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SPACE STABLE THERMAL CONTROL COATINGS

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1.0 INTRODUCTION

The potential that zinc orthotitanate possesses as a pigment for spacecraft thermal control applications has been thoroughly demonstrated in past studies at IITRI (Reference 1-3). The practical realization of this potential hinges most importantly on pigment stoichiometry and also on the production process and optimized preparative conditions associated with it. The "MOX" method, i.e., the use of zinc and titanium oxalate precursors, has the distinct advantages of simple and rapid processing, and of controlled pigment particle size. The primary goals of this program for obtaining a specification quality zinc orthotitanate are:

1) Determination of the chemical identity of TiOX ("titanium oxalate").

2) Effect of Zn/Ti ratio for Zn_2TiO_4 on the reflectance spectra and stability to ultraviolet irradiation in vacuum.

3) Optimized processing parameters for reproducibly obtaining a pigment of the most desirable optical properties and behavior.

The ultimate goal of obtaining a specification thermal control coating appears well within achievable reality. The studies discussed in this report are designed to yield a Zn_2TiO_4 paint as an engineering material for use on future spacecraft.

During this period, Zn_2TiO_4 pigments of varying Zn/Ti ratios (1.85 to 2.05) were prepared at 600° to 1050°C for optical studies. The results of UV-vacuum studies on silicate-bonded Zn_2TiO_4 paints have been analyzed, and these data are presented in the following sections.

2.0 PAINT STUDIES

In the current studies to obtain a highly reflective and stable Zn_2TiO_4 pigmented thermal control coating, an inorganic silicate vehicle (as opposed to a polymeric silicone binder) has been chosen for prime consideration. This choice is due to several desirable characteristics of silicate coatings: 1) lower solar absorptance, α_s; 2) higher emittance, ε; 3) greater stability in UV-vacuum; 4) no outgassing problems; and 5) higher electrical conductivity, minimizing charge buildup problems.

Historically, the objections to a silicate-bonded coating have been based on two disadvantages: 1) difficulties in spray technique to achieve a flaw-free, well-bonded coating; and 2) difficulty in cleanability. However, the use of Z93 (silicate-bonded ZnO) on large areas of the Gemini early in the space program attests to its applicability. The cleanability problem may be circumvented through the use of protective polymeric films. Studies (Ref. 4) at IITRI have shown that storage under plastics such as Mylar, Lexan, Type A Teflon, and Tedlar for periods up to 14 months maintains the excellent stability of Z93 to UV-vacuum.

2.1 Preparation of Samples

Zinc orthotitanate powders having Zn to Ti ratios of 1.85/1, 1.90/1, 1.95/1, 2.00/1, and 2.05/1 were prepared by the MOX method. Mixtures of zinc oxalate-"TiOX" composition were dryblended in polypropylene containers using nylon balls. A 500°C/2 hr pre-calcination was followed by final reaction at 900°C/2 hr or 1050°C/2 hr, using the flash calcination method of direct insertion of the powder into a furnace at temperature, followed by removal to room temperature conditions. This method minimizes heat up and cool down which can add to an undesirable increase in particle size due to sintering.

Paint formulations were prepared by ball-milling of pigment - PS7 potassium silicate - water mixtures having a pigment to binder ratio (PBR) of 4.26 by weight. Coatings were applied by conventional spray painting techniques and cured in air at room temperature. Samples were prepared on both IITRI and MSFC paint coupons for evaluation at both facilities.

2.2 Optical Studies

A tabulation of initial reflectance values at 350 and 450 nanometers for the various samples appears in Table 1. The 350 nm values show the position of the "knee" which indicates the amount of free ZnO in the Zn_2TiO_4, and the 450 nm values show the peak reflectance. In general, there is fairly good correlation between IITRI and MSFC values.

The 350 nm values for the 900°C calcined pigment paints are graphically illustrated in Figure 1, along with those for the pigments alone. The pigment samples show a trend of lower values (or increasing free ZnO content) with increasing Zn/Ti ratios. However, the paints do not follow this trend.

With the samples which have been acid leached to remove free ZnO, the R_{350} values are higher as expected. A trend toward higher values with increasing Zn/Ti ratio is indicated for the acid washed samples (Figure 1), suggesting greater amounts of

TABLE I

REFLECTANCE OF Zn_2TiO_4 PAINTS OF VARYING STOICHIOMETRY

	R_{350}		R_{450}			R_{350}		R_{450}	
Zn/Ti Ratio	MSFC	IITRI	MSFC	IITRI	Zn/Ti Ratio	MSFC	IITRI	MSFC	IITRI
5-9:*					5-9-A-9:*				
1.85	31.0	33.0	88.0	85.0	1.85	50.0	58.5	91.0	90.0
1.90	51.5	56.0	87.5	86.0	1.90	57.0	62.0	89.5	89.0
1.95	40.0	43.0	85.0	84.0	1.95	55.5	62.5	89.0	89.0
2.00	42.5	47.0	87.5	86.0	2.00	63.0	71.0	88.5	89.0
2.05	35.0	37.0	87.0	86.0	2.05	65.0	71.5	88.5	90.0
5-10.5:*					5-10.5-A-10.5:*				
1.85	55.5	60.0	86.0	85.0	1.85	59.5	69.0	90.0	87.5
1.90	60.0	63.0	86.0	84.5	1.90	60.0	67.5	88.0	85.5
1.95	48.0	48.0	87.5	84.0	1.95	62.5	69.0	87.5	87.0
2.00	45.5	47.0	88.0	87.0	2.00	63.0	69.0	89.0	87.0
2.05	36.5	38.5	86.0	85.0	2.05	62.5	65.0	87.0	84.5

