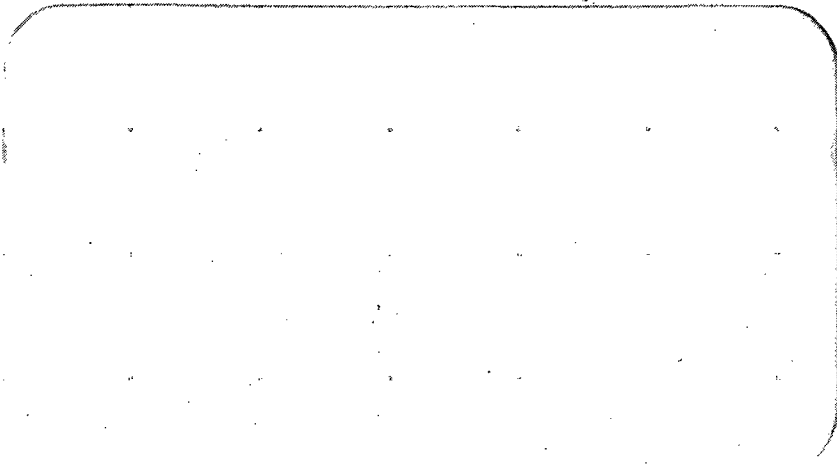


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Contract No. NAS8-26791
Report No. IITRI-C6233-8
(Triannual Report)

DEVELOPMENT OF SPACE STABLE THERMAL
CONTROL COATINGS FOR USE IN LARGE
SPACE VEHICLES

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FOREWORD


This is Report No. IITRI-C6233-8 (Triannual Report) of IITRI Project C6233, Contract No. NAS8-26791, entitled "Development of Space Stable Thermal Control Coatings for Use in Large Space Vehicles." This report covers the period from May 1 through August 31, 1971.

Major contributors to the program during this period include: Mr. J.E. Gilligan, Project Leader; Mr. Rodney M. Leas, strippable coatings preparation and evaluation; Mr. Yoshiro Harada, Mr. Wm. R. Logan, Mr. E.J. Onesto and Mr. R. Steuhmer, pigment preparation and characterization; Dr. Nicholas A. Ashford and Mr. Frank H. Jarke, EPR measurements, solid state consultation; Mr. F.O. Rogers, paint preparation; Mr. Robert F. Boutin, irradiation experiments and reflectance measurements; and Mr. Gene A. Zerlaut, general consultation and administrative management.

The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.


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Respectfully submitted
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ABSTRACT

The preparation and evaluation of zinc orthotitanate and of several new pigments and the environmental testing and evaluation of these pigments and of coatings made from them constitute the bulk of the work accomplished. New pigments have been prepared and EPR spectra of pigments and their precursor compounds have been studied. Results of extensive testing of commercially-available, strippable, protective coatings are reported; Owens-Illinois 650 glass resin has been stabilized against progressive mechanical failures; definite improvements have been noted. A zinc oxide pigmented lithium silicate paint has demonstrated very good ultraviolet stability.

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Report No. IITRI-C6233-8
(Triannual Report)

DEVELOPMENT OF SPACE STABLE THERMAL
CONTROL COATINGS FOR USE IN LARGE SPACE VEHICLES

1. INTRODUCTION

The research effort in passive spacecraft temperature control has, historically, been concentrated on the development of the class of surfaces known as solar reflectors - that is, surfaces with high reflectance for solar radiation and with high emittance in the thermal (infrared) spectrum. Basically, these surfaces must be stable in the total environment that they will experience. This requirement means that once we have achieved a high level of intrinsic stability of these materials in the laboratory we must be able to produce them in large quantities, and we must make certain that this stability is preserved in the process and will exist and can be protected in the practical sense as well. Applications on large space vehicles, therefore, present new R&D problems - not simply traditional problems in greater dimensions.

The program consists of four major tasks: pigment development, binder development, environmental effects evaluations, and general coatings investigations. The relative emphasis in each of these tasks varies according to the urgency of the problems elucidated in our investigations, and, of course, with the availability of time and funds. Our efforts have been expended mainly on pigment development, EPR studies, and environmental testing and evaluation activities. Strippable coatings evaluations, binder development and activities of a more general nature are continuing at a comparatively low level of effort. The improvement of the physical properties of Owens-Illinois 650 glass resin, as reported in the preceding triannual report on the program (Ref. 1), is essentially complete.

2. PIGMENT DEVELOPMENT

2.1 Introductory Remarks

The excellent optical properties and stability to ultraviolet radiation exhibited by zinc orthotitanate, Zn_2TiO_4 , (Ref. 2) make it apparent that means to produce this pigment in its most stable form be developed. As we have discussed at length in Reference 2, the stoichiometry of the preparative mixture and the subsequent surface treatment of the powder are highly important with respect to pigment stability. We expect that these same conclusions will obtain in the case of other pigments prepared by co-reaction of precursor compounds. The efforts in this task have involved mainly pigment preparation, new pigment screening, and EPR analyses of synthesized pigments.

Our interest in pigments other than zinc orthotitanate has diminished because of the increasing difficulty in justifying "long-shots". We will continue, as time and funding permit, to screen white pigments in the hope of finding one which has stable low α_s and requires little or no special treatment to stabilize it against ultraviolet radiation. However, since experience dictates that pigment materials are not stable in commercial form, the probability of discovering such a pigment for practical applications is virtually nil. Continuing the screening process, nevertheless, provides many insights regarding the mechanisms of ultraviolet damage.

The use of EPR in our pigment development efforts has been rewarding in two significant ways. It has provided a separate and somewhat independent means of studying fundamental properties of materials. Also, for certain materials, results of EPR studies appear to be correlatable with the optical changes occurring upon irradiation, thus opening up the possibility of directly quantifying radiation-induced optical damage.

2.2 Zinc Orthotitanate Synthesis

The purpose of these synthesis studies was to prepare a stable zinc orthotitanate of appropriate particle size at moderate temperatures. Two methods were used in synthesis: coprecipitation and reaction sintering. The results of these studies are discussed in the following sections.

2.2.1 Coprecipitation

The coprecipitation method consists of precipitating zinc oxalate and titanium oxalate as a mixture, designated (Ti,Zn) C_2O_4 , by adding a mixed $TiCl_4 - ZnCl_2$ solution to an oxalic acid solution. (The notation Zn,Ti (C_2O_4) represents a mixture of, and is an abbreviation for, the chemical formulae $Zn(C_2O_4) \cdot 2H_2O$ and $Ti_2(C_2O_4)_3 \cdot 10H_2O$.) The first step in this process is the preparation of $TiCl_4$ solution by slowly adding the liquid $TiCl_4$ to water which is cooled to $10^\circ C$ to prevent hydrolysis. This solution is then mixed with the $ZnCl_2$ solution, also at a temperature of $10^\circ C$. The mixed chloride solution is then added slowly to oxalic acid in water ($\sim 80^\circ C$), and as an alternate route, to oxalic acid in methyl alcohol ($45^\circ C$). The mixed oxalate precipitate is then filtered, washed and dried at $80-90^\circ C$.

A summary of the coprecipitation studies is shown in Table 1. Initial experiments (series A) conducted with water solutions of oxalic acid yielded precipitates of zinc oxalate, oxalic acid, or a combination. Calcination of this material produced zinc oxide in all cases. It appears from these experiments that titanium oxalate is water soluble.

Other studies were made using an alcohol solution of oxalic acid in order to eliminate this partial solubility of the mixed oxalate. As is shown in Table 1, the series-B precipitate exhibited a crystal structure which appeared to be an expanded lattice of zinc oxalate. Calcination of the 2 Zn: 1 Ti composition yielded Zn_2TiO_4 with an excess of TiO_2 , suggesting a slight solubility of zinc oxalate in methyl alcohol.

Table 1

SUMMARY OF COPRECIPITATION STUDIES

Series	Mol Ratio, Zn:Ti	Solvent for Oxalic Acid	Heat Treatment Time, °C	Heat Treatment Time, hrs	Phases Present in Product (x-ray diffraction analysis)
A	2:1	H ₂ O	Room		ZnC ₂ O ₄ · 2H ₂ O
			600	2	ZnO
B	2:1	CH ₃ OH	Room	2	ZnC ₂ O ₄ · 2H ₂ O (expanded lattice)
			400	2	ZnO + TiO ₂ (anatase)
			600	2	Zn ₂ TiO ₄ + TiO ₂ (anatase)
C	Precipitate (B) + ZnC ₂ O ₄ · 2H ₂ O, 3:1 Weight Ratio				
			400	2	ZnO + TiO ₂ (anatase)
			600	2	Zn ₂ TiO ₄ + ZnO (faint) + TiO ₂ (anatase, faint)
D	4:1	CH ₃ OH	Room	8	Zn ₂ TiO ₄ + ZnO (very faint)
			400	2	ZnC ₂ O ₄ · 2H ₂ O
			600	2	ZnO
			600	2	Zn ₂ TiO ₄ + ZnO
			600	8	Zn ₂ TiO ₄ + ZnO (faint)
			900	8	Zn ₂ TiO ₄ + ZnO (faint)

The excess TiO_2 was eliminated by two different methods. The first involved mixing of the series-B precipitate with zinc oxalate in a 3:1 weight ratio. Calcination of this mixture (Series C, previously designated EJO-Mix.) at 600°C for 2 hr yielded Zn_2TiO_4 with small amounts of TiO_2 and ZnO . Further heating at 600°C to a total of 8 hr produced a Zn_2TiO_4 material in which x-ray diffraction patterns revealed no lines for TiO_2 and only very weak lines for ZnO .

