaldehyde and melamine-formaldehyde paints have occasionally shown good resistance to ultraviolet irradiation, attempts were made to prepare four aliphatic polyurea-type resins. (1) The reaction of hexamethylenediisocyanate (HMDC) with diethylenetriamine at room temperature resulted in the formation of a white solid which apparently is predominantly linear. A smaller amount of a cross-linked product resembling an elastomer was also formed. (2) A white solid was formed by the solvent reaction of HMDC with urea. (3) HMDC reacted rapidly with hexamethylenediamine at room temperature to form a white solid, which upon standing turned pale beige. (4) HMDC and melamine were refluxed in pyridene; a viscous colorless polymerlike material formed. All the reaction products were insoluble in common laboratory solvents.

The ultraviolet stability of these materials will be evaluated by casting from solution if possible or by working with the materials in powder form. Further synthetic work with these materials will not be attempted unless they are found to be reasonably resistant to ultraviolet.

Attempts to prepare organic primer coatings for the inorganic paints have not been successful to date. The problem is wettability of the organic material by the aqueous inorganic paint. Wetting and surface-active agents which have been tried have acted as "parting agents" for the cured film. This work was initiated in order to provide corrosion protection for the relatively porous potassium silicate paints.

V. SPACE SIMULATION AND EFFECTS

A. Ion-Pump Space-Simulation System

An ion-pump solar-simulation chamber was constructed and was used for the longer-term tests. The system provides a convenient means of obtaining a clean ultrahigh vacuum. The chamber dimensions are given in Figure 25. The chamber is provided with a quartz window and a liquid-cooled sample table. The sample table, shown in Figure 26, can be cooled with liquid nitrogen, ice water, or tap water, and can accommodate six 1 ¼ x 1-inch specimens. The system, which is shown in Figure 27, consists of a 400 liter/sec Varian VacIon pump, which is prepumped with both a molecular-sieve sorption pump and a mechanical pump. A General Electric AH-6 mercury-arc lamp is mounted over the quartz window (shown in place in Figure 27). Reproducible equivalent solar factors as determined with a temperature compensating thermopile from 4 to 18 intensities (2000 to 4000 A) have been achieved. A plot of $1/D^2$ (D = distance from lamp to sample) resulted in a straight-line relation. The wide-angle thermopile is shown in Figure 28.

B. Space-Simulation Test Data

The pertinent data on the various space-simulation tests are presented in Table 26.

C. Photolysis Studies

1. Attenuated Total Reflectance

This new and potentially very useful technique is based upon the variation of the refractive index in the region of an absorption band. It is well known that total internal reflection occurs when a beam of light crosses an interface at an angle greater than the critical angle. This angle is determined by the