* 5-9: 500°C/2 hr + 900°C/2 hr
5-9-A-9: 500°C/2 hr + 900°C/2 hr + acid leach + 900°C/ 2 hr
5-10.5: 500°C/2 hr + 1050°C/2 hr
5-10.5-A-10.5: 500°C/2 hr + 1050°C/2 hr + acid leach + 1050°C/2 hr

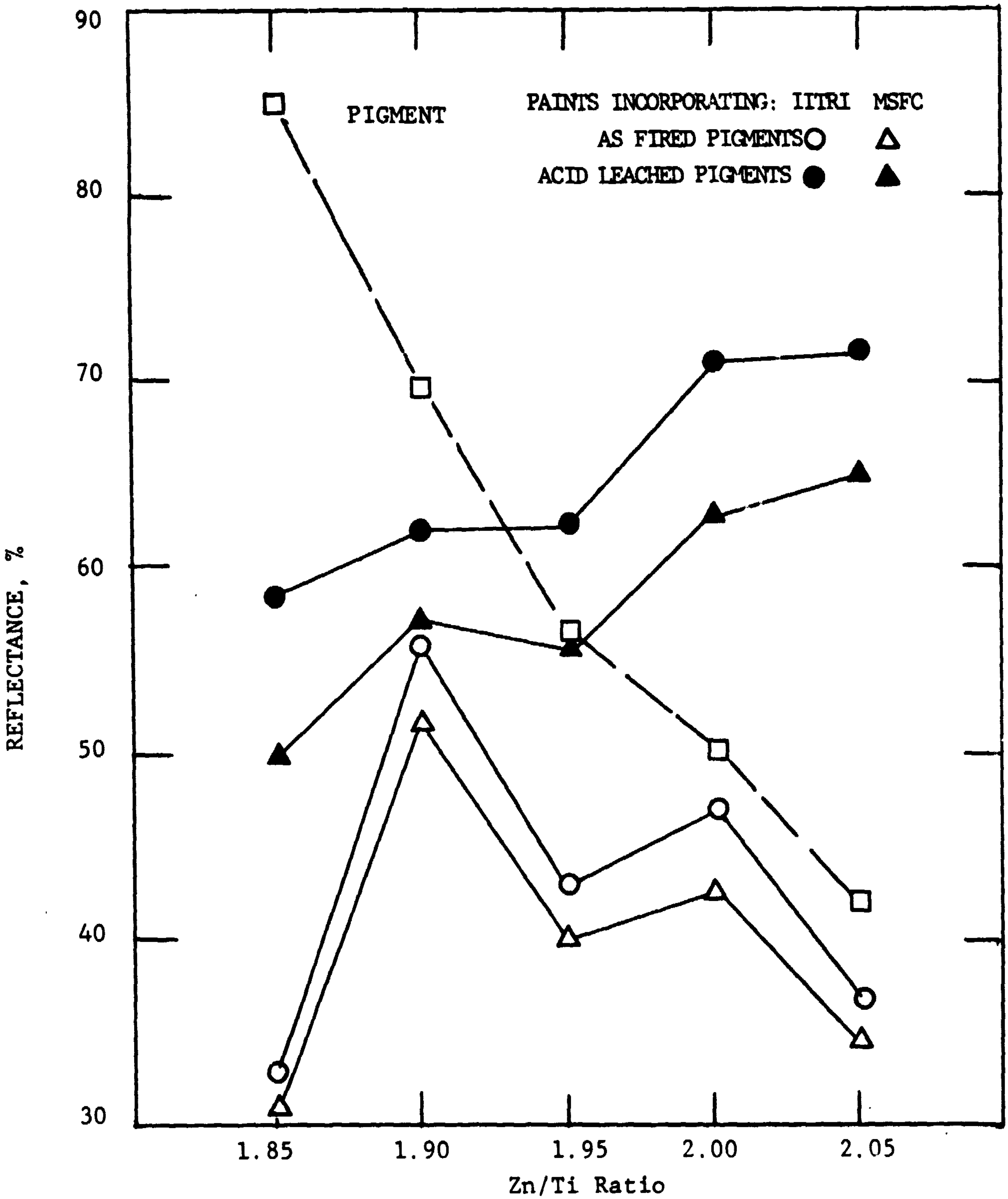

FIGURE 1 REFLECTANCE AT 350 NANOMETERS FOR Zn_2TiO_4-SILICATE PAINTS (PIGMENT CALCINED AT 900°C)

free ZnO remaining in the powders at the lower (.185, 1.90) stoichiometric ratios. The acid washing studies had shown (Figure 2) lesser amounts of ZnO removal with decreasing Zn/Ti ratio as can be expected. The reflectance data show, however, that the ZnO removal may not have been complete for the lower Zn/Ti ratio powders. Additional experiments are being conducted to investigate this anomaly.

Another observation is that the R_{350} values for the paints, both with acid-leached or untreated pigment, are lower than those of the pigment. This lower reflectance for the paints as compared to the pigments also maintains at higher wavelengths. Thus, the high reflectance potential exhibited by the pigment has not yet been achieved in a paint. As described later in this report, work is now underway to achieve higher reflectance with paints.

Shown in Figure 3 are the R_{350} values for pigments calcined at 1050°C and paints incorporating these pigments. These paints exhibit the expected trend, i.e., lower values with increasing Zn/Ti ratio. The data for the paints pigmented with acid-leached pigments also show expected behavior, i.e., the values were all about the same, reflecting ZnO removal to form a relatively pure Zn_2TiO_4 regardless of initial stoichiometry.