A second procedure used to preclude the TiO_2 excess involved the use of a 4:1 mol ratio of Zn to Ti, designated series D (previously ROB-I mix), in Table 1. Calcination of this material at 600°C yielded Zn_2TiO_4 with an excess of ZnO .

Series-C and series-D precipitates were also calcined at 800°C for 8 hr. A preliminary ultraviolet-vacuum test suggests that they are quite stable (see Table 2). Furthermore, the particle size of the calcined powders was still rather fine, and it would appear at this stage of the studies that comminution would not be necessary to adjust particle size. Reflectance spectra before and after 1200 ESH of ultraviolet irradiation of the series-C and -D pigment powders which have been calcined at 900°C for 8 hr are shown in Figures 1 and 2, respectively. These powders were subjected in a later IRIF test to 1200 ESH of simulated solar ultraviolet irradiation. The initial solar absorptance (α_s) values were 0.196 and 0.205, respectively, and 0.214 each for their post-irradiation solar absorptance values. The respective α_s changes are 0.018 and 0.009 after 1200 ESH of simulated solar ultraviolet irradiation.

2.2.2 Reaction Sintering

The reaction sintering technique involves the use of compounds which first decompose to or form the oxides of titanium and zinc. These in turn react to form the mixed oxide which in this case is Zn_2TiO_4 . The advantage of this synthesis method is that when a salt such as ZnCO_3 decomposes to the oxide at 300°C , a very fine powder (one which is very reactive because of its

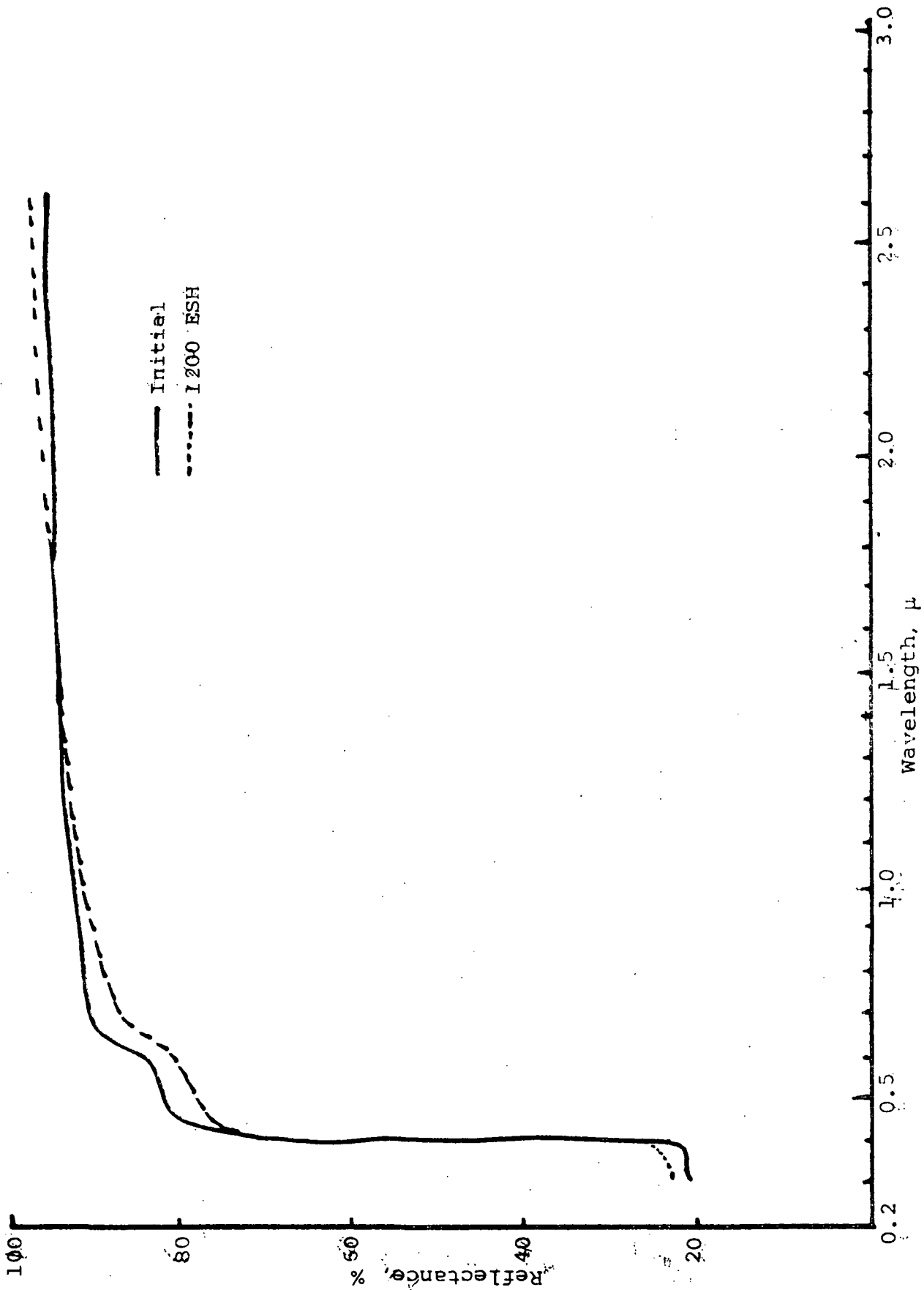


Figure 1 EFFECT OF ULTRAVIOLET RADIATION ON SERIES C ZINC ORTHOTITANATE POWDER (EJO-Mix)

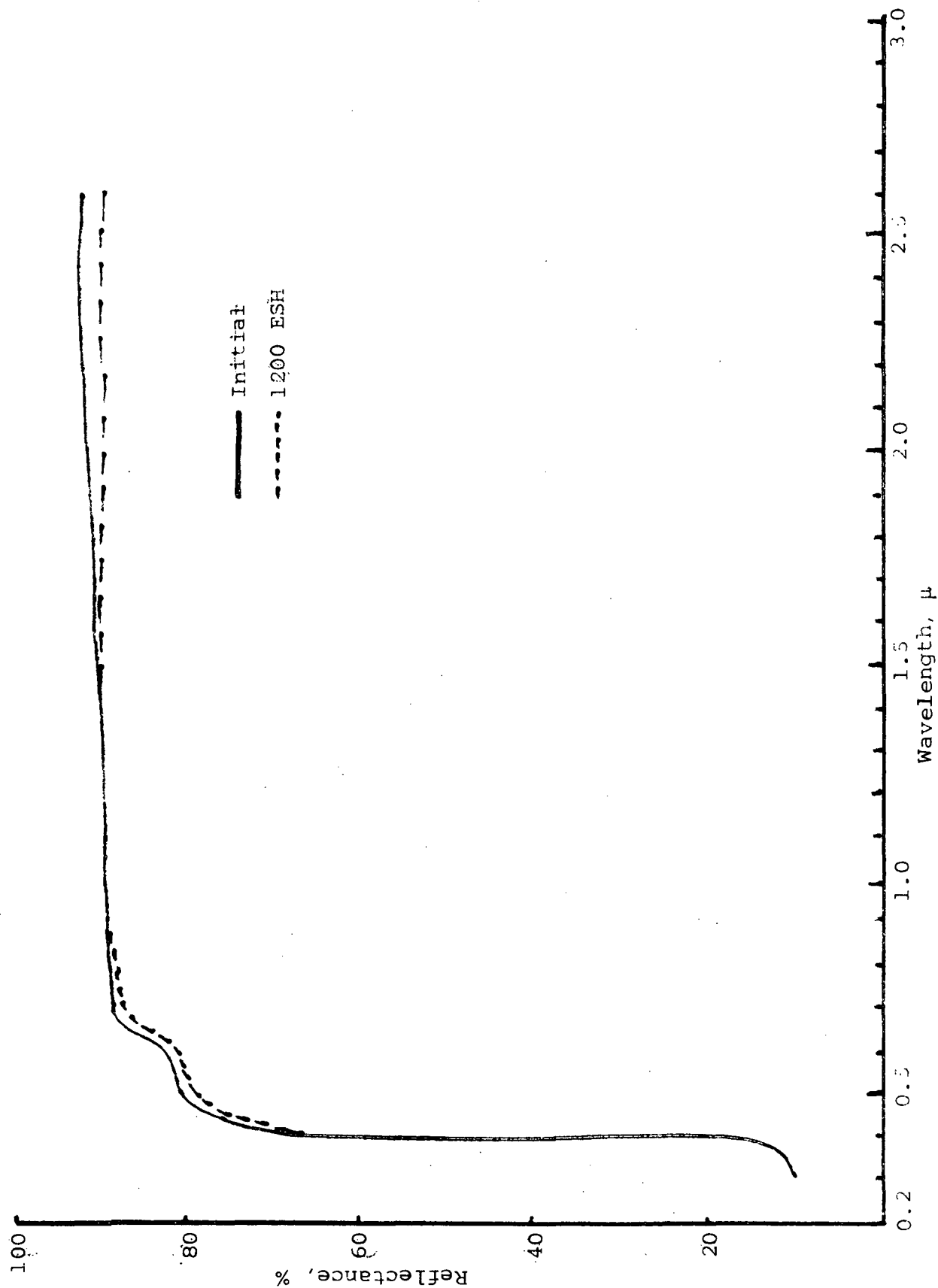


Figure 2 EFFECT OF ULTRAVIOLET RADIATION ON SERIES D ZINC ORTHOTITANATE POWDER (ROB-I Mix)

Table 2

EFFECT OF 576 ESH ON COPRECIPITATED ZINC ORTHOTITANATE POWDERS

	Wavelength, microns						
	0.4	0.5	0.6	0.7	1.0	2.0	2.6
EJO-Mix	78.0	86.0	90.3	91.6	91.0	91.9	93.0
600°C/8 hr	70.7	79.5	82.3	81.7	75.6	88.7	89.0
ROB-I	60.3	88.9	90.3	89.6	85.9	85.7	81.3
600°C/8 hr	57.3	85.0	85.7	83.3	76.0	83.1	77.3

Note: The reflectance values before and after irradiation are the upper and lower figures, respectively, in the set.

high surface area) is produced which forms reaction products more readily than commercially available materials such as SP500 ZnO.