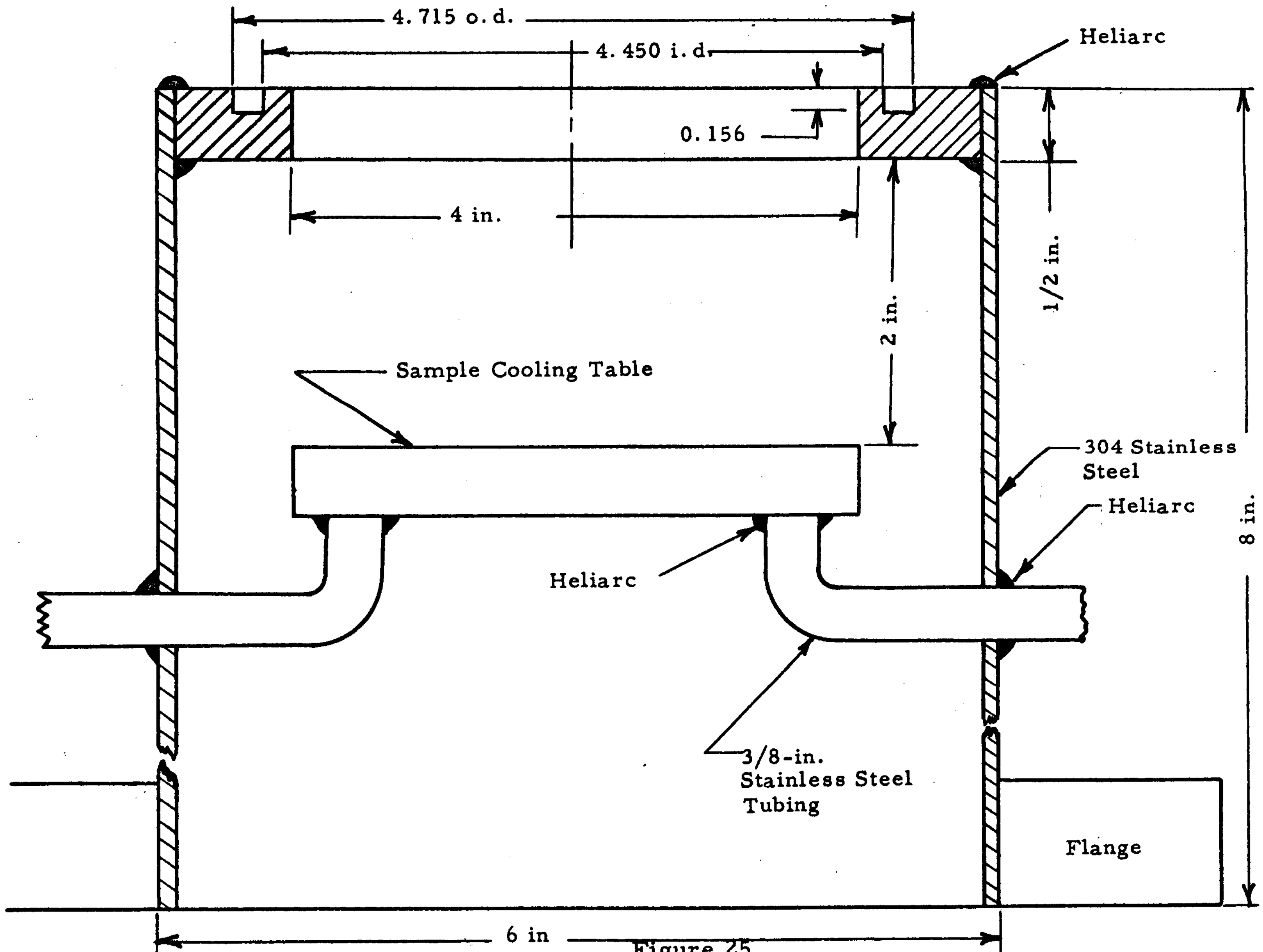

Figure 25

DIAGRAM OF ION-PUMP SPACE-SIMULATION CHAMBER

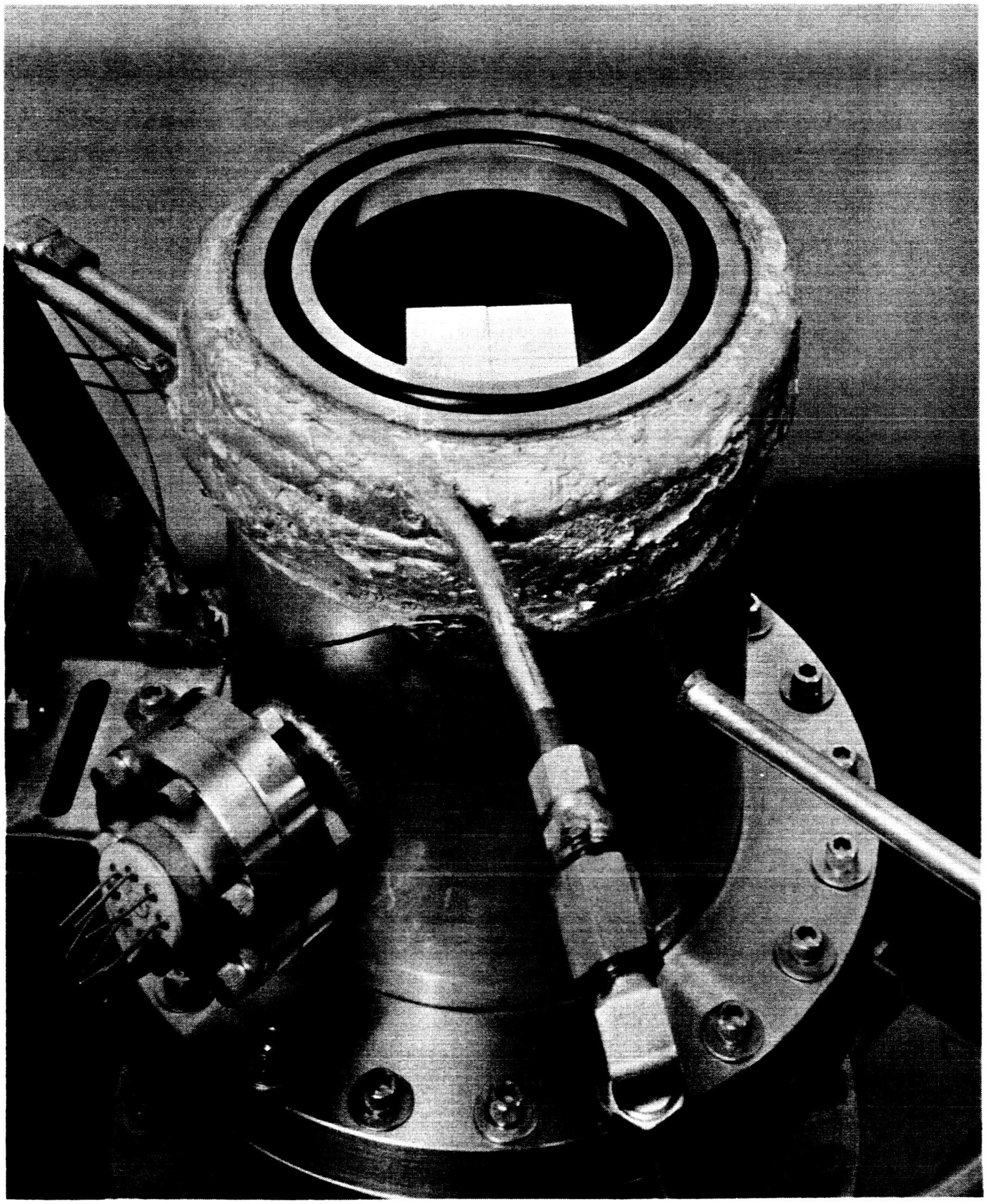

Figure 26

ION-PUMP SPACE-SIMULATION CHAMBER WITH SAMPLES IN PLACE

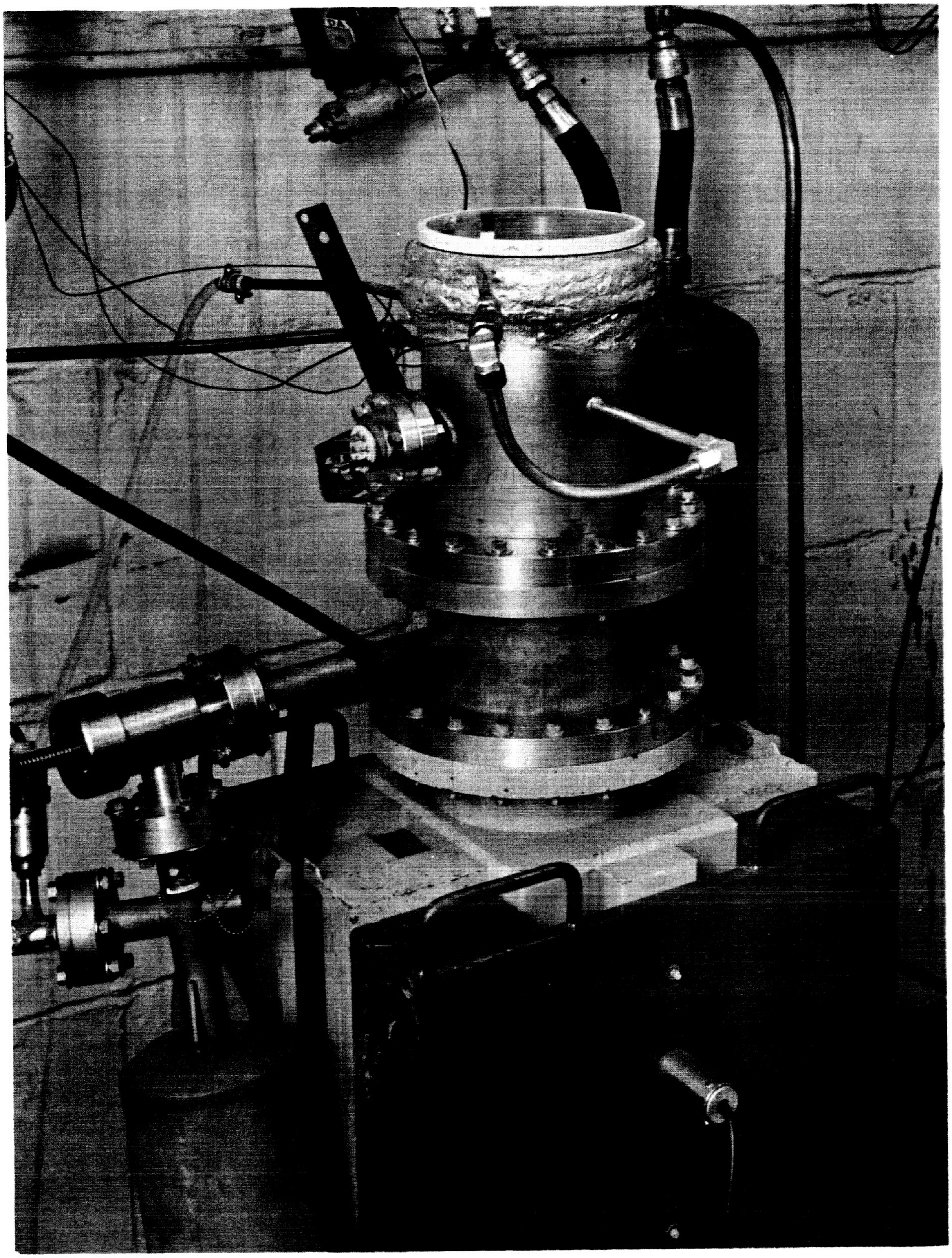

Figure 27

ION-PUMP SPACE-SIMULATION SYSTEM

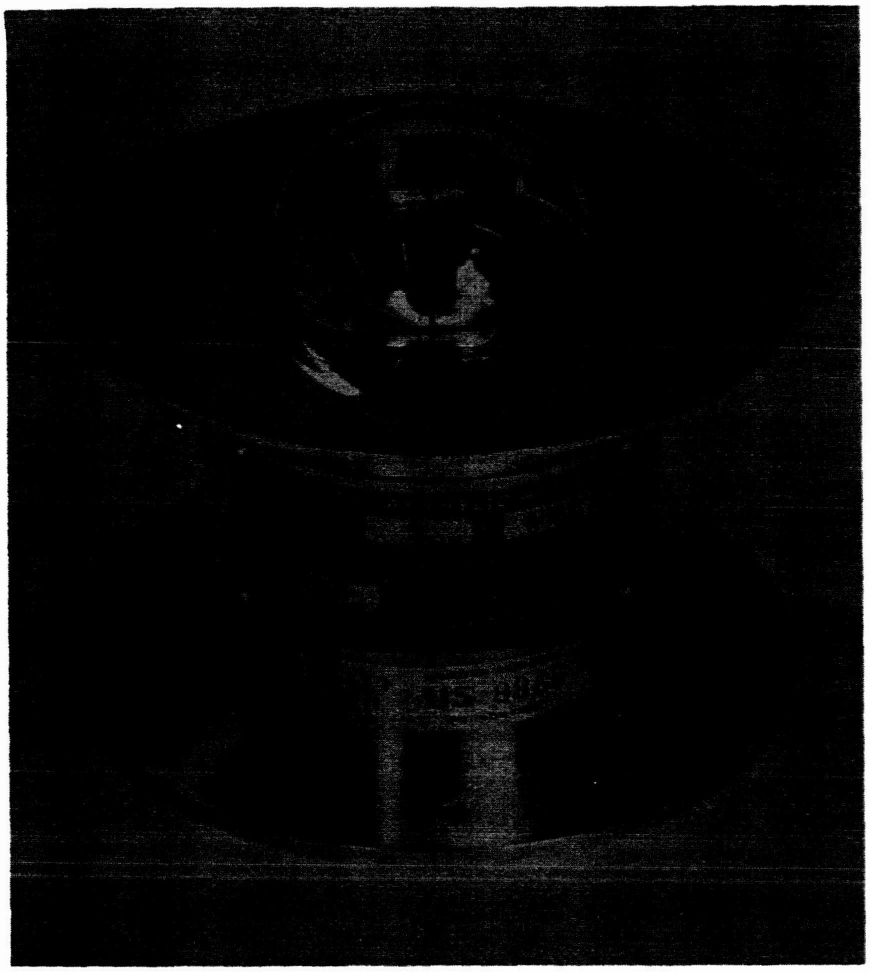

Figure 28

WIDE-ANGLE THERMOPILE
FOR MEASURING EQUIVALENT SOLAR-ULTRAVIOLET FACTOR

Table 26

SPACE-SIMULATION TEST CONDITIONS

Test	System	Ultimate Pressure, torrs	Avg. Sample Temp., °F	Equivalent Solar Factor	Exposure Time, hours	Equivalent Sun-Hours
D	Diffusion pump	$\sim 1.6 \times 10^{-6}$	190-250	3	100	300
E	Diffusion pump	$\sim 1.6 \times 10^{-6}$	190-250	2.5	100	250
F	Diffusion pump	1.6×10^{-6}	190-250	3.5-4.0	90	315-360
	Ion pump	$\sim 2 \times 10^{-8}$	70	10	45	450
	Ion pump	2.8×10^{-8}	71-76	10	210	2100
	Ion pump	2.0×10^{-8}	70	8.7	195	1700
	Ion pump	3.7×10^{-8}	70	10	120	1200
	Ion pump	$\sim 2 \times 10^{-8}$	70	10	310	3100
	Ion pump	$\sim 2 \times 10^{-8}$	70	10	160	1600