2.3 UV-Vacuum Studies

The results of UV-vacuum testing are summarized in Figure 4 for the 900°C pigment paints. No definite trend in stability as a function of stoichiometry, appears to exist for either the acid leached or untreated pigment coatings. For paints pigmented with 1050°C as-calcined powders (Figure 5) stability was similar for

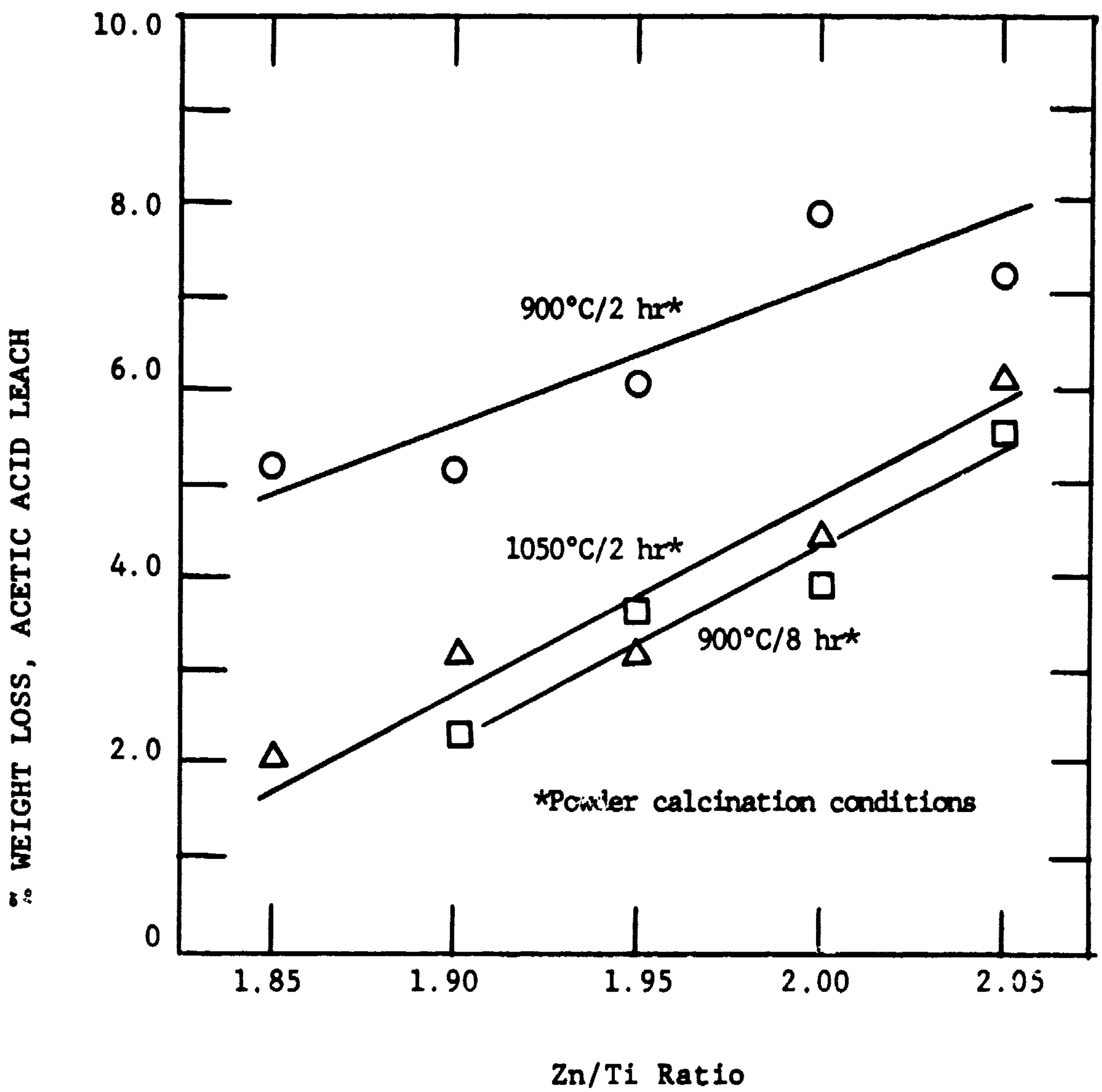