The results of these studies are summarized in Table 3. Reactions between anatase titania and various zinc salts at temperatures up to 600°C failed to produce zinc orthotitanate; only zinc oxide and anatase were detectable by x-ray diffraction evaluation. However, substitution of TiH for TiO₂ did result in a limited yield of Zn₂TiO₄. Experiments at 900°C using TiH or Ti metal powder also indicated incomplete reaction.

Additional work in this area should consider other precursors of TiO₂ such as the oxalate or the oxysulfate. This is suggested by the fact that titanium hydride, for example, undergoes a decomposition reaction to form a finely divided metal that (above 410°C) oxidizes to form TiO₂, which is also finely divided, and thus has extremely reactive nascent surfaces.

2.2.3 Conclusions

The co-precipitation method of preparing zinc orthotitanate holds considerable promise. The results indicate that particle sizes, although not optimum, are not unacceptable, and that stability is excellent. The needs now are to determine the ideal Ti/Zn starting ratio, and to minimize solar reflectance. The reaction sintering approach has not been as rewarding. Higher

Table 3

SUMMARY OF REACTION SINTERING STUDIES

Ti Source	Reactants		Heat Treatment		Phases Present in Product (x-ray diffraction analysis)
	Zn Source		Temp, °C	Time, hrs	
TiO ₂ *	ZnCO ₃		400	2	ZnO + TiO ₂ (anatase)
			600	2	ZnO + TiO ₂ (anatase)
TiO ₂ *	ZnC ₂ O ₄ ·2H ₂ O		400	2	ZnO + TiO ₂ (anatase)
			600	2	ZnO + TiO ₂ (anatase)
TiO ₂ *	Zn(NO ₃) ₂ ·6H ₂ O		400	2	ZnO + TiO ₂ (anatase)
TiO ₂ *	Zn(C ₂ H ₃ O ₂) ₂ ·2H ₂ O		400	2	ZnO + TiO ₂ (anatase)
TiH	ZnCO ₃		600	2	ZnO + Zn ₂ TiO ₄ (faint)
TiH	Zn(NO ₃) ₂ ·6H ₂ O		600	2	ZnO + Zn ₂ TiO ₄ (faint)
TiH	Zn(C ₂ H ₃ O ₂) ₂ ·2H ₂ O		600	2	ZnO + Zn ₂ TiO ₄ (faint)
TiH	ZnCO ₃		900	8	ZnO + Zn ₂ TiO ₄ (faint)
TiH	ZnC ₂ O ₄ ·2H ₂ O		900	8	ZnO + Zn ₂ TiO ₄ (moderate) + TiO ₂ (rutile)
Ti	ZnCO ₃		900	8	ZnO + Zn ₂ TiO ₄ (faint)
Ti	ZnC ₂ O ₄ ·2H ₂ O		900	8	ZnO + Zn ₂ TiO ₄ (moderate) + TiO ₂ (rutile)

*Anatase titanium dioxide (DuPont Tipure Type FF)

**-325 mesh (produced at IITRI under a different program)

***-325 mesh (Fansteel Metallurgical Corp.)

temperatures will probably be necessary to increase product yield. Even though reaction sintering is at least potentially the better method in terms of both ease of operation and adaptability to production, it has not been sufficiently successful to warrant any further studies within the time and funding of this program. Of the two methods, coprecipitation has obviously progressed the further.

2.3 New Pigment Materials

2.3.1 Initial Screening

Twelve potentially-stable white pigments were irradiated in IRIF test I-43 at six suns intensity to a total ultraviolet exposure of 575 ESH. The pre- and post-test spectral hemispherical reflectance curves have been studied to determine whether the materials have acceptably low solar absorptances and whether they are sufficiently stable. Table 4 lists the samples along with spectral reflectance values at selected wavelengths before and after irradiation. Solar absorptance values were not calculated, because it was obvious that most of the materials were unstable and few would have solar absorptance (α_s) values competitive with currently available stable systems.

The untreated commercial materials zinc borate, zinc silicate and zinc stannate (obtained from Alfa Inorganics) exhibit high α_s values and, with the exception of zinc borate, poor stability. Of the Pemco frits, only No. P-1A44P was reasonably stable. The frit, No. P-1805P, obviously is very attractive from the standpoint of its initial α_s value, but cannot be considered further because of its very poor stability. The IITRI zinc zirconate powders were prepared by a solid-solid reaction at 1800°C for 5 min and a post heat treatment of 1000°C for 10 min. They exhibited poor α_s values and serious instability. No further investigations of the zinc zirconates are planned.

Table 4

SPECTRAL REFLECTANCE VALUES BEFORE AND
AFTER ULTRAVIOLET IRRADIATION* OF NEW PIGMENT MATERIALS

Untreated Commercial Materials	Wavelength, microns						
	0.4	0.5	0.6	0.7	1.0	2.0	2.6
Zinc	80.0*	81.0	80.8	80.2	88.2	70.5	50.7
Borate	74.0*	79.8	79.4	79.8	88.0	71.9	51.2
Zinc	84.0	82.3	79.9	78.0	74.3	69.5	62.0
Silicate	59.0	69.2	73.3	74.4	72.8	69.0	60.7
Zinc	80.5	87.0	88.8	89.2	87.2	67.3	49.8
Stannate	63.2	80.1	85.8	87.3	86.4	64.0	45.7
Pemco Frits							
P-1805-P	88.5	88.8	88.6	88.4	87.2	89.5	84.5
	72.0	81.2	84.7	86.6	87.2	88.6	84.5
P-1P32P	79.9	89.1	88.9	88.3	86.0	81.9	77.0
	65.5	80.5	84.5	86.0	85.3	81.9	77.0
P-1A43P	80.6	82.9	82.4	81.8	80.9	83.5	84.5
	70.6	79.0	80.7	80.9	81.0	83.5	83.9
P-1A44P	79.0	88.0	88.3	88.0	86.0	88.2	84.9
	72.0	85.3	87.0	87.6	85.7	88.2	84.3
IITRI Zinc Zirconate Powders							
25 wt% ZnO·75 wt% ZrO ₂	78.9	89.5	92.8	93.2	93.7	95.9	97.2
	68.6	81.9	87.4	90.2	92.9	95.9	97.2
50 wt% ZnO·50 wt% ZrO ₂	77.1	88.0	91.3	91.9	92.0	93.2	95.1
	65.0	80.2	86.9	89.3	91.5	93.2	94.5
75 wt% ZnO·25 wt% ZrO ₂	74.8	83.4	85.2	85.6	86.1	89.2	91.8
	63.8	75.7	80.6	82.6	84.2	88.8	94.5

*The spectral reflectance values before and after 575 ESH of UV irradiation are the upper and lower figures, respectively, in each set.

2.3.2 Subsequent Tests

After some brief purification and calcination treatments some of the more promising materials from the test previously discussed were subjected to 1200 ESH in IRIF test I-45. Table 5 lists the pigments, their treatments, and the solar absorptance values. The spectral reflectance spectra for the untreated zinc borate sample are shown in Figure 3; those for the sample treated at 900°C for four hours, in Figure 4.

Table 5

SOLAR ABSORPTANCE VALUES OF
NEW PIGMENTS BEFORE AND AFTER 1200 ESH

Sample	Solar Absorptance		
	Initial	1200 ESH	$\Delta\alpha_s$
Untreated Zinc Borate	0.203	0.236	0.033
Zinc Borate, 500°C/8 hr	0.232	0.263	0.031
Zinc Borate, 700°C/8 hr	0.287	0.336	0.049
Zinc Borate, 900°C/8 hr	0.179	0.244	0.065
Pemco Frits			
No. P-1A43P	0.233	0.295	0.062
No. P-1A44P	0.179	0.200	0.021
No. P-1A44P, 400°C/4 hr	0.133	0.180	0.047

2.3.3 Conclusions

None of the new pigments tested merit any further consideration. Zinc borate even though its initial properties are very nicely improved by a 900°C calcination, suffers severe degradation. The Pemco frits likewise have, or can be treated to have, good initial properties, but they lack ultraviolet stability. In general, all of the new pigments tested, if made into paint systems, would not be expected to compete successfully with available paint systems. No further consideration will be given to any of these pigments. In making this judgement we always consider stability to be the primary criterion of performance. Initial properties depend upon sample thickness, particle size, etc., hence usually can be simply improved upon; the same is far from true regarding improvements in ultraviolet stability.