ratio of the refractive indices of the phases separated by the interface, and total internal reflection can only occur when radiation passes from a medium of high refractive index to one of lower refractive index. Therefore the critical angle varies with the refractive index of the second phase, if the refractive index of the first phase remains constant. Since the refractive index of a substance is anomalous in the region of an absorption band, it is to be expected that the reflectance of light near the critical angle will be a function of the absorption spectrum of the second phase.

Since this is an interfacial phenomenon, it is sensitive only to the surface composition of the second phase. This is a particular advantage in the study of the photolysis of solid materials, since the reaction has been shown to be confined to the surface of the material. Even if the coatings of interest to this project were transparent to infrared radiation (which they cannot be because of the requirements of high emissivity), a conventional transmission study of the changes produced by the photolysis would be relatively insensitive to changes produced on the surface, since conventional transmission techniques characterize the bulk of the material. In principle, then, this technique seems uniquely suitable for this investigation.

In practice there are difficulties of a practical nature, the greatest of which is obtaining true optical contact between the high refractive index prism (Figure 29) and the specimen. Various devices have been suggested, as, for example, a film of Nujol or some other transparent liquid, but none have thus far given the necessary degree of reproducibility. In order to detect small differences in samples before and after photolysis, the possibility of artifacts must be carefully excluded. Many of the coatings of interest to this project are highly pigmented and therefore do not have optically smooth surfaces.

Some are even sufficiently porous that excessive amounts of Nujol are required to exclude air from the interface, and the spectrum thereby loses definition. At present, the best procedure involves the use of a silver chloride prism, which is clamped against the specimen for 8 hours before the spectrum is obtained. Since silver chloride is relatively soft, it deforms under continued pressure, and eventually a reproducible spectrum is obtained. These spectra, however, have not been of sufficient quality to show, for example, changes in functional group concentration produced by photolysis.

The source of difficulty is clearly in the nature of the specimens. When a polymer solution is applied directly to the prism and an adhering film is formed by evaporation, excellent characteristic spectra are obtained. Figure 30 shows such a film and the effect of varying the angle of incidence. The spectrum is scarcely sensitive to the angle of incidence once the critical angle is exceeded, but below this angle the spectrum is predictably poor.

