Report No. IITRI-U6002-42
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

George C. Marshall Space Flight Center
National Aeronautics & Space Administration
Huntsville, Alabama

IIT RESEARCH INSTITUTE

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

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FOREWORD

This is Report No. IITRI-U6002-42 (Triannual Report) of IITRI Project U-6002, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." This report covers the period from January 20 through June 20, 1966. Previous Triannual Reports were issued on October 25, 1963; March 5, 1964; July 20, 1964; December 21, 1964; February 23, 1965; July 20, 1965; November 9, 1965 and February 21, 1966.

Major contributors to the program during this period include Gene A. Zerlaut, Project Leader; Dr. G. A. Rubin and William R. Logan, inorganic coatings and pigment studies; Noel D. Bennett, reflectance measurements and space simulation tests; and Wayne Ridenour and W. C. Courtney, design of new irradiation facilities. Dr. T. H. Meltzer, Manager of Polymer Research, provided administrative supervision. The work reported herein was performed under the technical direction of the Research Projects Laboratory of the George C. Marshall Space Flight Center with Daniel W. Gates acting as Project Manager.

Data are recorded in IITRI Logbooks C13423, C13736, C13802 and C14176.

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Respectfully submitted,
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ABSTRACT

The objective of the research reported herein is the development of thermal-control surface coatings which possess very low but stable ratios of solar absorptance (α_s) to infrared emittance (ϵ_H). The work reported consists of (1) completion of the heat-treatment studies of the double zirconium silicate pigments, (2) an investigation of the effect of heat treatment on potassium silicate-treated zinc oxide and silicone paints prepared therefrom, and (3) additional space simulation test involving in situ reflectance measurement capabilities.

Of the three double zirconium silicate pigments (i.e., calcium, magnesium and zinc), calcium zirconium silicate exhibits the best stability. In general, heat treatment of the double silicate paints after application increases stability whereas heat treatment of the pigment prior to incorporation in the vehicle decreases stability.

Heat treatment of the potassium silicate-treated zinc oxide prior to incorporation into the silicone elastomer has apparently eliminated the shelf problem of S-13G gellation.

Non-stoichiometric zinc titanate and zinc titanate-pigmented RTV-602 paints do not possess the oxygen-bleachable infrared degradation exhibited by zinc oxide and zinc oxide-pigmented RTV-602. Excellent stability to 500 ESH of ultraviolet in vacuum was achieved with a zinc titanate-RTV paint at 32% PVC. The solar absorptance of the paint prepared at 32% PVC was 0.14; that of a paint prepared at 43% PVC was 0.11.

Author

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DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

The general requirement under this contract is for the development of thermal-control surface coatings which possess very low but stable ratios of solar absorptance (α_s) to infrared emittance (ε_H). The program has been divided historically into three major phases: (1) inorganic technology, (2) silicone photolysis investigations, and (3) general coatings investigations.

The relative emphasis placed upon each of these three major tasks has varied during the course of the program in accordance with the urgency of the various problems elucidated by our investigations, as well as the availability of both funds and personnel. For example, the use of S-13 on the Saturn S-IV stages of the Pegasus spacecraft necessitated the urgent development of manufacturing scale-up procedures. Similarly, discovery of the oxygen-bleachable infrared degradation associated with zinc oxide photolysis necessitated the urgent examination and rectification of the problem as related to S-13.

These ancillary investigations have unavoidably diverted funds from the three major tasks outlined above. For example, it was necessary to temporarily suspend the silicone-photolysis studies during the past 8-month period as a consequence of the investigation of the infrared degradation of zinc oxide and the S-13-type coatings. Indeed, these studies have revealed the urgency for more sophisticated in situ measurements of the optical properties of thermal coatings materials; they have, along with the results of other investigators, also prompted the construction of "in situ" facilities at IITRI and elsewhere in the aerospace industry.

The work reported herein consists of (1) completion of the heat-treatment studies of the double zirconium silicate pigments, (2) an investigation of the effect of heat treatment on potassium silicate-treated zinc oxide and silicone paints prepared therefrom, and (3) additional space simulation tests involving in situ reflectance measurements. A funding lapse of approximately 10 weeks occurred in this report period. During this time we (1) completed the design and began fabrication of the IRIF (In Situ Reflectometer/Irradiation Facility), (2) designed an irradiation chamber aimed at the in situ measurement of total hemispherical emittance*, and (3) moved our entire thermal coatings facilities into new and larger laboratories.

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*Both the IRIF and the facility for measurement of hemispherical emittance in situ are being constructed with IITRI funds.

II. INORGANIC TECHNOLOGY

A. Zinc Oxide Paints

A series of potassium silicate-bonded zinc oxides were prepared from as-received, newly developed SP-500 zinc oxide (New Jersey Zinc). The average grain size for three lots varies as follows:

Sample	5221	5222	5223
Grain Size (Microns)	0.52	0.47	0.56

Table 1 shows the ultraviolet degradation of three Z-93 paints, also designated 5221, 5222 and 5223, prepared from the newly developed SP-500. This new material is heat treated at a temperature between 600 and 700°C for one hour, presumably in air.

Table 1

COMPARISON OF Z-93 PAINTS PREPARED FROM NEWLY DEVELOPED NJZ SP-500 ZINC OXIDE PIGMENTS (TEST Q-18 - 1650 ESH @ 7X)

		Solar Absorptance			
Sample No.	Exposure ESH	α_1	α_2	α_s	$\Delta\alpha_s$
5221	0	.076	.052	.128	
	1650	.101	.051	.152	.024
5222	0	.081	.060	.141	
	1650	.106	.059	.165	.024
5223	0	.091	.064	.155	
	1650	.112	.063	.175	.020

The change in solar absorptance is relatively high compared to values previously obtained on paints containing standard SP500 zinc oxide. Typical of the results is the $\Delta\alpha_s$ of -0.016 reported for specimen 7173 of Z93 reported in Table 1 of Triannual Report No. IITRI-U6002-31 (November 9, 1965).

B. The Double Zirconium Silicates

The results of test Q-19 on several double zirconium silicates are presented in Table 2. Of significance are the nearly identical increases in solar absorptance for duplicate specimens of both calcium and zinc zirconium silicate. This was observed for specimens which possessed greatly different initial solar absorptances (i.e., 0.136 and 0.092 for $CaZrSiO_5$ and 0.156 and 0.098 for $ZnZrSiO_5$). These specimens were powder compacts and the differences in initial solar absorptance are therefore not surprising.