FIGURE 2 ZINC OXIDE REMOVAL ON ACID LEACHING OF ZINC ORTHOTITANATE AS FUNCTIONS OF Zn/Ti RATIO AND SYNTHESIS PARAMETERS

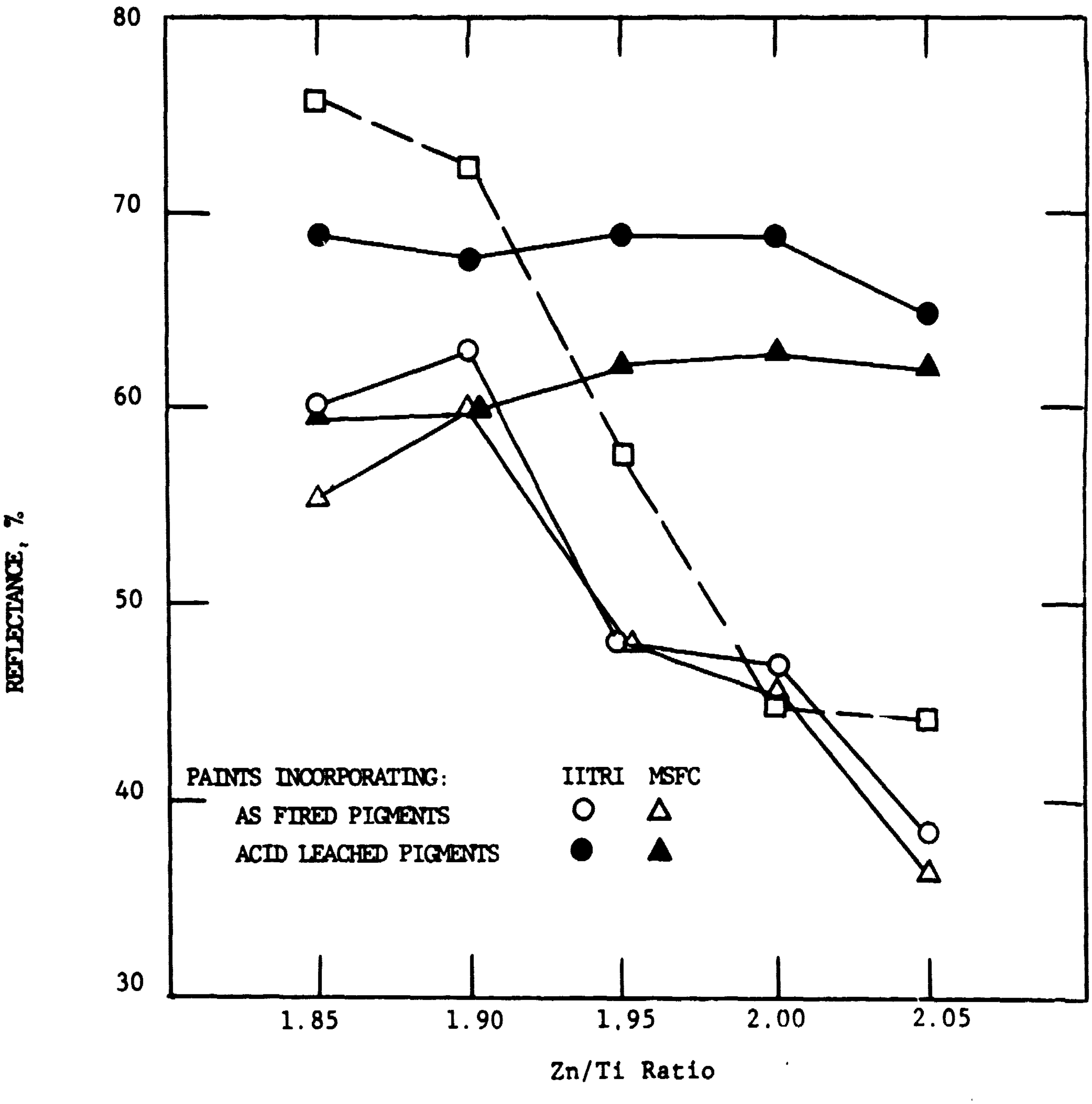

FIGURE 3 REFLECTANCE AT 350 NANOMETERS FOR Zn_2TiO_4-SILICATE PAINTS (PIGMENT CALCINED AT 1050°C)

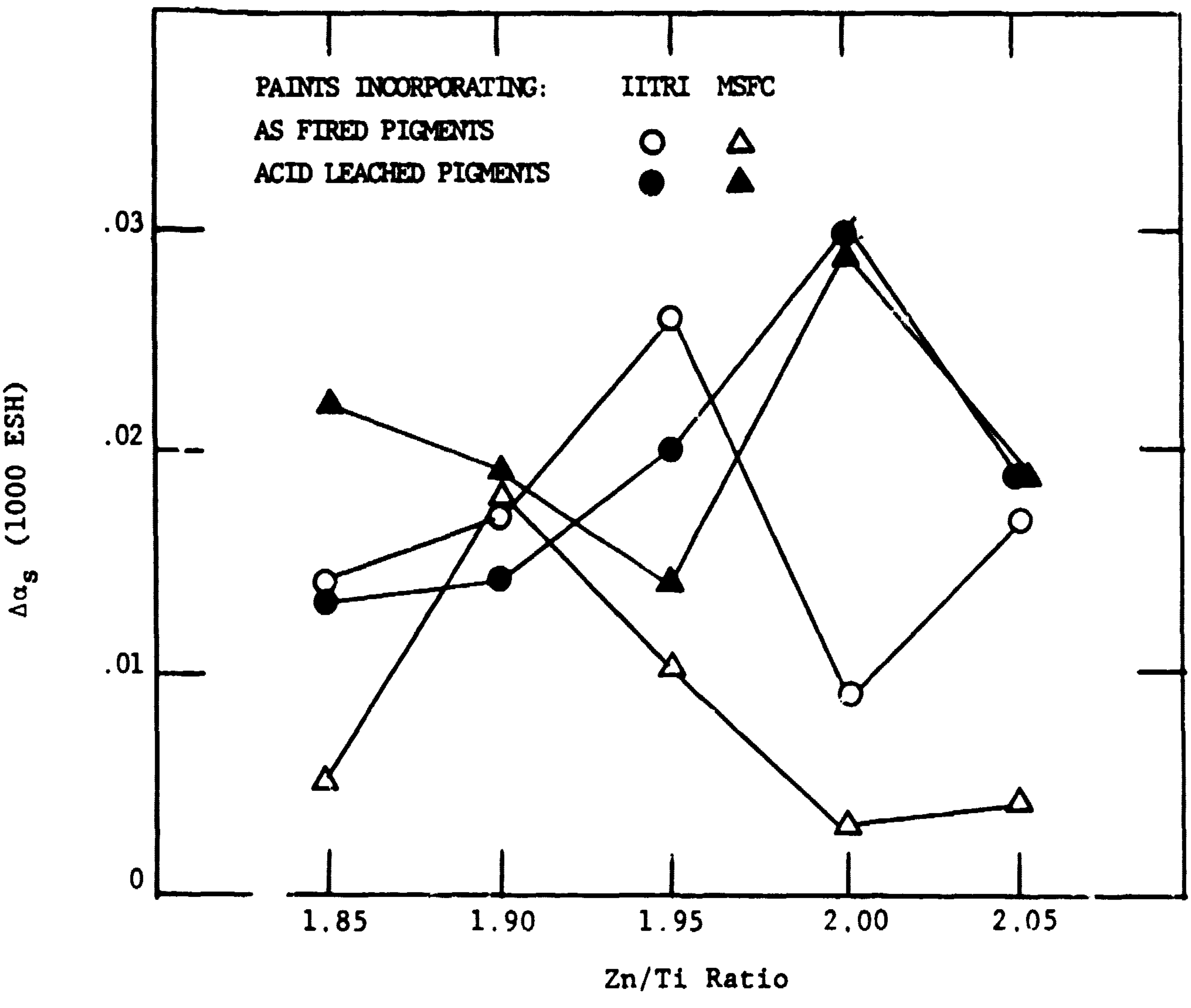

FIGURE 4 SOLAR ABSORPTANCE CHANGES (1000ESH) FOR Zn_2TiO_4-SILICATE PAINTS (900°C CALCINED PIGMENTS)