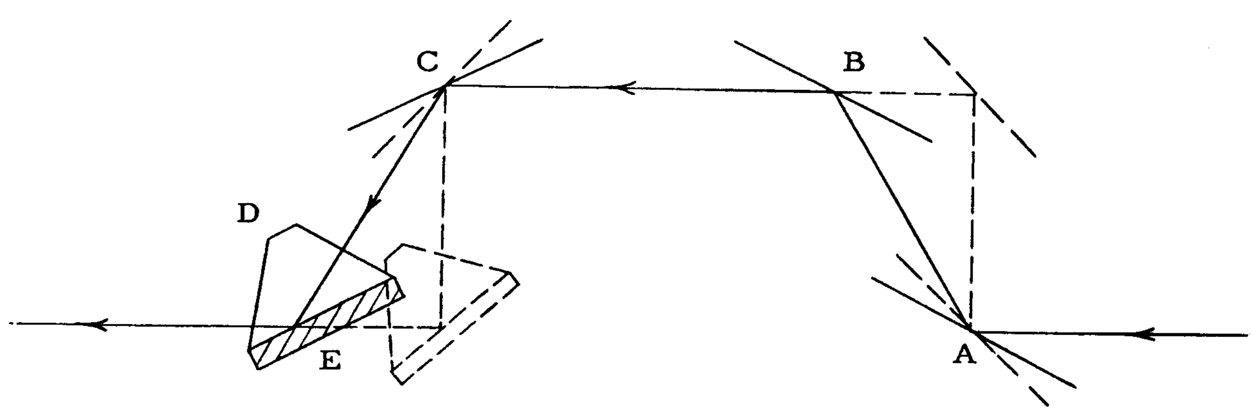

Figure 29

ATTENUATED TOTAL REFLECTANCE

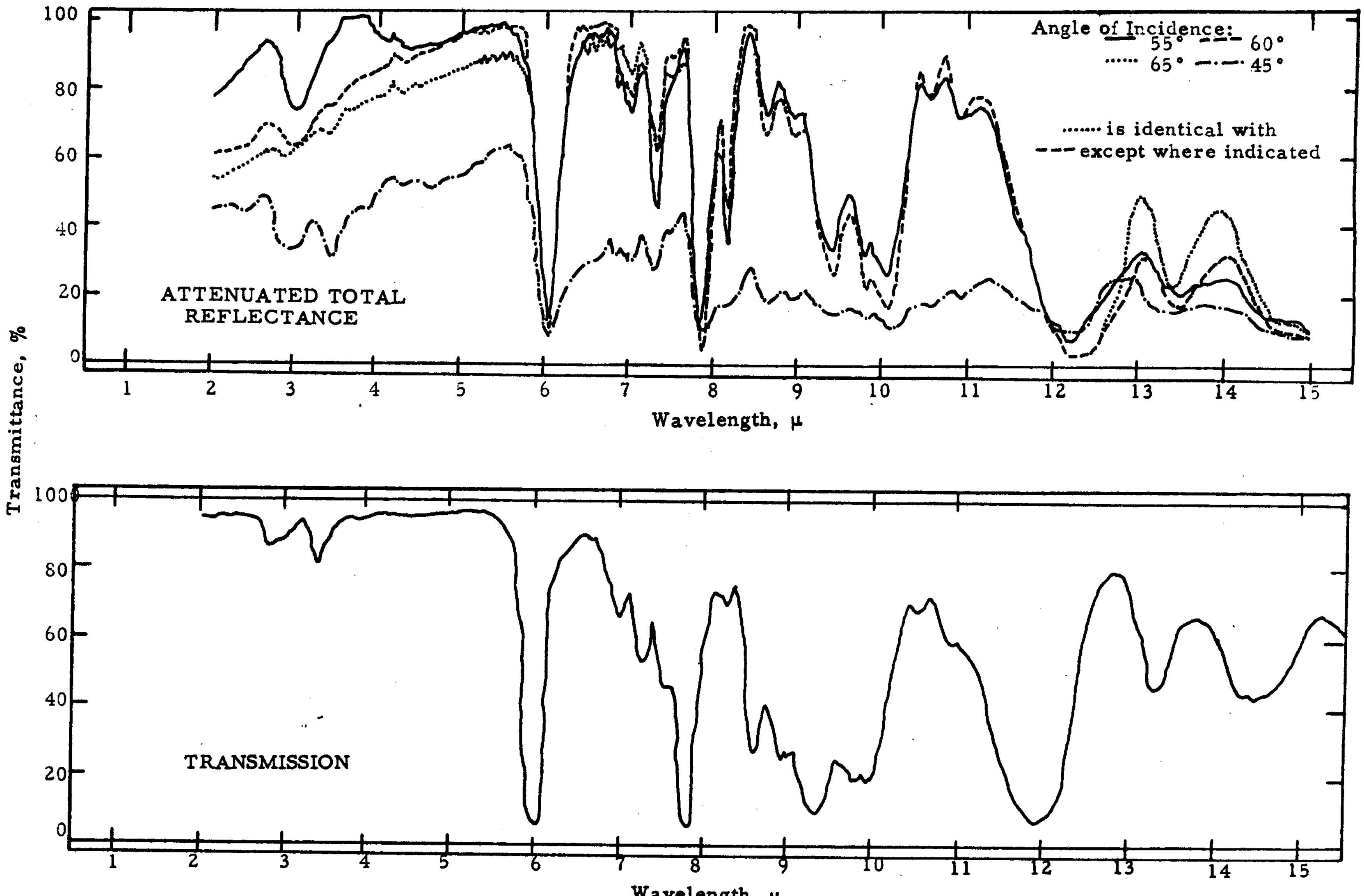

Figure 30

COMPARISON OF ATTENUATED-TOTAL-REFLECTANCE AND TRANSMISSION SPECTRA

2. Zinc Oxide

Studies of the basic mechanism of photolysis in zinc oxide are proceeding in two areas: (1) a method for analysis of interstitial Zn^+ and excess Zn^0 is being developed and (2) samples of zinc oxide are being photolyzed in vacuum for the analyses.

Two analytical methods are under consideration. One consists of dissolving the zinc oxide in hydrochloric acid in the presence of hydrogen iodide and a known quantity of iodine (in the form of a complex ion). The excess iodine, which is not reduced by the Zn^+ and Zn^0, is titrated. The other method, which we prefer, consists of dissolving the zinc oxide in hydrochloric acid in a vacuum system which is designed to measure the hydrogen evolved.[5] We have performed similar analyses before and have found such gas-measuring techniques to be accurate and sensitive. Hydrogen is one of the better gases for such a method because almost all other gases can be trapped at liquid nitrogen temperatures.