The data from Table 2 was abstracted and used in Table 3 to compare with the results of other space-simulation tests. Examination of the compilation presented in Table 3 demonstrates that the solar absorptance, α_s, of unirradiated paints, as well as the change of solar absorptance due to irradiation, varies considerably with the heat treatment applied. It has previously been observed that a decrease in $\Delta\alpha_s$ due to temperature annealing of pigments or paints is combined with an increase in the solar absorptance of the unirradiated material, and vice versa, a decrease in α_s is combined with an increased $\Delta\alpha_s$. This trend

Table 2

EFFECT OF 2000 ESH EXPOSURE TO UV IRRADIATION IN VACUUM ON SEVERAL DOUBLE ZIRCONIUM SILICATES (TEST Q19 - 2000 ESH @ 8X)

Sample		Exposure		Solar Absorptance			
No.	Material	ESH	SF	α_1	α_2	α_s	$\Delta\alpha_s$
5230	$CaZrSiO_5$	0	0	.081	.055	.136	
	(Powder)	2000	8	.154	.062	.216	.080
5237	$CaZrSiO_5$	0	0	.072	.020	.092	
	(Powder)	2000	8	.151	.020	.171	.079
5231	$MgZrSiO_5$	0	0	.102	.065	.167	
	(Powder)	2000	8	.162	.065	.227	.060
5233	$ZnZrSiO_5$	0	0	.089	.067	.156	
	(Powder)	2000	8	.165	.075	.240	.084
5234	$ZnZrSiO_5$	0	0	.077	.021	.098	
	(Powder)	2000	8	.160	.024	.184	.086
5235	$CaZrSiO_5$	0	0	.083	.053	.136	
	(PS7-Paint)	2000	8	.183	.052	.235	.099
5236	$MgZrSiO_5$	0	0	.110	.066	.176	
	(PS7-Paint)	2000	8	.175	.066	.241	.065
5232	$ZnZrSiO_5$	0	0	.103	.083	.186	
	(PS7-Paint)	2000	8	.185	.077	.262	.076

Table 3

EFFECT OF TREATMENT ON UV-STABILITY OF DOUBLE ZIRCONIUM SILICATES

Material	Treatment*	Binder	α_s Non-Irradiated	$\Delta\alpha$ (ESH)
$ZnZrSiO_5$	A	None	.123	.058 (2000)
	B	None	.156	.084 (2000)
	C	PS7	.154	.097 (1000)
	D	PS7	.176	.104 (2650)
	E	PS7	.212	.032 (2000)
	F	PS7	.186	.076 (2000)
$CaZrSiO_5$	A	None	.115	.044 (2000)
	B	None	.136	.080 (2000)
	C	PS7	.165	.012 (1000)
	D	PS7	.138	.126 (2650)
	E	PS7	.178	.021 (2000)
	F	PS7	.136	.099 (2000)
$MgZrSiO_5$	A	None	.102	.058 (2000)
	B	None	.167	.060 (2000)
	C	PS7	.138	.067 (1000)
	D	PS7	.171	.064 (2650)
	E	PS7	.145	.032 (2000)
	F	PS7	.176	.065 (2000)

*Treatment:
A - As received, powder compact.
B - Heat treated 800°C/12 hr powder compact.
C - As received pigment, paint.
D - Pigment heat treated 800°C/12 hr, paint.
E - Pigment as received, paint heat treated 500°C/1 hr.
F - Pigment heat treated 800°C/12 hr, paint heat treated 500°C/1 hr.

however is not so obvious from the data of Table 3. These data indicate that annealing of the paint may cause a more significant improvement of the paint than calcination of the pigment alone. The calcination of the paint probably results in a better pigment-vehicle bond and thus in the formation of a more effective adsorption-desorption barrier with respect to the surface of the pigment particles. Calcination of the pigment powder on the other hand essentially reduces the surface free energy of the pigment and may give rise to an improved ultraviolet stability of powder compacts due to a lower concentration of surface defects. A lower surface free energy of the pigment powder however, may also result in a decreased chemical activity and consequently in a poorer pigment-vehicle bond in the paint with the resultant possibility of photoinduced desorption of gases from the pigment particles.

The following conclusions have been made from an examination of the compilation presented in Table 3:

1. Heat treatment of the double zirconium silicate powders increases $\Delta\alpha$. This might be due to "fresh" surfaces which are created in "breaking" the powder after the heat treatment. The largest increase in $\Delta\alpha$ occurred with $CaZrSiO_5$ which has the lowest MP and thus would "sinter" at lower temperatures than the other two zirconium silicates.

2. The paints tend to be less table than the pigment alone except for $CaZrSiO_5$. The $CaZrSiO_5$ paint may exhibit a better bond between the pigment and vehicle.

3. In general, pigments heat-treated prior to paint preparation, except for $MgZrSiO_5$, exhibited inferior stability to paint heat-treated after application.

4. Except for $CaZrSiO_5$, heat-treatment of the paint increases stability. Heat treatment of the paints (using non-heat-treated pigment) has the most favorable effect on $\Delta\alpha$.

C. General

Specimens of inorganic potassium silicate-based paints which were prepared at NASA's Goddard Space Flight Center were furnished by the Project Manager. They were irradiated in Test Q-18 for 1650 ESH at a solar factor of 7X. The results are presented in Table 4.

Table 4

PERFORMANCE OF GODDARD SPACE FLIGHT CENTER THERMAL CONTROL PAINTS AT 1650 ESH

			Solar Absorptance			
Sample No.	Pigment/Binder	Exposure ESH	α_1	α_2	α_s	$\Delta\alpha_s$
5218 CM-114	α-Al_2O_3/K-SiL	0 1650	.095 .174	.126 .120	.221 .294	 .073
5219 CM-118	ZnO/K-SiL	0 1650	.096 .129	.092 .094	.188 .223	 .035
5220 CM-119	r-TiO_2/K-SiL	0 1650	.115 .174	.102 .101	.217 .275	 .058

III. METHYL SILICONE PAINTS AND MISCELLANEOUS SPECIMENS

A. Post Exposure Evaluation of S-13-type Paints

The development of the modified S-13 paint systems employing silicate-treated zinc oxide has been continued in efforts to compare the protective effects of various modifications and treatments and to determine the problems inherent in these treatments. The results of ultraviolet-irradiation in vacuum on three modified S-13 paint systems are presented in Table 5.

Table 5

EFFECT OF UV IRRADIATION IN VACUUM ON
S-13G AND S-13H (TEST Q-18 & Q-19)

		Exposure		Solar Absorptance*			
Specimen	Material	ESH	Solar Factor	α_1	α_2	α_s	$\Delta\alpha_s$
5215	S-13G	0	0	.105	.107	.213	
		1650	7	.158	.111	.269	.056
5228	S-13G	0	0	.095	.092	.187	
		2000	8	.111	.092	.203	.016
5216	S-13H	0	0	.091	.081	.172	
		1650	7	.139	.081	.220	.048
5229	S-13H	0	0	.089	.072	.162	
		2000	8	.104	.072	.176	.014
5217	S-13L	0	0	.109	.100	.209	
		1650	7	.187	.102	.289	.080

*Obtained by post-exposure measurements.

These specimens were irradiated in Test Q-18 and Q-19 for 1650 ESH at 7X and 2000 ESH at 8X, respectively. All samples were maintained at 50°F during irradiation. The silicate-modified S-13 (G and H) specimens irradiated in Test Q-18 were much more severely degraded in 1650 ESH than in Test Q-19 for a longer exposure of 2000 ESH. Whether the entire test was more severe than the lamp monitoring indicated, or whether the severity was due to the inadvertant addition of too much SRC-05 catalyst to the three RTV-602 specimens has not been determined; we suspect the latter reason at this time. In both tests, however, the S-13G modification (standard S-13 pigmented with PS-7-treated SP-500 zinc oxide) was slightly inferior in both solar absorptance, α_s, and $\Delta\alpha_s$ to the more highly pigmented S-13H (RTV-602 pigmented at 40% PVC with PS-7-treated SP-500 zinc oxide). On the other hand, S-13L, which is the S-13 formulation prepared from 0.1% lithium doped SP-500 zinc oxide pigment, was clearly inferior to S-13G and S-13H.