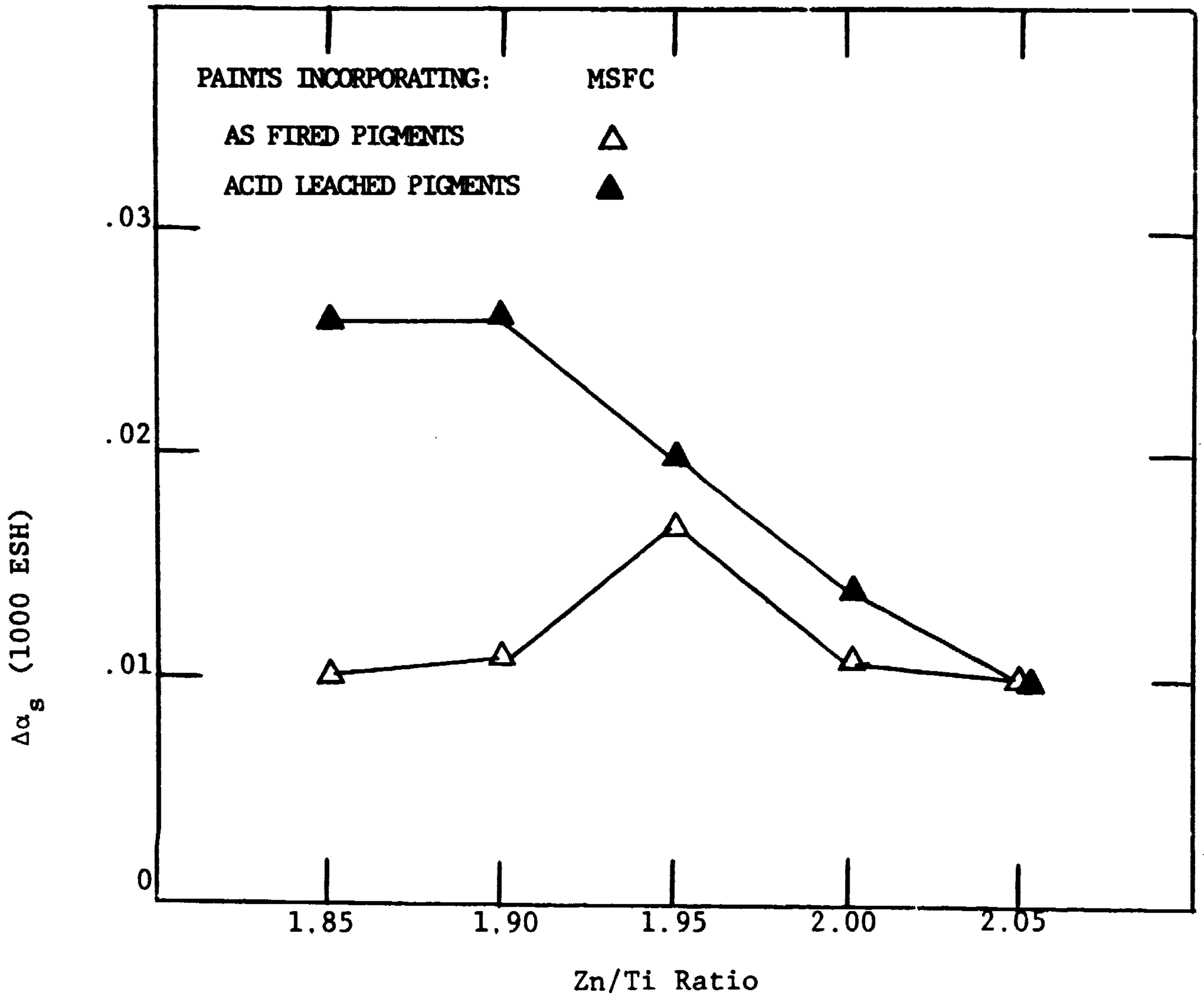

FIGURE 5 SOLAR ABSORPTANCE CHANGES (1000 ESH) FOR Zn_2TiO_4-SILICATE PAINTS(1050°C CALCINED PIGMENTS)

the various Zn/Ti ratio materials. The acid leached materials appeared less stable, especially for the lower Zn/Ti ratio paints. This may be explained in this manner: the lower Zn/Ti ratio has a higher proportion of a titanium component. Thus, acid leaching to remove free ZnO could yield a greater amount of free unreacted TiO_2, which can deleteriously affect stability.

Reflectance changes at particular wavelengths for both the IITRI and MSFC exposure for 1050°C pigment paints are shown in Table II. A summarization of these data appears in graphic form in Figure 6. These data points are obtained by adding the values of reflectance changes listed in Table II, and are used pending full reduction of IITRI data to solar absorptance values. A good indication of relative performance are obtained from these data.

Examination of the data in Figure 6 shows the following:

1. No particular trend in stability vs stoichiometry is observed for the non-acid treated pigment paints.

2. A trend toward improved stability with increasing Zn/Ti ratio is apparent for the acid-leached pigment paints.

3. At Zn/Ti ratios of 1.85-1.95, the paints pigmented with non-acid leached pigments appear more stable than those incorporating leached pigments; at ratios of 2.00 and 2.05, this difference is not readily evident.