Disks of zinc oxide were prepared for optical reflectance measurements and chemical analysis. Plots of change in reflectance versus the quantity of photolysis products are expected to have radically different forms for different materials.

The determination of excess zinc in zinc oxide (nonstoichiometry) will be performed according to the method developed by Allsopp.[5] This method, being a chemical one, distinguishes itself by its directness of approach from optical and electrical methods, where certain assumptions are involved.

The sample to be analyzed is dissolved in hydrochloric acid under vacuum. By this means the solid zinc oxide is completely disintegrated, giving the

[5] Allsopp, W. E., Analyst, 82, 474, 1957.

excess metal the best possible opportunity to react with the acid and to form an equivalent amount of hydrogen. After solution, the acid is evaporated to ensure that all the evolved gas is released. Hydrochloric acid vapors are condensed in liquid nitrogen traps; dry hydrogen chloride is absorbed by soda-asbestos. The pressure of the evolved gas is measured by a Pirani gauge. Any oxygen present is allowed to react with hydrogen on a platinum filament at 600°C, and the drop in pressure is measured. The remaining hydrogen is diffused to the atmosphere through a palladium tube at 350°C, and the drop in pressure is again measured. The total hydrogen present is found from the two pressure changes, and the zinc equivalent is then calculated.

The apparatus consists essentially of two parts, a reaction system and an analytical system. A schematic diagram is shown in Figure 31. The reaction system consists of four bulbs, which can be cooled with liquid nitrogen. Bulb 1 is provided with a side arm to house the sample and a sealed glass tube filled with iron powder to act as a "pusher." Bulb 2 is provided with a side arm through which 50% (v/v) hydrochloric acid can be added. Both side arms are sealed with a torch after the sample, the pusher, and the acid are put into the system. The reaction vessels are connected to the main apparatus by a cone and socket joint, A, and then via a mercury-vapor cold trap, trap 1, and tap T_1 to a three-stage mercury diffusion pump, P_1. This pump transfers the gases evolved from the reaction vessels to a small analytical system containing a palladium tube, a platinum filament, a Pirani gauge, a soda-asbestos bulb, a McLeod gauge, and a cold trap, 2. The palladium tube, soda-asbestos bulb, McLeod gauge, and cold trap can be isolated from the analytical system by taps. A second mercury diffusion pump, P_2, is used to evacuate the whole system and is backed by a conventional rotary oil pump. When necessary, the reaction vessels can be directly evacuated by this backing pump via tap T_7.