B. In Situ Space-Simulation Testing

Specimens of S-13G, S-13H, Z93 and Zn_2TiO_4 (A-54-2 powder obtained from New Jersey Zinc) were irradiated in the facility for making in situ reflectance determinations. This equipment was described in Figures 1 and 2 of Triannual Report IITRI-U6002-36 (February 21, 1966). The reflectance was measured as optical density, O.D., and the data are tabulated in Table 6. The negative ΔO.D. values at 2.0μ wavelength for Z93 are attributed to

Table 6

RESULTS OF 2400 ESH *IN SITU* SPACE SIMULATION TEST
(TEST I-1)

Sample No.	Material	Exposure ESH	ΔO.D. (Reflectance)[1]			
			0.4μ	0.7μ	1.0μ	2.0μ
5240	S-13H	225	.006	.000	.000	.010
		350	.006	.010	.040	.003
		550	.006	.000	.030	.003
		825	.016	.000	.030	.003
		2400	.036	.005	.024	.013
		ATMO	.036	.005	.008	.003
5241	S-13G	225	.000	.000	.005	.015
		350	.010	.005	.015	.020
		550	.005	.015	.008	.005
		825	.010	.010	.020	.020
		2400	.020	.010	.024	.040
		ATMO	.020	.010	.004	.020
5242	Z-93	225	.000	.000	.005	+.005[2]
		350	.008	.000	.002	-.022
		550	.000	.008	.000	-.032
		825	.005	.008	.000	-.048
		2400	.040	.008	.007	+.015
		ATMO	.032	.006	.007	+.050
5243	Zn_2TiO_4 (Powder)	225	.005[3]	.000	.000	-
		350	.015	.000	-	-
		550	.025	.000	.000	.000[2]
		825	.030	.000	.000	.000
		2400	.050	.000	.000	.000
		ATMO	.040	.000	.000	.000

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[1] Compared to MgO.

[2] ΔO.D. determined for 2.5μ wavelength.

[3] ΔO.D. determined for 0.35μ wavelength.

a loss of water during the test; likewise the positive ΔO.D. on admission of air is attributed to the readsorption of water. The data in Table 6 has uncertainties due to the fact that the measurements were performed through a window. (The uncertainties are ± 0.005 O.D. units for S-13H and ± 0.010, ± 0.008 and ± 0.003 for S-13G, Z93 and Zn_2TiO_4 powder, respectively.) The ΔO.D. values are given for four wavelengths after 225, 350, 550, 825, and 2400 ESH as well as for a minimum of 30 minutes after admission of air to the irradiation chamber.

The data in Table 3 was used to compute the normalized reflectance corresponding to each ΔO.D. value. This was performed from the relation

$$\Delta\text{O.D.} = \log_{10}\left(\frac{R_o}{R_s}\right)_{UV} - \log_{10}\left(\frac{R_o}{R_s}\right)_i .$$

Normalized reflectance values were determined for 0 and 2400 ESH and for the reflectance after admission of air, only. These data are presented in Table 7. The reflectance values for S-13 after exposure to 1200 ESH are also shown in Table 7 for comparison.

Examination of the data presented in Table 7 indicates that the oxygen-bleachable infrared degradation has indeed been precluded by the silicate treatment of zinc oxide that is manifest in the S-13G and S-13H formulations. The specimen of Z93 also appears to be stable in the infrared region, as would be expected from the data and conclusions presented in Triannual Report IITRI-

Table 7

NORMALIZED REFLECTANCE COMPUTED FROM TABLE 3

Material	Exposure ESH	Normalized Spectral Reflectance $R_{.4\mu}$	$\Delta R_{.4\mu}$	$R_{.7\mu}$	$\Delta R_{.7\mu}$	$R_{1\mu}$	$\Delta R_{1\mu}$	$R_{2\mu}$	$\Delta R_{2\mu}$
S-13	0	77.0	-	94.5	-	91.5	-	82.5	-
	1200	67.0	10.0	93.5	1.0	88.2	3.3	54.5	28.0
	ATMO	67.0	10.0	93.5	1.0	90.8	0.7	81.0	1.5
S-13G	0	75.0	-	95.0	-	93.0	-	76.0	-
	2400	71.8	3.2	93.2	2.8	88.0	5.0	69.3	6.7
	ATMO	71.8	3.2	93.2	2.8	92.0	1.0	72.3	3.7
S-13H	0	76.0	-	94.5	-	95.6	-	80.5	-
	2400	71.0	5.0	93.3	1.2	90.5	4.1	78.0	2.5
	ATMO	71.0	5.0	93.3	1.2	93.5	2.1	80.0	0.5
Z93	0	75.0	-	93.0	-	93.5	-	71.5[1]	-
	2400	68.2	6.8	90.8	2.2	92.0	1.5	69.0	2.5
	ATMO	69.8	5.2	91.5	1.5	92.0	1.5	64.0	7.5
Zn_2TiO_4	0	72.0[2]	-	93.0	-	91.0	-	97.5[1]	-
	2400	64.0	8.0	93.0	0.0	91.0	0.0	97.5	0.0
	ATMO	65.2	6.8	93.0	0.0	91.0	0.0	97.5	0.0

[1] Reflectance at 2.5μ.

[2] Reflectance at 0.35μ.

U6002-36 (February 21, 1966). Of particular significance is the fact that the A-54-2 zinc titanate, Zn_2TiO_4, does not exhibit the infrared-degradation phenomenon associated with zinc oxides. The excellent optical properties and the fact that the loss in reflectance was only 8% at 0.4μ wavelength after 2400 ESH make this pigment an excellent candidate for more concentrated studies.

* * * * * * *

Because of the rather general plans to use S-13 on current hardware, the elucidation of S-13's bleachable-infrared degradation created a number of problems for those organizations committed to the use of S-13. IIT Research Institute immediately made S-13G available to the industry in small quantities at cost in order to help alleviate the problem created by S-13's infrared anomally. We accordingly initiated studies to scale-up the preparation of S-13G and H from half-pint laboratory batches to ½- to 1-gallon batches. Storage of control cans quickly indicated the silicate-treated pigment's propensity to settle into a redispersable cake, however.

It was subsequently learned that cans of S-13G either gelled in transit or soon after arrival at their destination -- although control samples of the liquid paints did not gell nearly as quickly as those shipped long distances. It was concluded that the gellation was due to a base-catalyzed polymerization of the RTV-602 silicone by the residual potassium "alkali" silicate from the treatment of the SP-500 zinc oxide. The neutralization of the basic character of the residual alkali silicate was therefore suggested. Since acid neutralization would have necessitated considerable washing to remove all the chloride, which has previously been found to be detrimental to stability, heat-treatment of the PS7-treated zinc oxide was chosen as a first course of action.