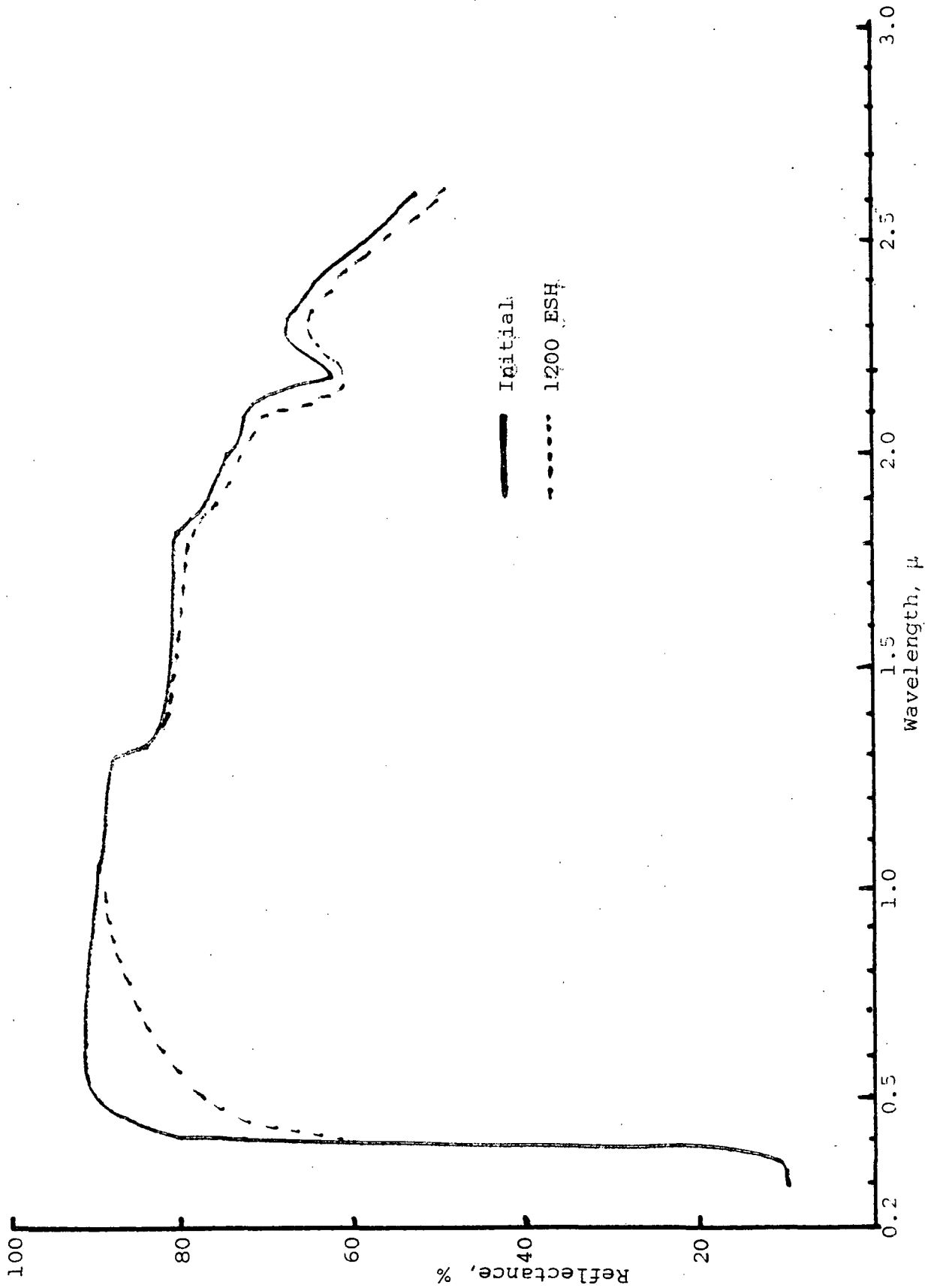


Figure 3 EFFECT OF ULTRAVIOLET RADIATION ON UNTREATED ZINC BORATE POWDER

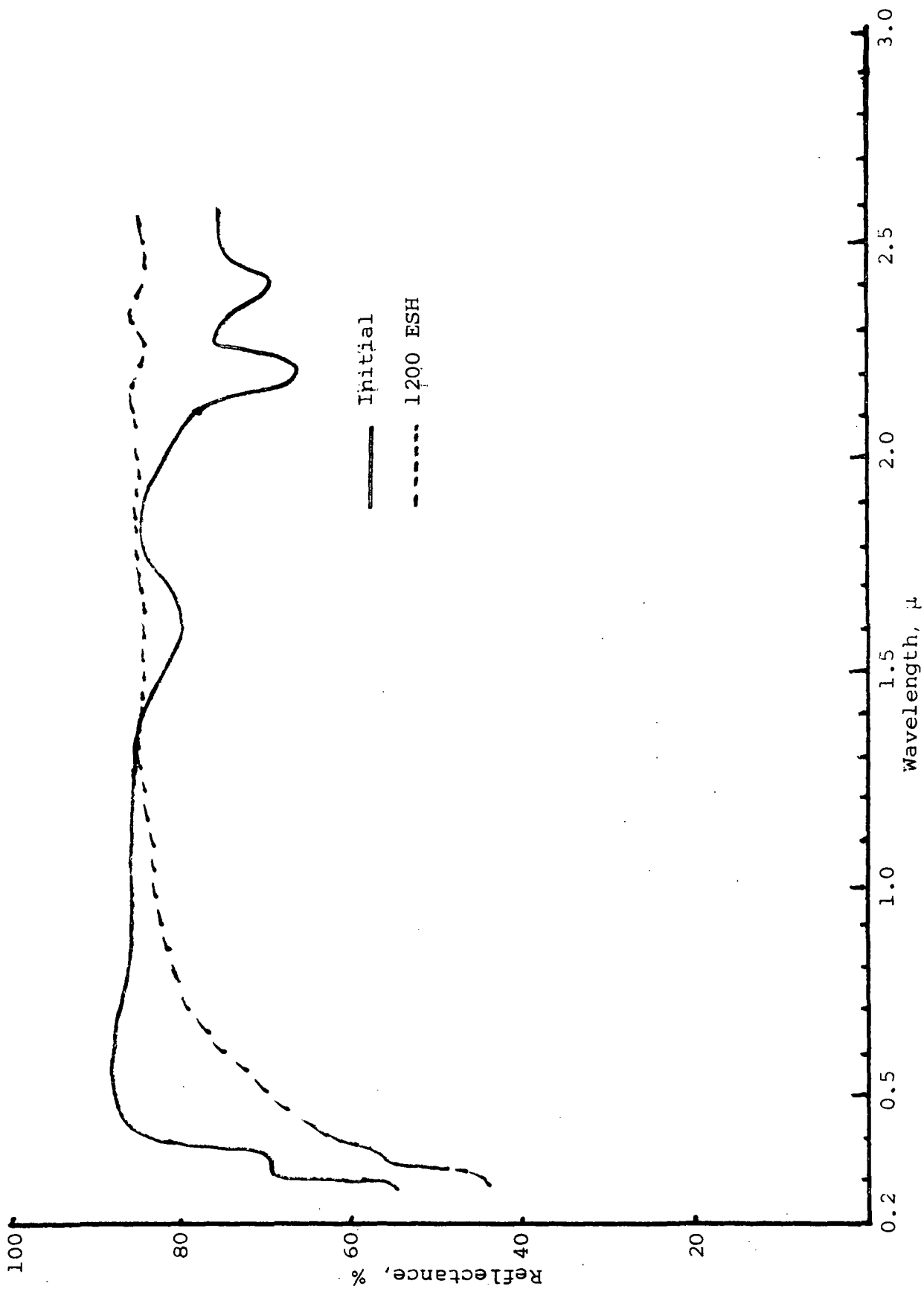


Figure 4 EFFECT OF ULTRAVIOLET RADIATION ON ZINC BORATE POWDER CALCINATED AT 900°C for 8 Hr.

2.4 Electron Paramagnetic Resonance (EPR) Investigations

2.4.1 Introduction

The research efforts conducted during this reporting period were greatly aided by the utilization of a new high-vacuum in situ irradiation facility which is mated to the EPR spectrometer. This facility is more fully described in the next section and was constructed and put into operation using IITRI in-house funds.

The efforts during this period confirm in part some of the results of earlier work, in which the conclusions were considered tentative due to poorer vacuum conditions (Ref. 1). In particular, the purposes of the investigations have been:

- a. The rationalization of the differences in optical damage in differently treated zinc orthotitanates both in terms of intrinsic defect structure and in terms of the presence of precursor-type oxides.
- b. The elucidation of the various Ti^{+3} species in Zn_2TiO_4 and of the importance of metastable species.
- c. The identification and characterization of the species responsible for the optical damage at ~ 0.9 microns.
- d. The clarification of the relationship of residual paramagnetic centers in ZnO to damage at ~ 363 nm and in the infrared.
- e. The correlation of centers detected by EPR spectroscopy with those which are optically important.

A comprehensive summary of previous EPR work is provided in Reference 1 and should be consulted for completeness.