4. The IITRI data indicate better stability for the various paints as compared to the MSFC results.

TABLE II

REFLECTANCE CHANGES FOR SILICATE PAINTS PIGMENTED WITH 1050°C Zn_2TiO_4 POWDERS (1000 ESH)

	WAVELENGTH, MICRONS								
SAMPLE	.330	.354	.444	.554	.700	.929	1.30	1.71	2.50
(5-10.5) Samples:									
MOX-85(I)	1.0	0.5	0	0	1.0	1.5	0	+1.0	+1.0
(M)	0	0	1.5	1.5	2.0	2.0	0.5	+1.0	+1.5
MOX-90(I)	0	0	0	0.5	1.0	1.0	+0.5	+2.0	+3.0
(M)	0	0	1.0	1.0	2.0	2.5	1.0	+0.5	+1.0
MOX-95(I)	1.0	1.5	1.5	1.0	1.0	0.5	0.5	+1.5	+1.0
(M)	0	0	2.0	2.0	2.0	2.5	0.5	+2.0	+2.0
MOX-00(I)	1.0	0	1.5	1.0	1.0	2.0	0.5	+0.5	+2.0
(M)	0	0	0.5	1.5	1.5	2.0	0.5	+1.0	+1.5
MOX-05(I)	0	0	0	0.5	+0.5	1.0	0	+1.0	0
(M)	0	0.5	0.5	1.5	1.5	2.0	0.5	+1.0	+1.0
(5-10.5-A-10) Samples:									
MOX-85(I)	0	1.0	2.0	2.0	2.0	2.0	0	0	0
(M)	0	0	3.0	3.5	4.5	5.0	2.0	+1.5	+1.0
MOX-90(I)	1.0	3.0	1.5	1.0	1.0	1.0	0	0	+1.0
(M)	0	0	2.5	3.5	4.0	4.5	2.0	+1.0	+1.5
MOX-95(I)	1.0	2.0	2.0	1.5	1.5	2.0	0.5	0	+0.5
(M)	0	0	2.5	3.0	3.0	3.0	1.5	+0.5	+1.0
MOX-00(I)	0	2.0	1.0	1.0	0	0	0	+1.0	+2.0
(M)	0	0	2.0	2.0	2.0	2.5	1.0	0	+1.5
MOX-05(I)	0	0	0	0	0	1.0	0	0	0
(M)	0	0	1.5	1.0	2.0	2.0	0	+2.0	+2.0

NOTE: (I) = IITRI

(M) = MSFC

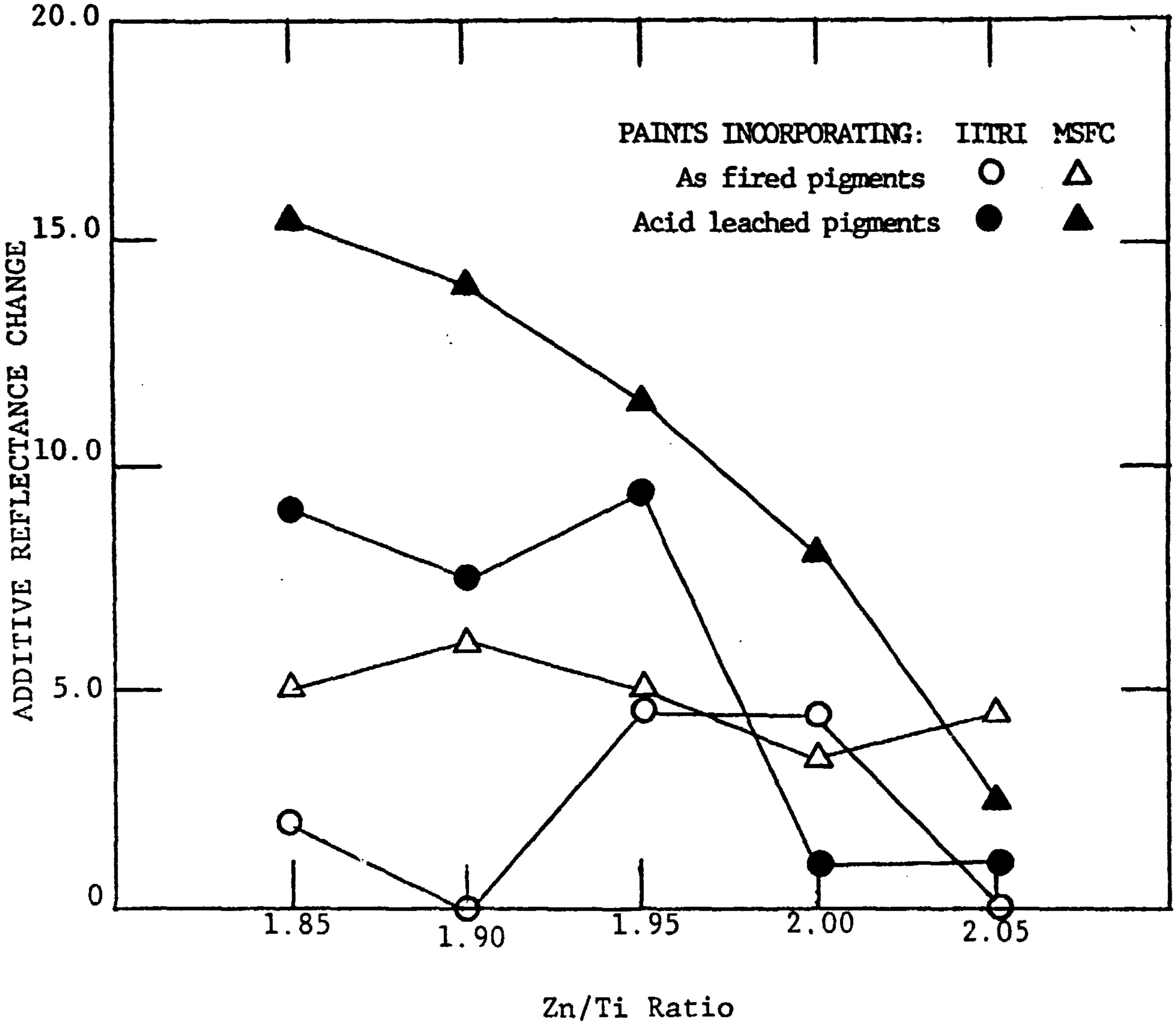

FIGURE 6 ADDITIVE REFLECTANCE CHANGES vs Zn/Ti RATIO FOR Zn_2TiO_4-SILICATE PAINTS (1000 ESH)

This is in contrast with the results for the 900°C pigment paints in which the reverse relationship was observed.