The heat-treated pigment was prepared as follows. Approximately 600 gms of SP500 zinc oxide were treated with PS7 potassium silicate in the usual manner. The pigment was divided into quarters with three portions heated at 500°F for 4 hours, 500°F for 16 hours and 700°F for 8 hours, respectively. Paints were prepared from each of these pigments and are designated S-13T1, S-13T2 and S-13T3, respectively. They were formulated on March 29, 1966. None of the three new formulations have exhibited silicone gelation as of July 11, 1966. A control paint prepared from the un-heat-treated silicate-treated zinc oxide has thoroughly gelled in the same period. The three formulations, T1, T2 and T3, have exhibited pigment settling; the pigment cake is easily redispersable, however.

Specimens of S-13T1, S-13T2 and S-13T3 were irradiated in Tests I-2 and I-3 utilizing the facility for making <u>in situ</u> reflectance measurements described earlier. Specimens of S-13, S-13G and a Zn_2TiO_4-pigmented RTV-602 (32% PVC) were also irradiated in these tests. The reflectance was measured as differential reflectance in an optical density mode and ΔO.D. was recorded directly by the Beckman DK-2A spectroreflectometer.

The data for these two tests are presented in Table 8. Because differential plots were obtained rather than optical density versus an MgO standard, as was the case in Test I-1, less scatter and uncertainty in the data was noted. The errors associated with making such measurements through a thick window are still the principle source of uncertainty, however.

The data in Table 8 was used to compute the normalized reflectance corresponding to each ΔO.D. value, just as was done for the data presented in Table 6. The results of the tests tabulated in Table 9 confirm the fact that the oxygen-bleachable infrared degradation of S-13 essentially can be eliminated by treatment of the SP-500 zinc oxide pigment with potassium silicate prior to incorporation into the silicone elastomer. Furthermore, the heat treatment of the silicate-treated zinc oxide prior to incorporation into the silicone appears to have improved the stability in the visible region at little or no expense to the behavior in the infrared region. The three coatings based on heat-treated pigment did suffer a slight, permanent decrease in reflectance at 2.0-μ wavelength, however. The reasons for this behavior are not known and more work is contemplated in the near future on the general subject of zinc oxide protection by potassium silicate treatment. The stability of the non-stoichiometric zinc titanate-pigmented RTV-602 was especially gratifying. An increase in reflectance at 2.0μ for this paint was recorded; no reason can be advanced at this time and additional tests are planned.

Table 8

RESULTS OF 500 ESH IN SITU SPACE SIMULATION TEST (TESTS I-2 AND I-3)

Sample No.	Material	Test	ΔO.D. (Reflectance)*			
			0.4μ	0.7μ	1.0μ	2.0μ
-	S-13	I-2	.018	.000	.000	.210
-	S-13	I-3	.018	.000	.020	.190
-	S-13G	I-2	.018	.000	.000	.008
5-13-6**	S-13G	I-3	.032	.000	.000	-.005
5246	S-13T1	I-3	.035	.000	.000	.010
5247	S-13T2	I-2	.014	.000	.000	.020
5248	S-13T3	I-2	.020	.000	.000	.020
-	Zn_2TiO_4***	I-3	.018	.000	.000	-.020

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*Obtained by differential reflectance techniques in the optical density mode using a control specimen of each sample as reference.

**Batch 5-13-6 was prepared from 2000 grams of PS-7-treated SP-500 zinc oxide.

***Prepared in RTV-602 at 32% PVC.

Table 9

NORMALIZED REFLECTANCE CHANGES COMPUTED FROM TABLE 8

			Normalized							
Material	Test	Exposure ESH	$R_{.4\mu}$	$\Delta R_{.4\mu}$	$R_{.7\mu}$	$\Delta R_{.7\mu}$	$R_{1\mu}$	$\Delta R_{1\mu}$	$R_{2\mu}$	$\Delta R_{2\mu}$
S-13	I-2	0	79.5	-	93.8	-	90.5	-	82.0	-
		500	76.5	3.0	93.8	0.0	90.5	0.0	50.6	31.4
S-13	I-3	0	81.0	-	94.0	-	90.0	-	73.5	-
		500	78.0	3.0	94.0	0.0	86.0	4.0	47.5	26.0
S-13G	I-2	0	76.0	-	91.8	-	89.3	-	78.6	-
		500	72.9	3.1	91.8	0.0	89.3	0.0	77.1	1.5
S-13G (5-13-66)	I-3	0	78.2	-	88.0	-	84.0	-	71.5	-
		500	73.0	5.1	88.0	0.0	84.0	0.0	72.3	+0.8
S-13T1 (500°F/4 hr)	I-3	0	88.0	-	93.0	-	88.5	-	76.8	-
		500	81.2	6.8	93.0	0.0	88.5	0.0	75.0	1.8
S-13T2 (500°F/16 hr)	I-2	0	85.5	-	94.0	-	90.0	-	76.7	-
		500	82.5	3.0	94.0	0.0	90.0	0.0	73.8	3.0
S-13T3 (700°F/8 hr)	I-2	0	85.5	-	93.0	-	88.5	-	77.0	-
		500	81.5	4.0	93.0	0.0	88.5	0.0	74.0	3.0
Zn_2TiO_4/ RTV-602	I-3	0	87.8	-	90.6	-	90.4	-	85.2	-
		500	84.2	3.6	90.6	0.0	90.4	0.0	89.0	+3.8

The optical data generated in Test I-3 are presented in Figures 1 through 6. Figure 1 shows the increase in optical density on irradiation as a function of wavelength. The plots were obtained as differential spectra by using control specimens of the sample in the reference beam. An initial spectra is required since the reflectance of the unirradiated specimen and that of the reference are seldom identical at all wavelengths. In addition, the fact that the specimen to be irradiated is measured through a quartz window tends to magnify the differences; indeed, Fresnel reflection from the window may account for the sudden decrease in O.D. observed at 3875 A, the region where zinc oxide begins to absorb almost totally. (The reference would therefore be considerably more absorptive below the absorption edge of zinc oxide.) Examination of the curves show that the absorption band generated commences at 7000 A and gradually increases with increasing wavelength.

Figures 2 and 3 are similar plots for S-13G and S-13Tl. The degradation at the zinc oxide adsorption edge, which is presumably the result of vehicular coloration, is shown clearly in these data.