2.4.2 Experimental

2.4.2.1 High-Vacuum In Situ Irradiation Facility

The new high vacuum equipment which will permit in situ irradiation and gas adsorbate studies under high vacuum in the EPR facility was completed and installed during this reporting period (with IITRI in-house funds). A photograph appears in Figure 5. The added equipment consists of a mounting structure

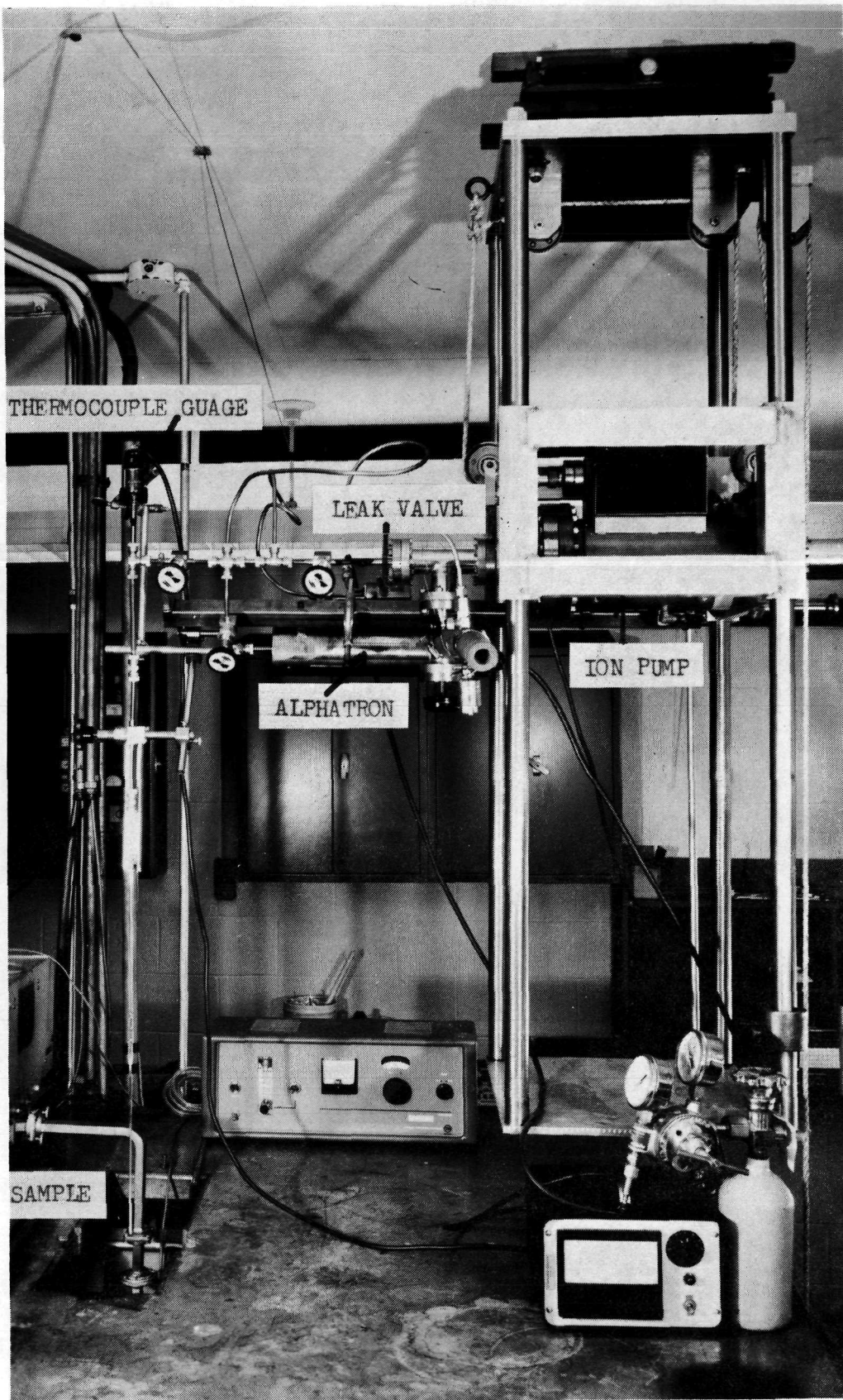


Figure 5 EPR FACILITY WITH NEW IN-SITU SAMPLE HANDLING CAPABILITY

(on the right in the photograph), a 20 liter/sec. ion pump (middle right), and valving and vacuum connections (middle left). The EPR tube (lower left) is mated to this equipment through a Cajon "O ring" connection and is easily removed and replaced. The mounting structure, which is suspended from the ceiling, is movable vertically so that the EPR tube may be raised and lowered into the Varian EPR spectrometer cavity between the pole pieces of the magnet. The latter lies below the table and is not visible in the photograph.

2.4.2.2 Samples and Materials

<u>Sample</u>	<u>Description</u>
ZnO	SP-500 New Jersey Zinc ZnO, as received
TiO ₂	Titanium Dioxide, DuPont Type FF (anatase) converted to rutile (Ref. 6).
3	Zn ₂ TiO ₄ with excess TiO ₂
B-229	Zn ₂ TiO ₄ with excess ZnO
B-454	Zn ₂ TiO ₄ with excess ZnO, Li ₂ SiF ₆ -treated

2.4.2.3 Ultraviolet Irradiation

Ultraviolet irradiation of the samples in suprasil EPR tubes was performed utilizing unfiltered light from an Osram 500 watt point-source lamp collimated with a four-inch diameter fused silica lens (focal-length four inches). The lens was placed at approximately twice the focal length from the lamp providing a one-to-one magnification of the point-source arc whose image was entirely contained within the polycrystalline sample area. Although no measurements have been made to compare the luminous flux with that provided by the IRIF facility, it is believed that overnight irradiation utilizing this collimated source provides the equivalent of 500 ESH in the IRIF.

Two configurations were utilized:

(a) Irradiation carried out for times up to an hour at 77°K in a suprasil quartz dewar placed in a Varian EPR multi-purpose cavity provided with a grating in the wall of the cavity.

(b) Irradiations carried out for longer times at ambient temperatures outside the dewar and cavity.

In both configurations, the samples were under high-vacuum in Varian suprasil EPR tubes with approximately 3mm ID. EPR measurements herein reported were carried out at liquid nitrogen temperatures, with the exception of an experiment in which metastable species were investigated.

2.4.2.4 Air or O₂ Bleaching Experiments

The admission of air or O₂ to the samples in EPR tubes was always accomplished with the samples at room temperature. In some cases this necessitated removing the sample from a dewar with liquid nitrogen in it, admitting the gas, re-pumping and then re-cooling to 77°K for EPR measurements. The bleaching experiments performed during this period were preliminary and served more of a diagnostic purpose than a detailed (dynamic) gas adsorbate EPR investigation. The way in which some of the bleaching experiments were performed thus necessitated an investigation of temperature effects and the role of metastable species to distinguish those effects from true adsorbate phenomena.

2.4.3 Results

2.4.3.1 ZnO

Untreated SP-500 ZnO gives a weak EPR signal as shown in Figure 6a. After 30 minutes of in situ irradiation at 77°K at a vacuum of 10^{-7} , the intensity is greatly increased as is shown in Figure 6b. Figure 7a shows the intensity of the $g = 1.9565$ signal after warming the irradiated material to and holding it at room temperature for 45 minutes (while under high vacuum); after then re-cooling to 77°K (for an EPR measurement), the signal intensity had decreased by about one-half (Figure 7b). Re-irradiation for 30 minutes at 77°K restored the previous (irradiation-produced) intensity (Figure 7c). Warming the sample to room temperature again and admitting O₂ at a pressure