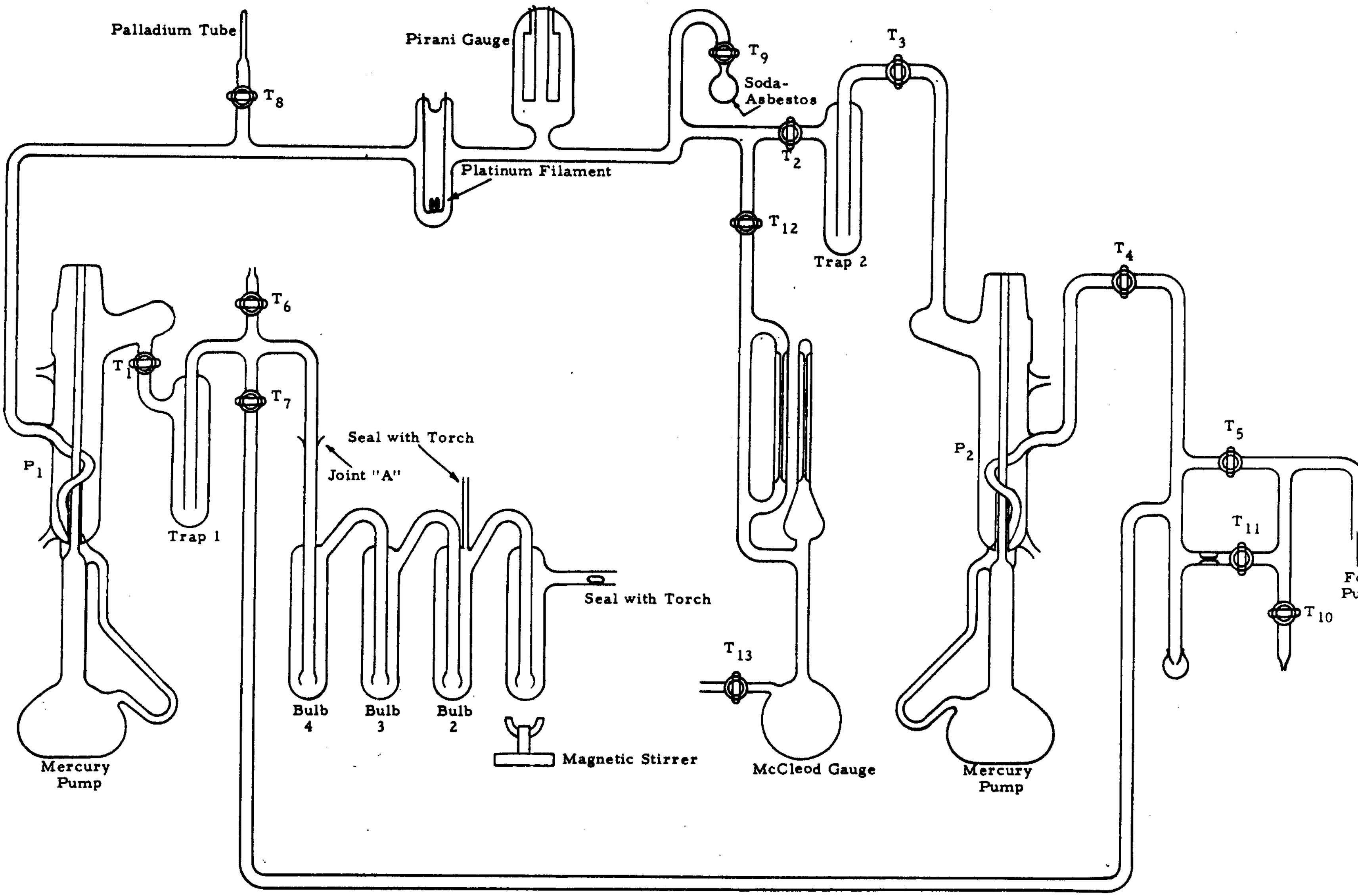

Figure 31

REACTION AND ANALYTICAL SYSTEM FOR DETERMINATION OF INTERSTITIAL Zn^+ AND EXCESS Zn^0 IN ZINC OXIDE

VI. SUMMARY AND FUTURE WORK

The studies conducted during this report period confirmed zinc oxide's exceptional resistance to ultraviolet irradiation in vacuum as well as its capacity to protect the medium in which it is dispersed. The inherent ultraviolet stability of the O-Si-O system was confirmed for both the inorganic potassium silicate and organometallic polydimethylsiloxane (or methyl silicone) zinc oxide systems. The limited search for other pigments did not unveil any material which might supplant zinc oxide. Possible substitutes may be zinc sulfide or stannic oxide, neither of which is as stable as zinc oxide. Investigations of these substitutes and other potentially stable systems will be continued.

Considerable emphasis was placed on the zinc oxide-potassium silicate paints. Their mechanical properties appear to be satisfactory, but their affinity to soiling is a problem. Future work will include efforts to overcome the soiling and cleaning problem, and application of the coatings on substrates other than aluminum will also be investigated. Of the variety of zinc oxides which were examined, New Jersey Zinc SP500 zinc oxide appears to be the most stable. Calcination of this material improves its ability to form a good inorganic paint but does not affect its stability.

Studies involving methyl silicone polymers as vehicles for zinc oxide showed that these resins tend to produce films with greater resistance to ultraviolet irradiation in vacuum than elastomeric materials, particularly at long exposures. Varying the Me/Si ratio affects physical properties and stability; at a lower Me/Si ratio both brittleness and stability increase. Studies with methyl silicone paints are proceeding along three lines: (1) characterization and purification of experimental resins, (2) determination of the effect of structure on ultraviolet stability and film properties, and (3) preparation of film-forming resins with the lowest possible Me/Si ratio.

Closer control of particle size and distribution may be beneficial in optimizing the physical properties of both the inorganic and organic coatings. The achievement of higher pigment concentrations may obviate the necessity for thick silicone coatings as well as decrease the degradation due to binder-rich layers. All these factors will be investigated in future work.

Spraying parameters will be studied in order to reduce variations in coatings. The effect of temperature on space stability will be investigated as will the extent to which the promising coatings obey photochemical reciprocity (in terms of change in solar absorptance).

Long-term space-simulation tests will be made as the final criterion for selection of paints. The construction of an ion-pump system and the use of a wide-angle thermopile have made possible longer, cleaner, and more accurately defined exposures to a simulated extraterrestrial ultraviolet environment.