Figure 4 is a plot of optical density before and after irradiation for the A-54-2 zinc titanate-pigmented RTV-602 paint. The graph shows the long wavelength tail of an absorption band in the ultraviolet at the wavelength limit of the test, i.e., 3375 A. Also, the increase in reflectance in the infrared on

S-13

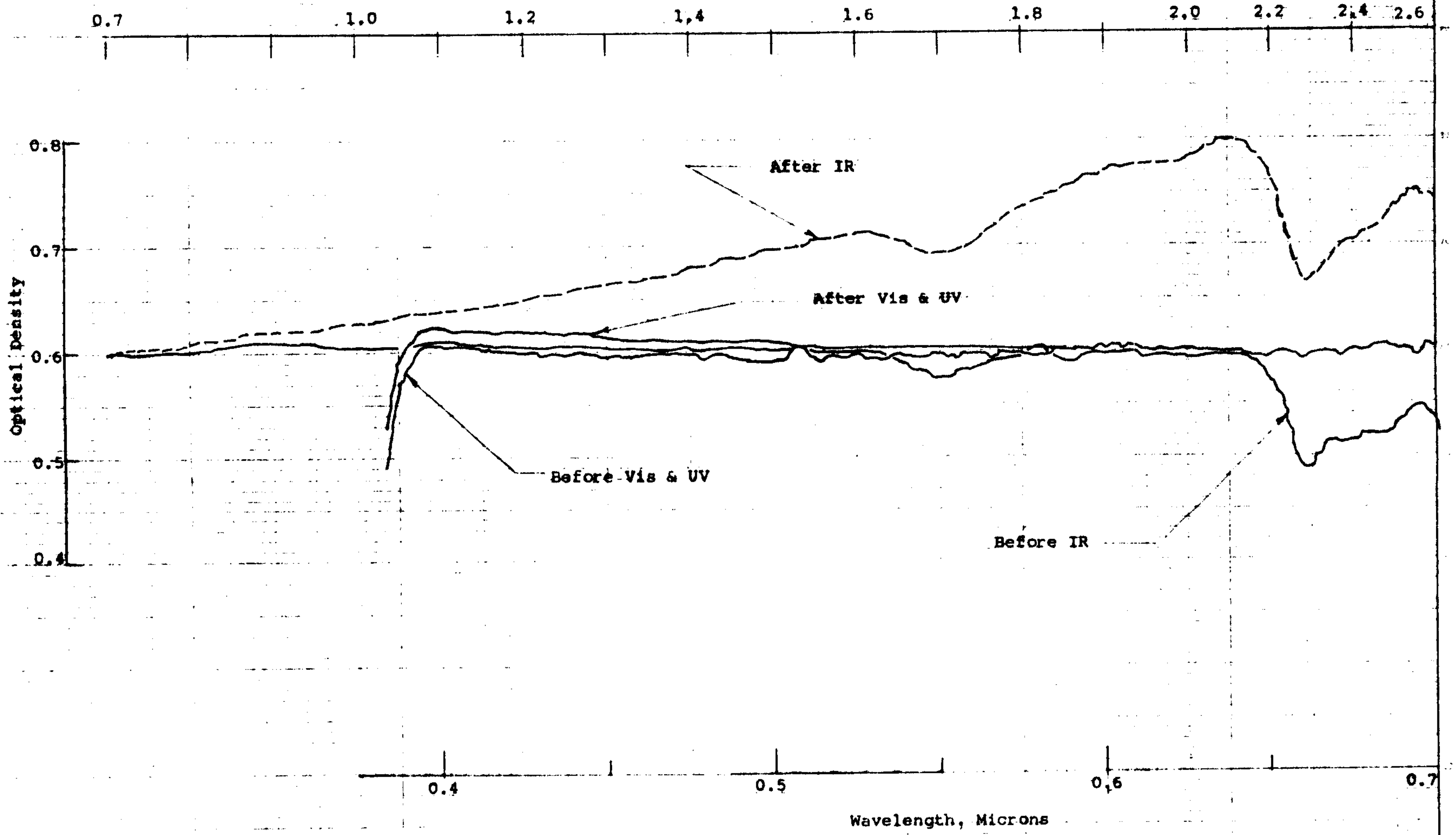

Figure 1

REFLECTANCE (AS OPTICAL DENSITY) OF S-13 BEFORE AND AFTER 500 ESH UV IRRADIATION IN VACUUM

S-13G Fig 2

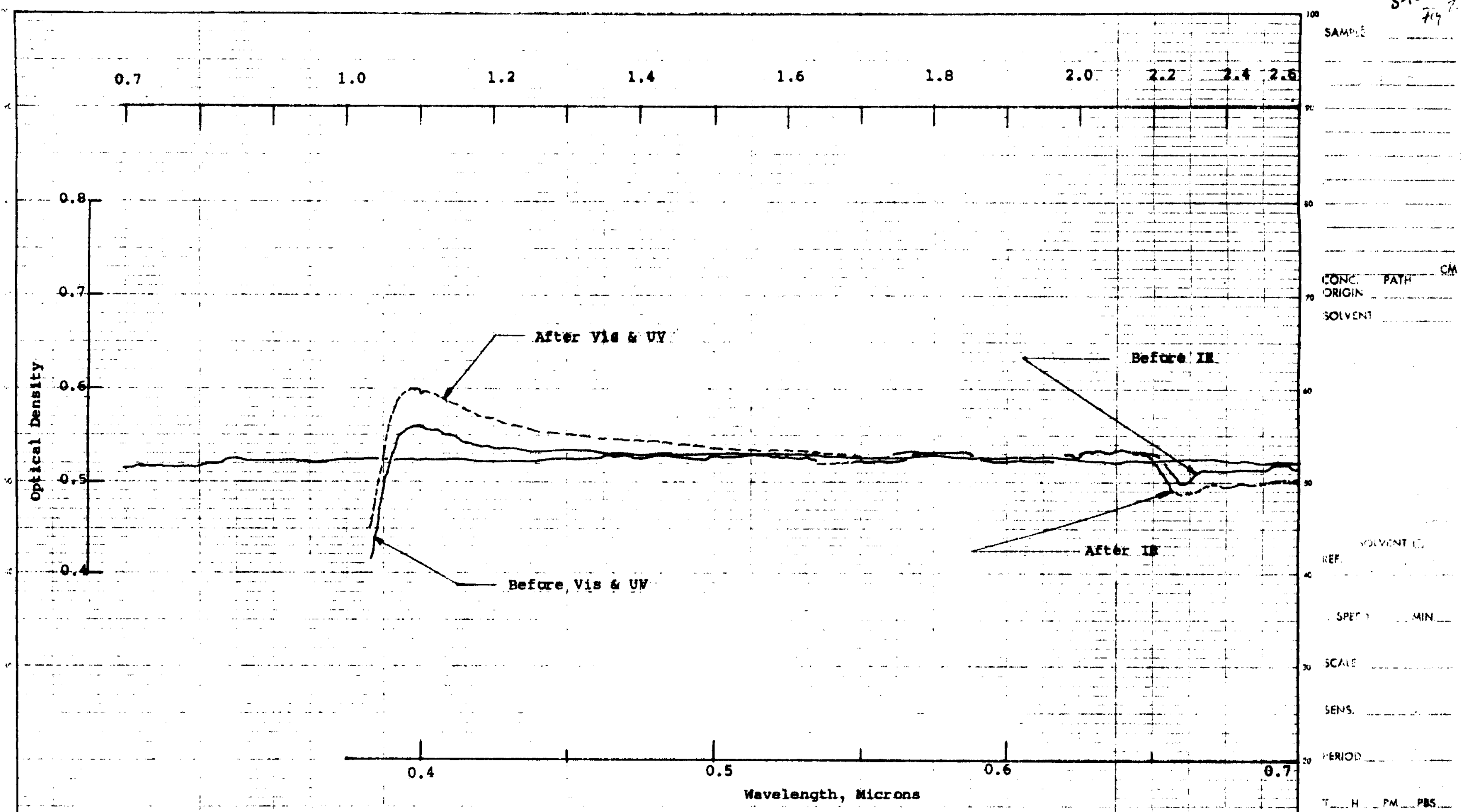

Figure 2

REFLECTANCE (AS OPTICAL DENSITY) OF S-13G BEFORE AND AFTER 500 ESH UV IRRADIATION IN VACUUM

5246

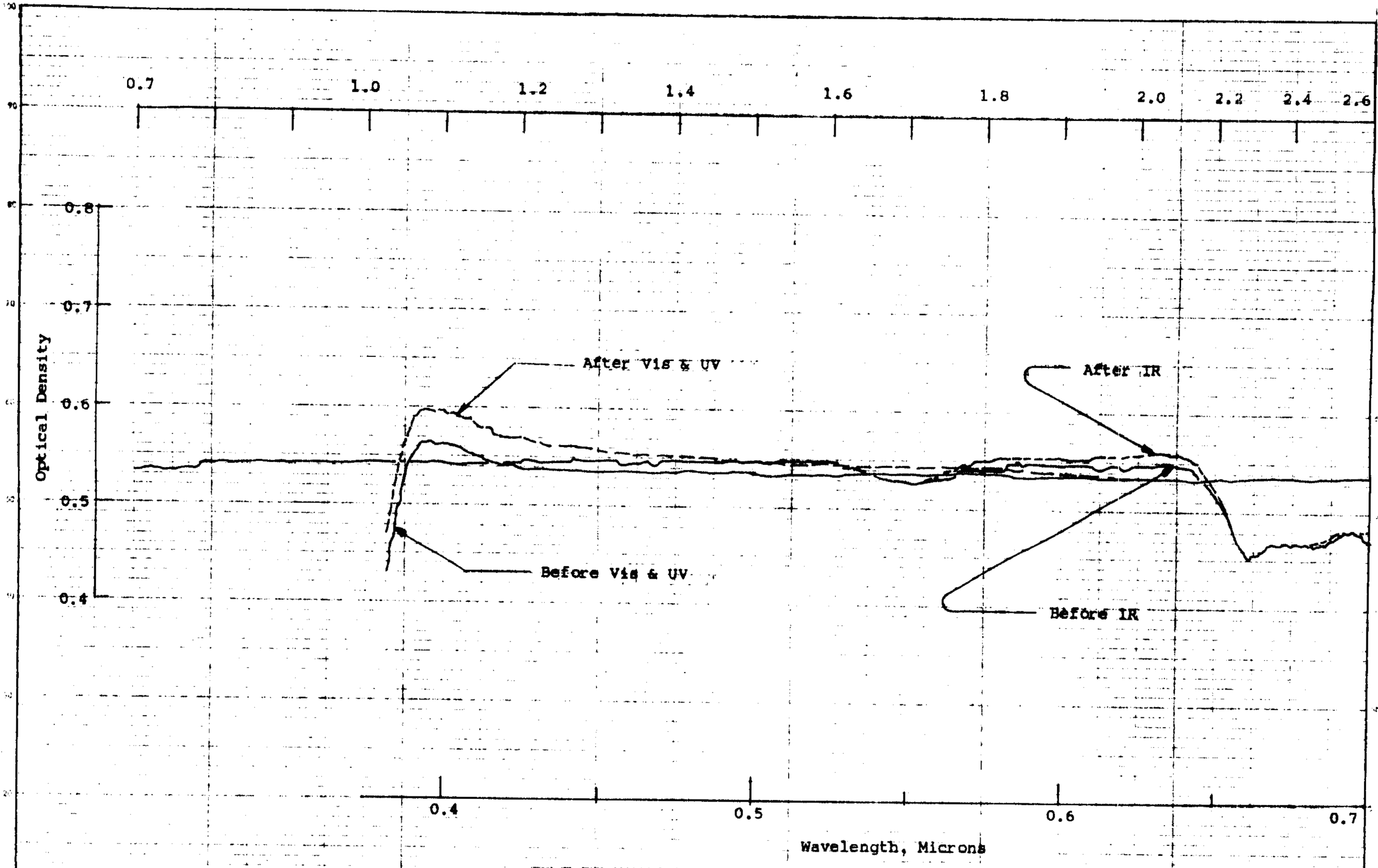

Figure 3

REFLECTANCE (AS OPTICAL DENSITY) OF S-13T1 BEFORE AND AFTER 500 ESH UV IRRADIATION IN VACUUM

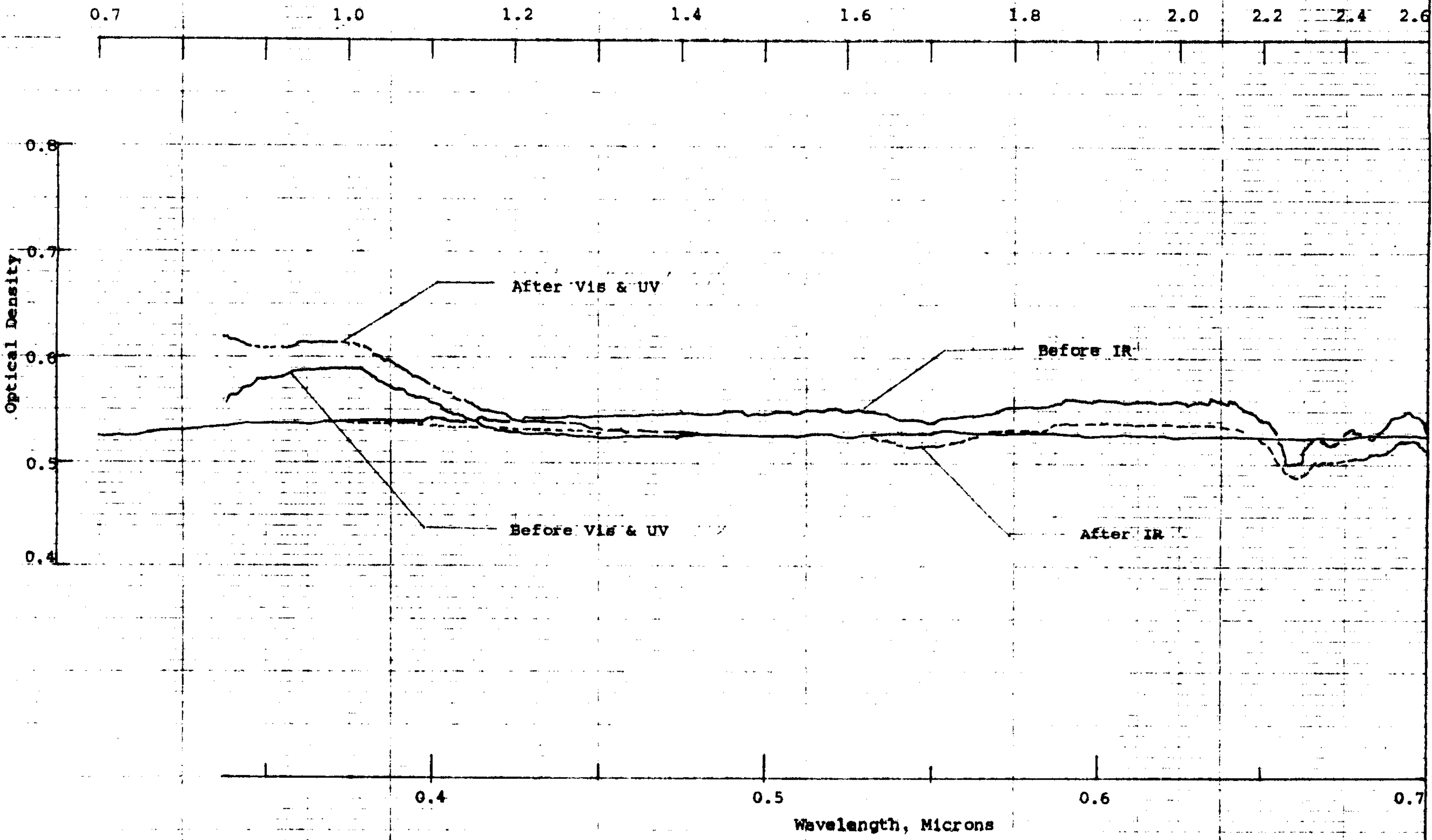

Figure 4

REFLECTANCE (AS OPTICAL DENSITY) OF A Zn_2TiO_4/RTV PAINT BEFORE AND AFTER 500 ESH UV IRRADIATION IN VACUUM

$ZnTiO_2$

SAMPLE 7-4

CONC. PATH CM
ORIGIN
SOLVENT

SOLVENT
REF.

λ SPEED MIN

SCALE

TENS

PERIOD

H PM PBS

ANALYST

DATE

irradiation is clearly shown by the decrease in optical density in that region. Figure 5 is a plot of the reflectance of the titanate paint before and after irradiation (measured versus magnesium oxide). The "after" curve was obtained by post exposure measurements. It will be noted that these curves do not agree with the calculated $\Delta R\lambda$'s that are presented in Table 9. This is due to the fact that two different MgO standards were used for each of the two measurements since the standards are prepared fresh each day; they are in turn compared to a calibrated Vitrolite primary standard. (It is noted that the Vitrolite values are used in the computer program used to obtain absolute reflectance and solar absorptance.) Curve C in Figure 5 is the reflectance of a zinc titanate-pigmented RTV-602 at a higher PVC of 43%. A rough calculation of the solar absorptance gave a value of 0.11 for this coating.

Figure 6 is a plot of the absolute reflectance of the 32% PVC zinc titanate/RTV-602 paint made on the Edwards-type integrating sphere constructed at IITRI. The solar absorptance of this coating was determined to be 0.14.