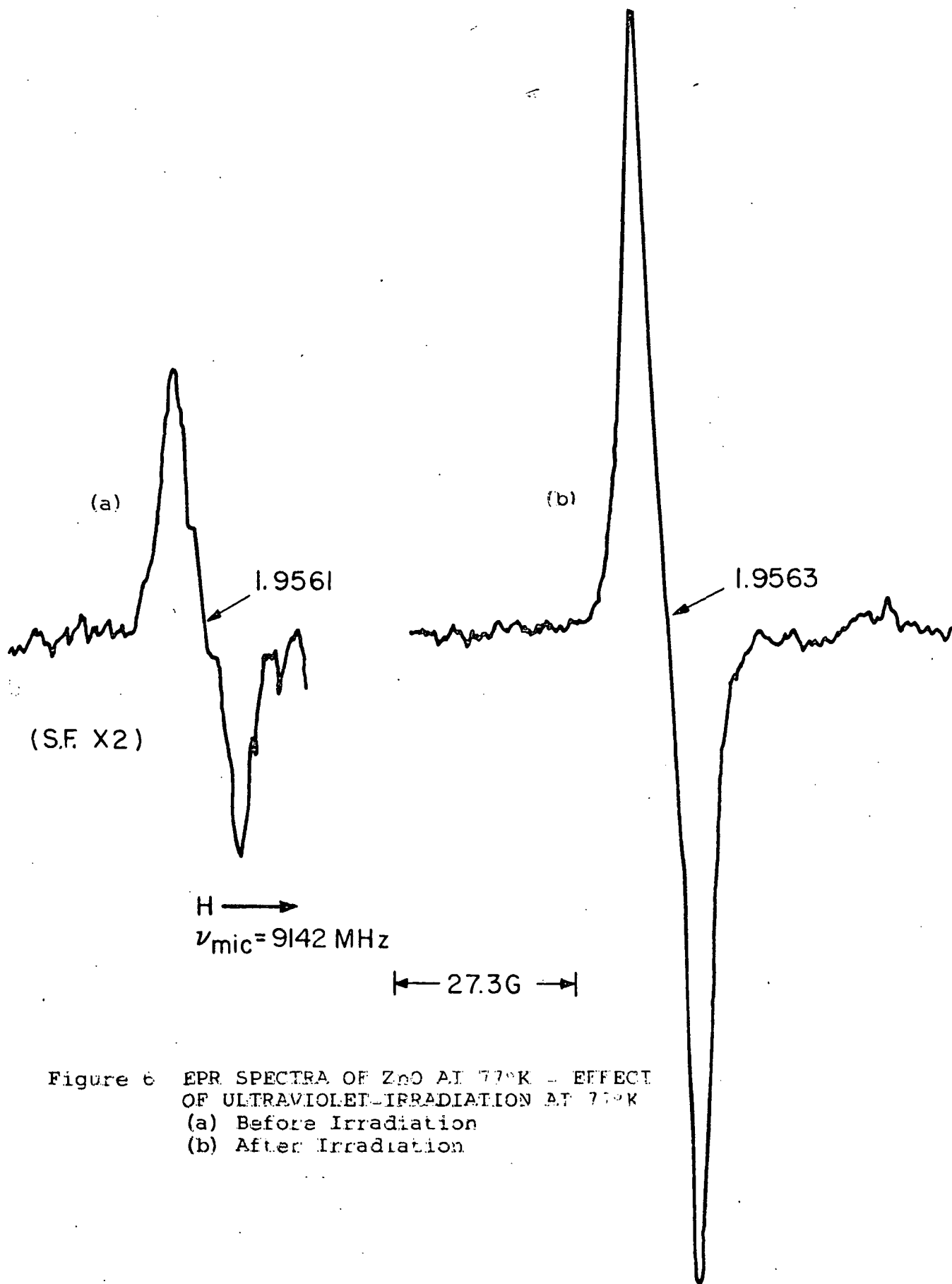


Figure 6 EPR SPECTRA OF ZnO AT 77°K - EFFECT OF ULTRAVIOLET-IRRADIATION AT 77°K
 (a) Before Irradiation
 (b) After Irradiation

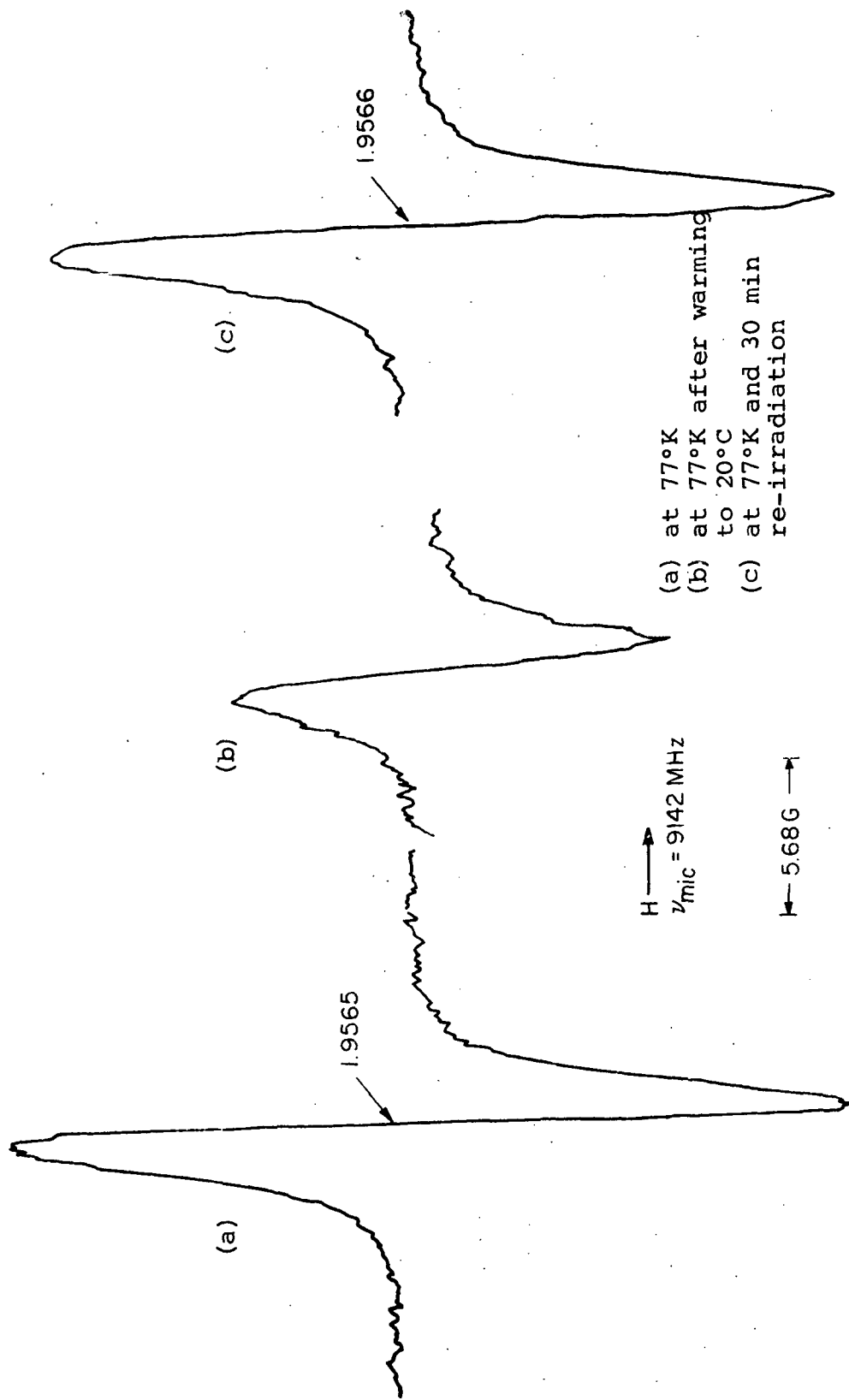


Figure 7 EPR OF ZnO AT 77°K
 EFFECT OF WARMING UV-CREATED
 CENTER TO ROOM TEMPERATURE

of ~ 0.1 torr after 15 minutes and a large decrease in the EPR signal (at 77°K) which could not be explained in terms of temperature effects. The original signal (before irradiation and O_2 bleaching) is shown in Figure 8a; after O_2 bleaching as Figure 8b indicates, the signal is actually smaller than the original signal.

2.4.3.2 Titanium Dioxide, Anatase Converted to Rutile (Ref. 1)

The EPR spectra of a titania which was partially converted from anatase to rutile at 10^{-7} torr are shown in Figure 9.

No additional centers were produced or destroyed by: (a) in-situ irradiation for 30 minutes at 77°K , (b) irradiation for 39 hours at ambient temperatures; or (c) admission of air.

2.4.3.3 Zinc Orthotitanate with Excess ZnO (IITRI Batch B-229)

2.4.3.3.1 Investigation of Metastable Species

The sample was irradiated in the EPR cavity at 10^{-7} torr and at room temperature, and the EPR spectrum was observed simultaneously. The spectrum was noisy but it was apparent that two signals not present in the ground state were created, one at $g = 2.00$ and one at $g = 1.98$. Liquid nitrogen was added to the dewar while irradiating and the signal-to-noise improved (as expected). Warming the sample to room temperature for ~ 15 minutes and re-cooling resulted in the disappearance of the $g = 1.98$ signal only. Re-irradiation at 77°K re-created the signal at $g = 1.98$; the spectra are shown in Figure 10a. After rewarming the sample to room temperature for ~ 22 minutes and re-cooling, both photo-created signals had disappeared as is shown in Figure 10b. The large signal in both spectra is the y' center(s) in ZnO.

2.4.3.3.2 Room Temperature Irradiation

The sample was evacuated to 10^{-7} torr and EPR spectra was obtained initially (Figure 11a), and after one hour room

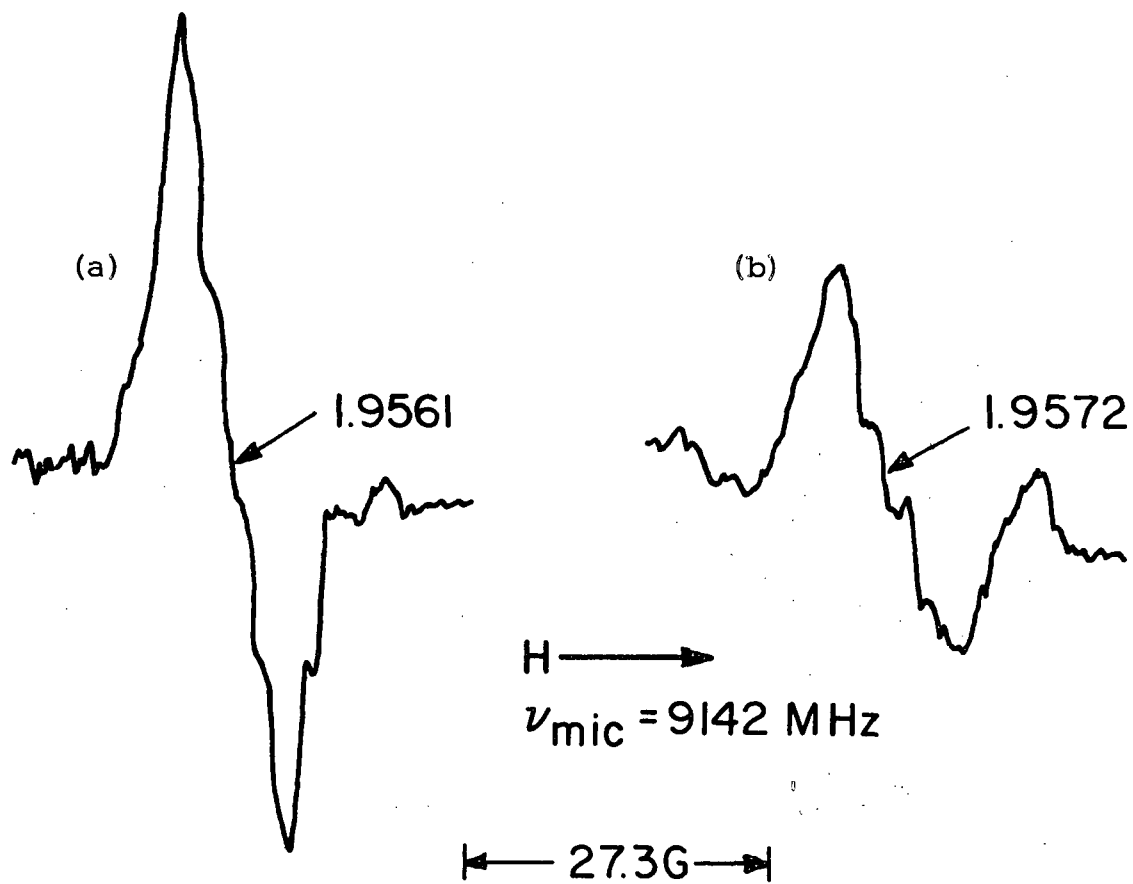


Figure 8 EPR SPECTRA OF ZnO AT 77°K - EFFECT OF O₂ (ONE TORR) ON ULTRAVIOLET-CREATED CENTER
 (a) Original, before irradiation and O₂ bleaching
 (b) After irradiation and O₂ bleaching