In summary, the variability and lack of trends in optical behavior as a function of stoichiometry for the 900°C pigments is somewhat puzzling. The paints incorporating 1050°C pigments exhibit more predictable behavior. It is possible that the 900°C pigments are in a metastable form due to the limited reaction times (2 hours at 900°C). Experiments involving longer reaction times up to 16 hours are being pursued to examine this behavior.

A very desirable result with the silicate-bonded paints is their good stability. Previous work with silicone paints generally yielded $\Delta\alpha_s$ values of greater than .02, up to as high as .10. It is believed that in the current work, a superior Zn_2TiO_4 product is being produced through better processing procedures, and this, along with the use of a silicate binder, is providing a more stable paint.

2.4 Effect of Pigment to Binder Ratio

Studies have been initiated to obtain paints of higher reflectance by increasing the pigment to binder ratio (PBR). Samples with PBR's of 4.26 (used in above-mentioned paints), 4.73 and 5.32 were prepared, along with a water spray sample. Thicknesses were about 6 mils.

Reflectance values at particular wavelengths are shown in Figure 7. An increase in reflectance with increasing PBR can be seen, particularly at wavelengths of 350 nm and 2000 nm. The R_{350} value for the 4.73 PBR is the only one that does not fit the general trend; additional work is needed to check this anomaly.

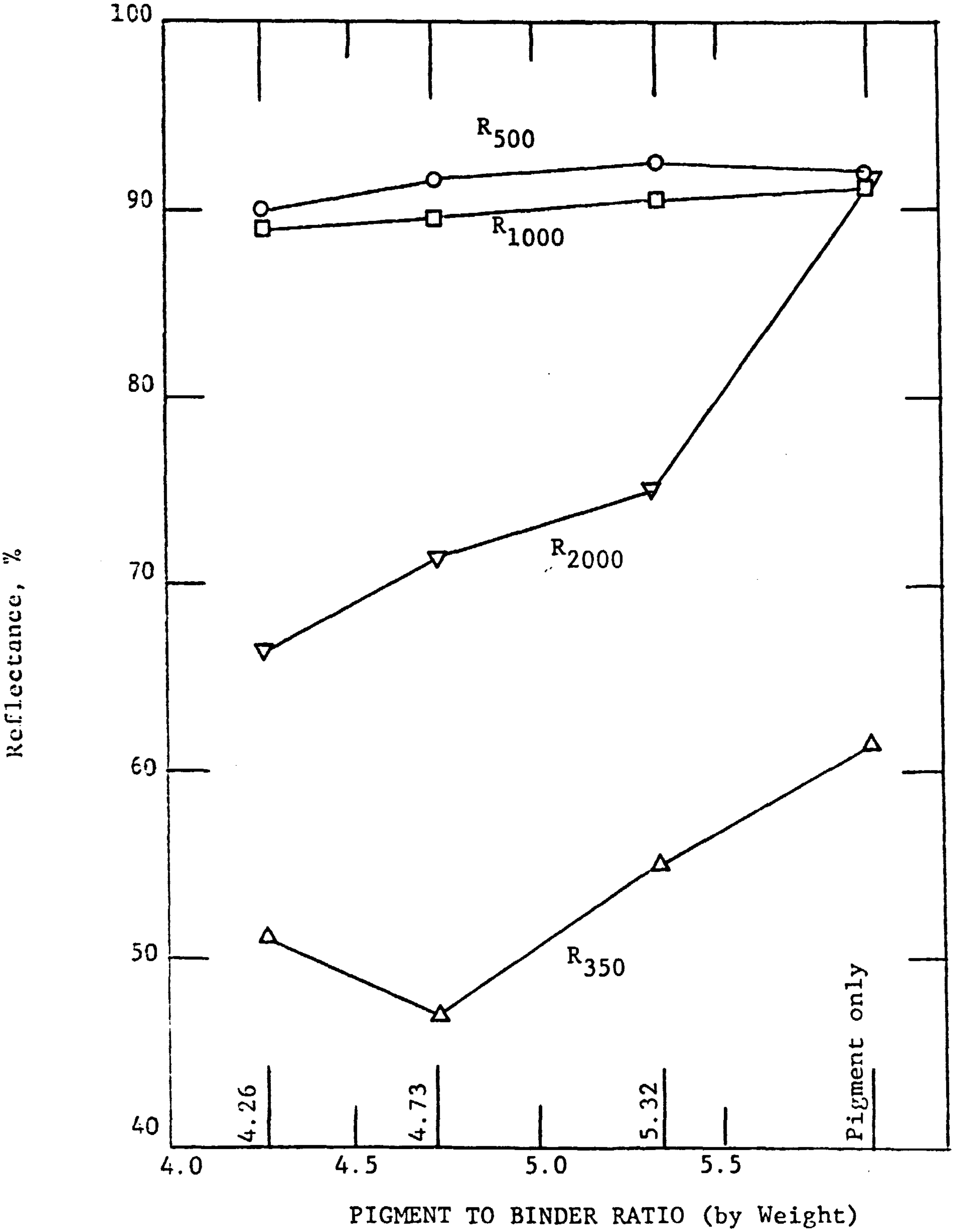

FIGURE 7 REFLECTANCE OF Zn_2TiO_4-SILICATE PAINTS AS A FUNCTION OF PIGMENT TO BINDER RATIO

Examination of the samples revealed good integrity and reasonable coating hardness for even the 5.32 PBR samples. It may be possible to increase the PBR even more to achieve reflectance approaching that of the pigment; such experiments will be conducted in the near future.