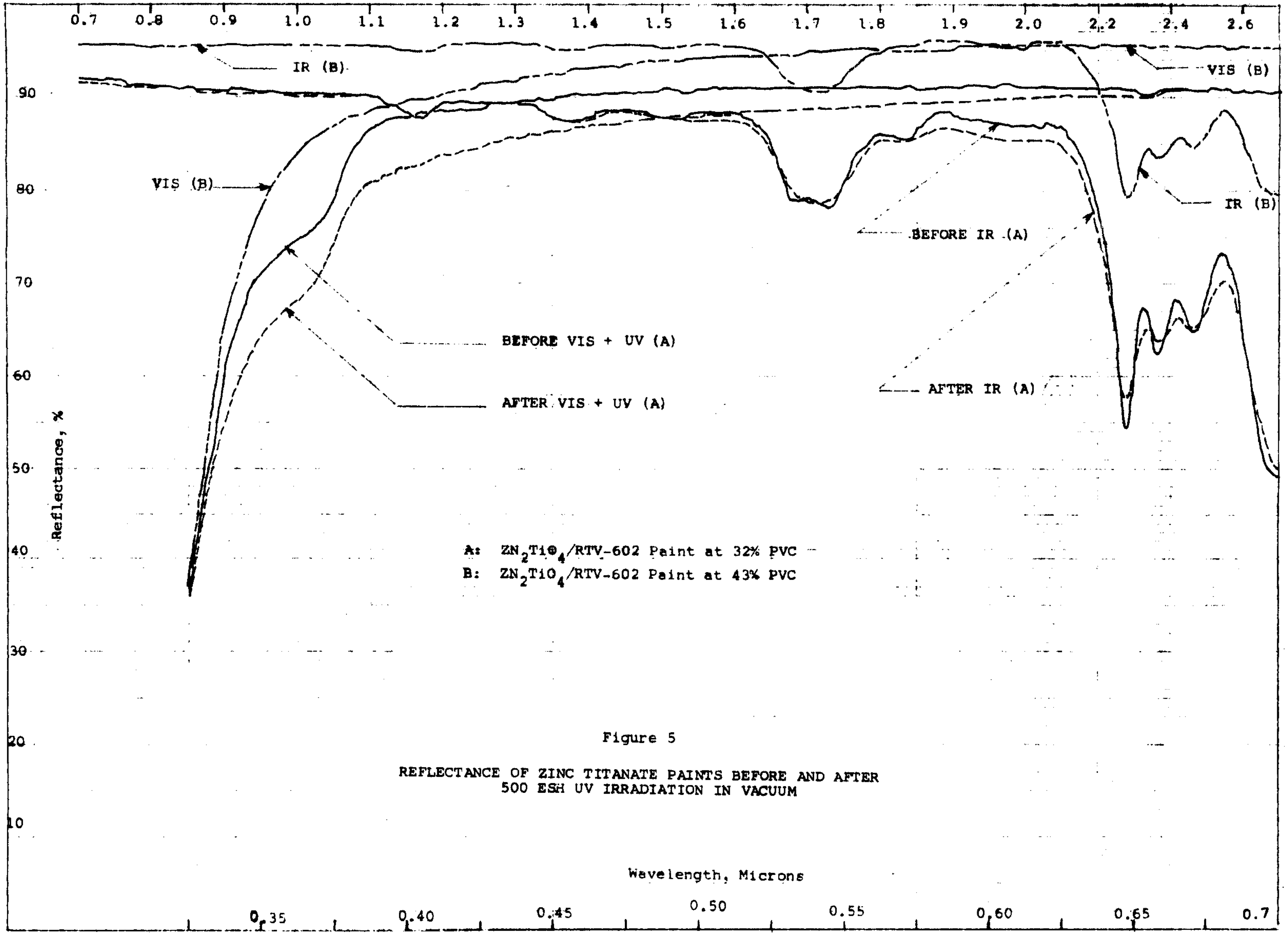

Figure 5

REFLECTANCE OF ZINC TITANATE PAINTS BEFORE AND AFTER 500 ESH UV IRRADIATION IN VACUUM

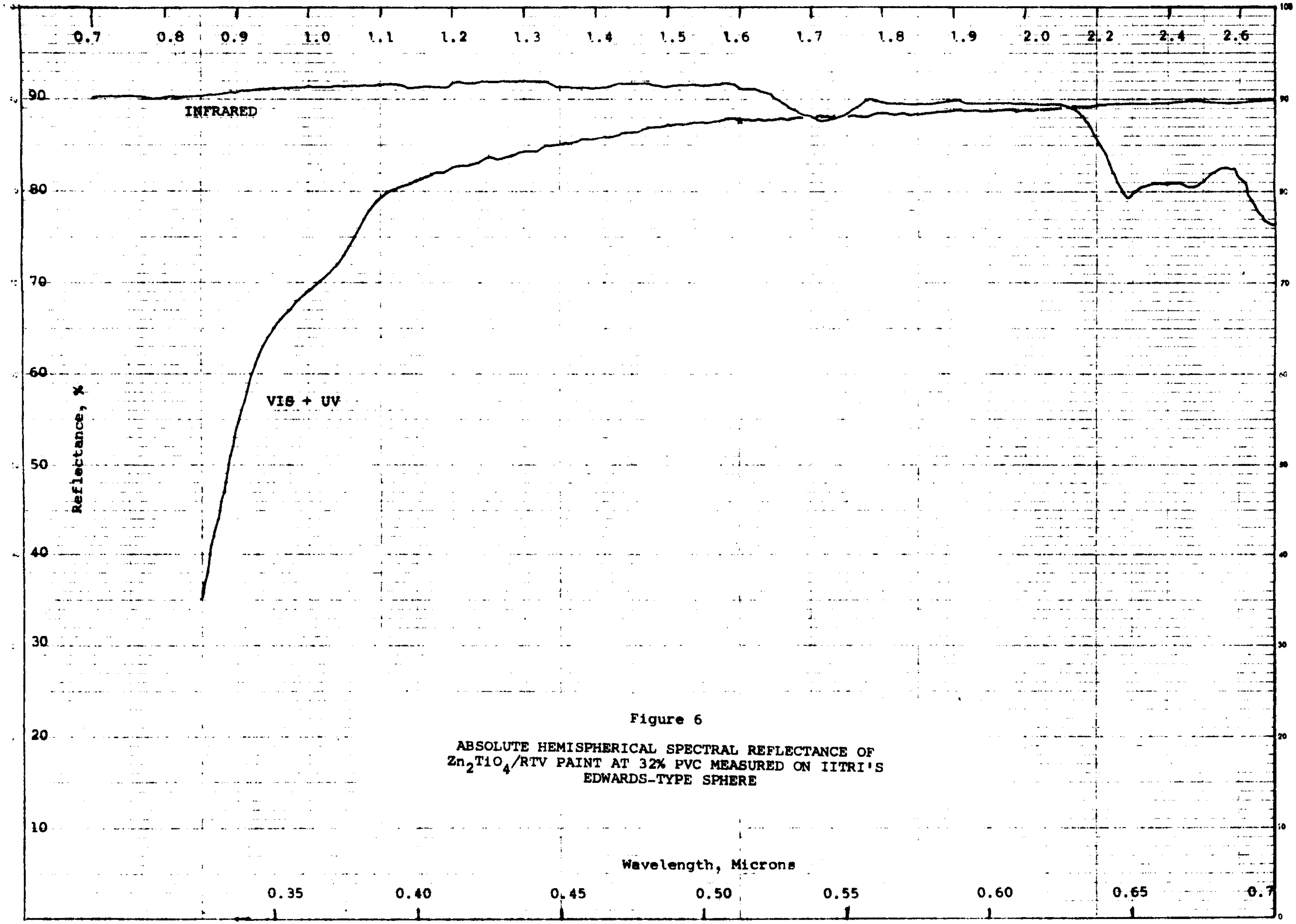

Figure 6

ABSOLUTE HEMISPHERICAL SPECTRAL REFLECTANCE OF Zn_2TiO_4/RTV PAINT AT 32% PVC MEASURED ON IITRI'S EDWARDS-TYPE SPHERE

SAMPLE Fig 6

Zn_2TiO_4/RTV
@ 32% PVC

CONC. PATH CM
ORIGIN
SOLVENT

$\alpha_s = 0.14$

SOLVENT ☐
REF. Absolute

SPEED MIN
SCALE
SENS.
PERIOD
T H PM PBS
ANALYST
DATE

IV. OTHER STUDIES

A. In Situ Reflectometer/Irradiation Facility (IRIF)

The construction of a multiple-sample ultraviolet-simulation facility with *in situ* hemispherical-spectral-reflectance-measurement capabilities has been 90% completed. A schematic of the facility was presented as Figure 12 of the last Triannual Report (IITRI-U6002-36). It is planned that the facility will be used for initial tests of all coatings and for all pigment screening studies. It will also be used to prepare comprehensive degradation rate information on all promising thermal-control coatings.

B. Methyl Silicone Photolysis

The new photolysis train will be attached to the Hitachi RMU-6D mass spectrometer during the month of July. Photolysis studies will commence in early August and it is intended to greatly emphasis this phase of the program in order to complete these studies within 6 months. Indeed, the general coatings studies involving the IRIF and the silicone photolysis investigation will receive primary emphasis during the current 6-month funding period.

V. CONCLUSIONS

The data presented in this report greatly supports the concept that the stability of a given pigment/binder system is a strong function of the degree to which the pigment is encapsulated, i.e., the intimacy of the pigment-binder interface. While for zinc oxide this may be due to the orthosilicate reaction product, the stability is probably to a large extent dependent upon the degree to which the binder inhibits diffusion and adsorption at the interface. Not only has this been shown to be true for the so called "infrared anomally", but