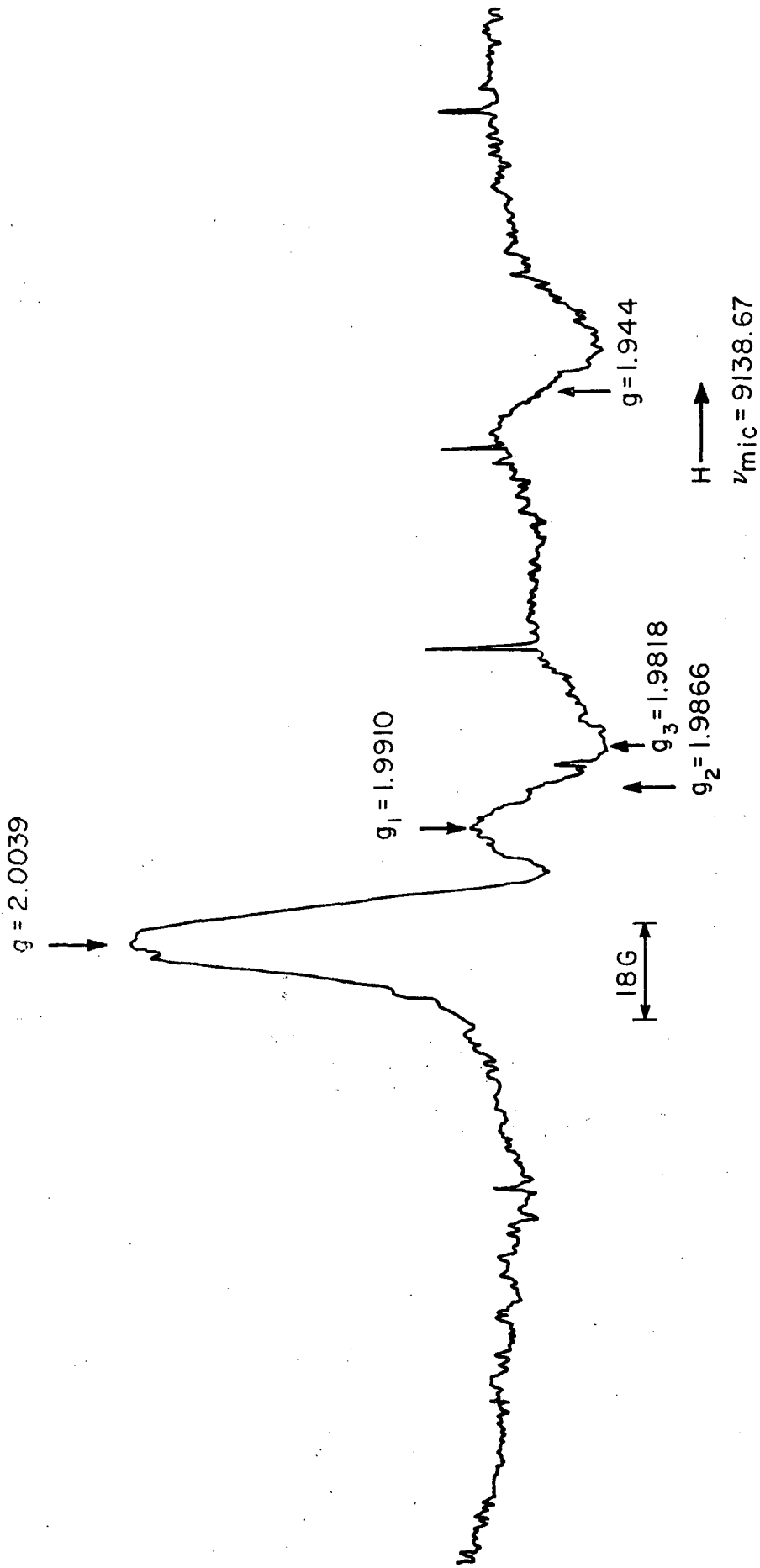


Figure 9 EPR OF FF (ANATASE) - RUTILE AT 77°K

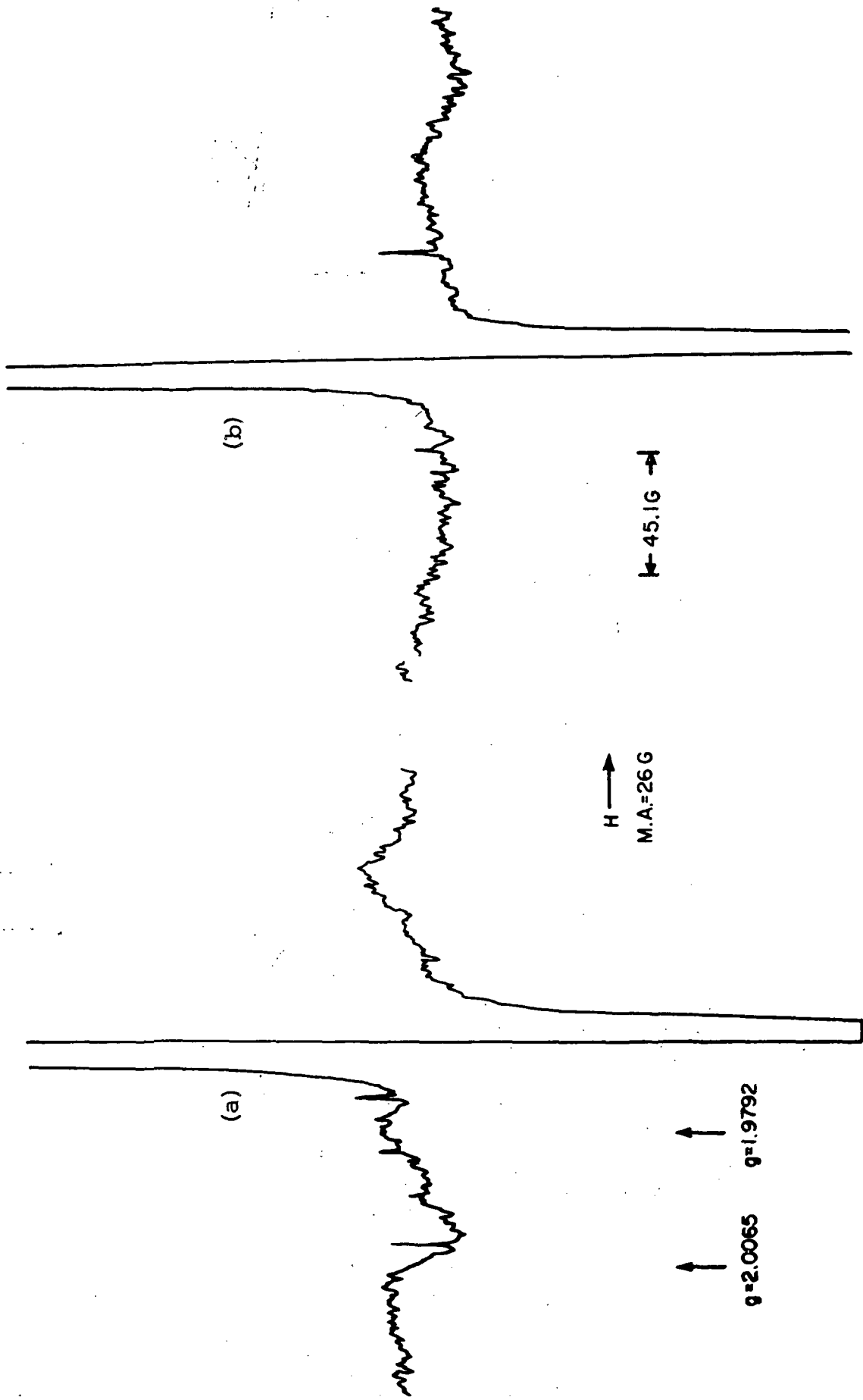


Figure 10 EPR SPECTRA OF ZnO-EXCESS PRODUCED Zn_2TiO_4 INVESTIGATION OF METASTABLE CENTERS (a) After Irradiation, (b) After re-warming to $\sim 20^\circ C$ and re-cooling to $77^\circ K$