3.0 PIGMENT STUDIES

The preparation of pigments remains an ongoing function on this program. This involves: 1) preparation of $ZnCl_2$ and $TiCl_4$ solutions; 2) reacting with oxalic acid to form the oxalate precursors; 3) dry ball milling of zinc oxalate with "TiOX" in a plastic media; 4) precalcination at 500°C/2 hrs; and 5) production of Zn_2TiO_4 using flash calcination at 900°C or 1050°C. The various pigments prepared during this report are described in the following sections.

3.1 Zn_2TiO_4 Synthesis at 600°-800°C

A series of calcinations were conducted at 600°-800°C to determine if Zn_2TiO_4 can be fully formed, i.e., completeness of the ZnO + TiO_2 reaction, at lower temperatures by using longer reaction times. The use of lower temperatures should result in products of finer particle size and thus could provide higher reflectance materials.

The results of gravimetric and x-ray analyses for these materials are shown in Table III. The weight percent residue values decrease very slightly with increasing calcination temperature, and all are quite close to the theroetical value.

X-ray analysis showed the presence of Zn_2TiO_4 and ZnO in the powders calcined at 600°C. The line intensity in the X-ray pattern indicates an approximate composition of 60% Zn_2TiO_4 -

TABLE III

SUMMARY OF LOW TEMPERATURE SYNTHESIS OF Zn_2TiO_4

SAMPLE	CALCINATION: TEMP, °C	TIME, HRS.	WT % RESIDUE: ACTUAL	THEORETICAL	X-RAY ANALYSIS
MOX-00 (6/8)	600	8	46.67	46.45	$Zn_2TiO_4 + ZnO$
MOX-00 (6/16)	600	16	46.76	46.45	$Zn_2TiO_4 + ZnO$
MOX-00 (7/8)	700	8	46.38	46.45	Zn_2TiO_4
MOX-00 (7/16)	700	16	46.41	46.45	Zn_2TiO_4
MOX-00 (8/2)	800	2	46.32	46.45	Zn_2TiO_4
MOX-00 (8/8)	800	8	46.35	46.45	Zn_2TiO_4
MOX-00 (8/16)	800	16	46.35	46.45	Zn_2TiO_4

40% ZnO. No TiO_2 lines were in evidence. At the 700°C and 800°C levels, all samples exhibited patterns for Zn_2TiO_4 with no evidence of free ZnO. This shows a level of about 5% or less of ZnO in these powders.

The various samples will be analyzed optically to determine if greater reflectance is exhibited by lower temperature (finer particles) powders. The amount of free ZnO will be evaluated using the "knee" data, i.e., reflectance at 350 nm, to determine the completeness of the $ZnO-TiO_2$ reaction.

3.2 Zn_2TiO_4 Synthesis at 900°C

In examining the reflectance spectra of paints pigmented with Zn_2TiO_4 calcined at 900°C (see Report No. IITRI D6118-10), the expected trend of increasing reflectance at 350 nanometers as a function of decreasing Zn/Ti ratio was not observed. This expected trend was observed with paints pigmented with 1050°C calcined powders.

It was speculated that the 900°C/2 hr calcination conditions might have been too short to produce a fully reacted material. Therefore, a series of pigment samples were prepared at various hold times for optical evaluation. The matrix for these preparations is shown in Table IV, along with the results of gravimetric analysis. The data show no clear trend of increased weight loss as a function of time, suggesting that the extent of reaction is essentially complete after 1 hour.

These samples, along with Zn_2TiO_4 powders prepared at 600°C, 700°C, and 800°C, are being evaluated, and the results will appear in the next report.

TABLE IV

WEIGHT PERCENT RESIDUE VS CALCINATION TIME AT 900°C IN PREPARATION OF Zn_2TiO_4 FROM PRECURSOR OXALATES

Zn/Ti Ratio	Calcination Time, Hours					Theoretical
	1	2	4	8	16	
1.85	46.29	46.18	46.40	46.39	46.20	46.65
1.90	46.31	45.99	46.02	46.03	46.04	46.58
1.95	46.19	46.22	46.22	46.20	46.21	46.51
2.00	46.19	46.24	46.26	46.18	46.15	46.45
2.05	45.91	45.91	45.71	45.88		46.39

Other pigments which have been prepared during this reporting period are as follows:

SAMPLE	WT% RESIDUE AFTER CALCINATION	
	Actual	Theoretical
2MOX-95(9-5)	46.32	46.51
2MOX-00(9-5)	46.49	46.45
2MOX-05(9-5)	46.56	46.39
2MOX-95(5-10.5)	46.70	46.51
2MOX-00(5-10.5)	46.47	46.45
2MOX-05(5-10.5)	46.14	46.39

These materials will be used in paint studies to examine effects of stoichiometry, thickness, and pigment-to-binder ratio on optical behavior.

4.0 SUMMARY

Efforts to develop an engineering paint on this program are now being concentrated on inorganic silicate-bonded systems as opposed to the silicone coatings heretofore studied. The UV-vacuum stability of potassium silicate-Zn_2TiO_4 paints have been shown to be quite good; work is now well underway to optimize the reflectance of these systems by maximizing thickness and pigment-to-binder ratio.

Personnel who have contributed to this work include J. E. Brzuskiewicz, Jr., J. E. Gilligan, and W. R. Logan.

Respectfully submitted,

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