the improvement in the stability at visible wavelengths (i.e., at about 4000 A) afforded by the potassium silicate treatment of zinc oxide is of considerable significance, if real. Indeed, these observations appear to be analogous to the excellent stability exhibited by vitreous enamel, in which case the reprecipitated microcrystalline opacifier is most certainly protected by a dense, rigid diffusion barrier!

Heat treatment of the double zirconium silicate powders decreases stability -- presumably due to "fresh" surfaces which are created in grinding the powder after the heat treatment. Of the three double zirconium silicates -- zinc, magnesium and calcium -- calcium zirconium silicate suffered the greater decrease to stability on heat treating. In general, the heat treatment of the paint after application increases stability whereas heat treatment of the pigment prior to paint preparation decreases stability. Best stability was achieved with calcium zirconium silicate-pigmented potassium silicate paints which were irradiated without heat treatment (although heat treatment still resulted in the second best stability achieved).

Heat treatment of the potassium silicate-treated zinc oxide used to prepare S-13G has apparently eliminated the problem of coating gellation. This was accomplished at little or no expense to stability in the infrared region of the spectrum. Indeed, the stability at visible wavelengths may be improved by heat treatment of the silicate-modified zinc oxide at 700°F for 8 hrs.

One of the most significant results of the studies during this report period is the optical properties and the stabilities achieved with zinc titanate (Zn_2TiO_4) paints based on RTV-602. Not only does zinc titanate not show the oxygen-bleachable infrared degradation exhibited by zinc oxide, but RTV-602 coatings were prepared with solar absorptances as low as 0.11. Long range tests are planned to determine the stability of zinc titanate pigmented silicone paints at exposures to at least 2000 ESH.

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