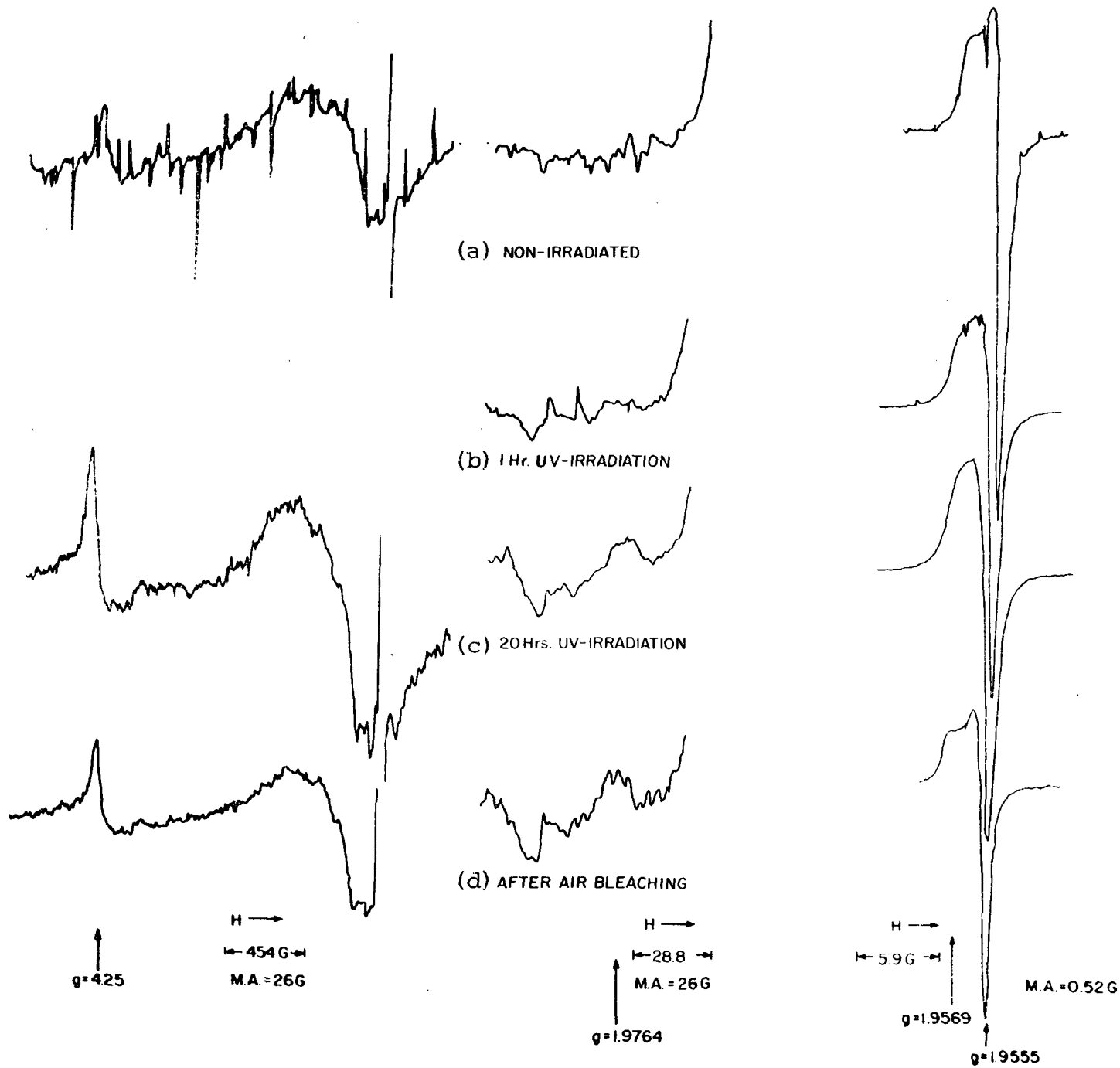


Figure 11 EPR SPECTRA OF Zn_2TiO_4 WITH EXCESS ZnO

temperature irradiation (Figure 11b), 20 hours room temperature irradiation (Figure 11c), and after admission of air at 760 torr (Figure 11d). A new signal at $g = 4.25$, which seemed to be affected by irradiation was detected but not fully investigated. Only after extensive irradiation was the center x detected, and it did not alter even after three days in air. On the other hand the signal y' attributed to centers in ZnO did indicate a photocreated, air bleachable component.

2.4.3.4 Zinc Orthotitanate with Excess ZnO, Li_2SiF_6 Treated (IITRI Batch B-454)

In contrast to the above results, this sample contains no centers attributed to ZnO and after 14 hours of irradiation at room temperature, no new centers are created. Four unidentified centers (shown in Figure 12) are observed with mean g 's of 2.0840, 2.0664, 2.0018 and 1.9572. An EPR signal at $g = 4.25$ was observed but was weaker than that found in irradiated, untreated zinc orthotitanate.

2.4.4 Zn_2TiO_4 with Excess TiO_2 (Sample No. 3)

The sample was evacuated to less than 10^{-7} torr and subjected to room temperature irradiation and subsequent air bleaching at one torr for 51 minutes. The spectra are shown in Figure 13. Figure 13a shows the spectrum of the sample prior to irradiation. In contrast to the results obtained in irradiation Zn_2TiO_4 with an excess of ZnO, 2 hour room temperature irradiation of this material created the signal at $g = 1.98$ (Figure 13b) and 19 more hours of irradiation further increased the signal (Figure 13c). Additionally, the center was partly bleached (Figure 13d) by exposure to air for 51 minutes at a pressure of one torr. Centers attributable to ZnO were not detected in Sample 3, but the center at $g = 4.25$ was intense.

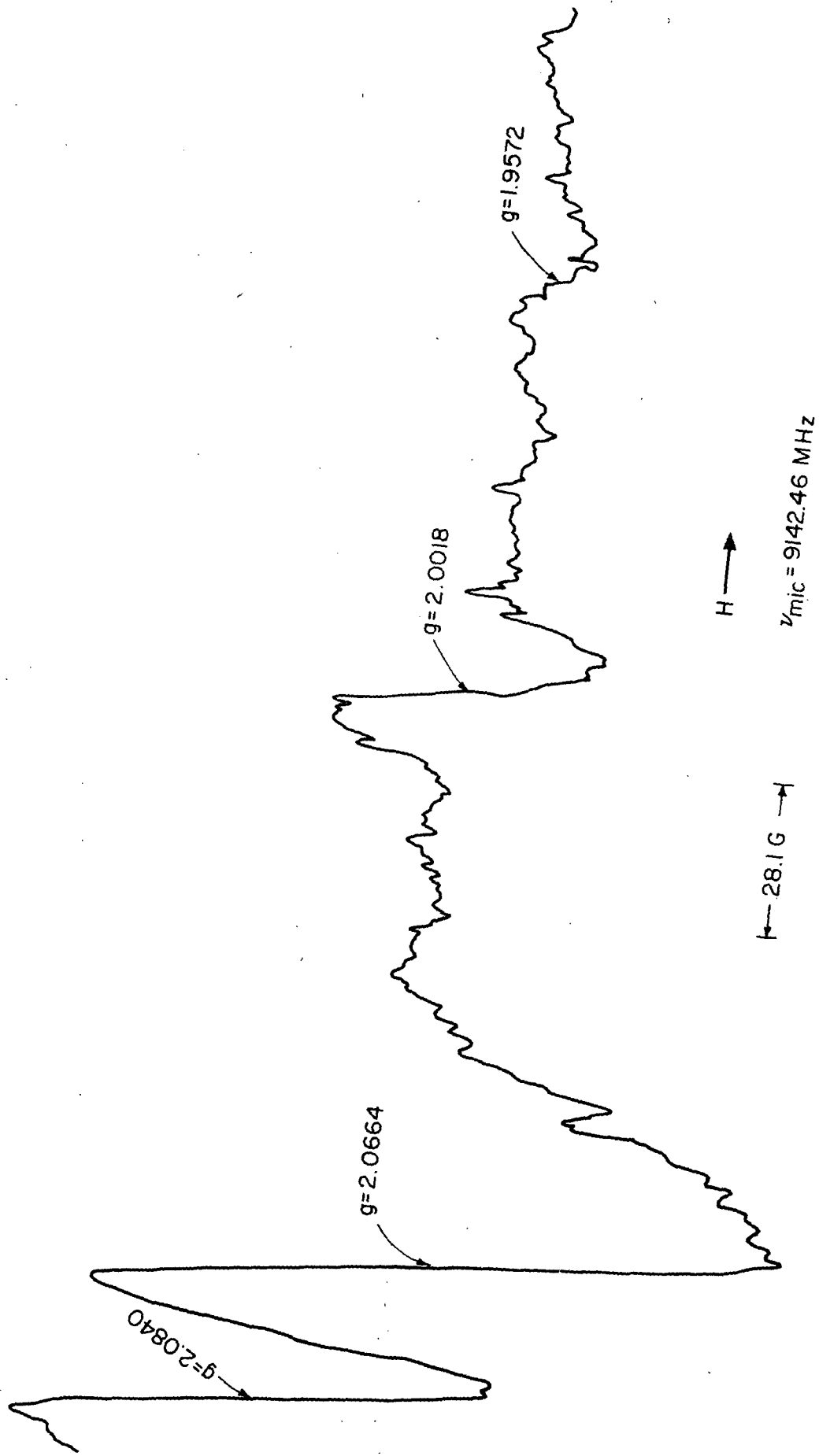


Figure 12 EPR AT 77°K OF Li_2SiF_6 -TREATED Zn_2TiO_4 (B-454)

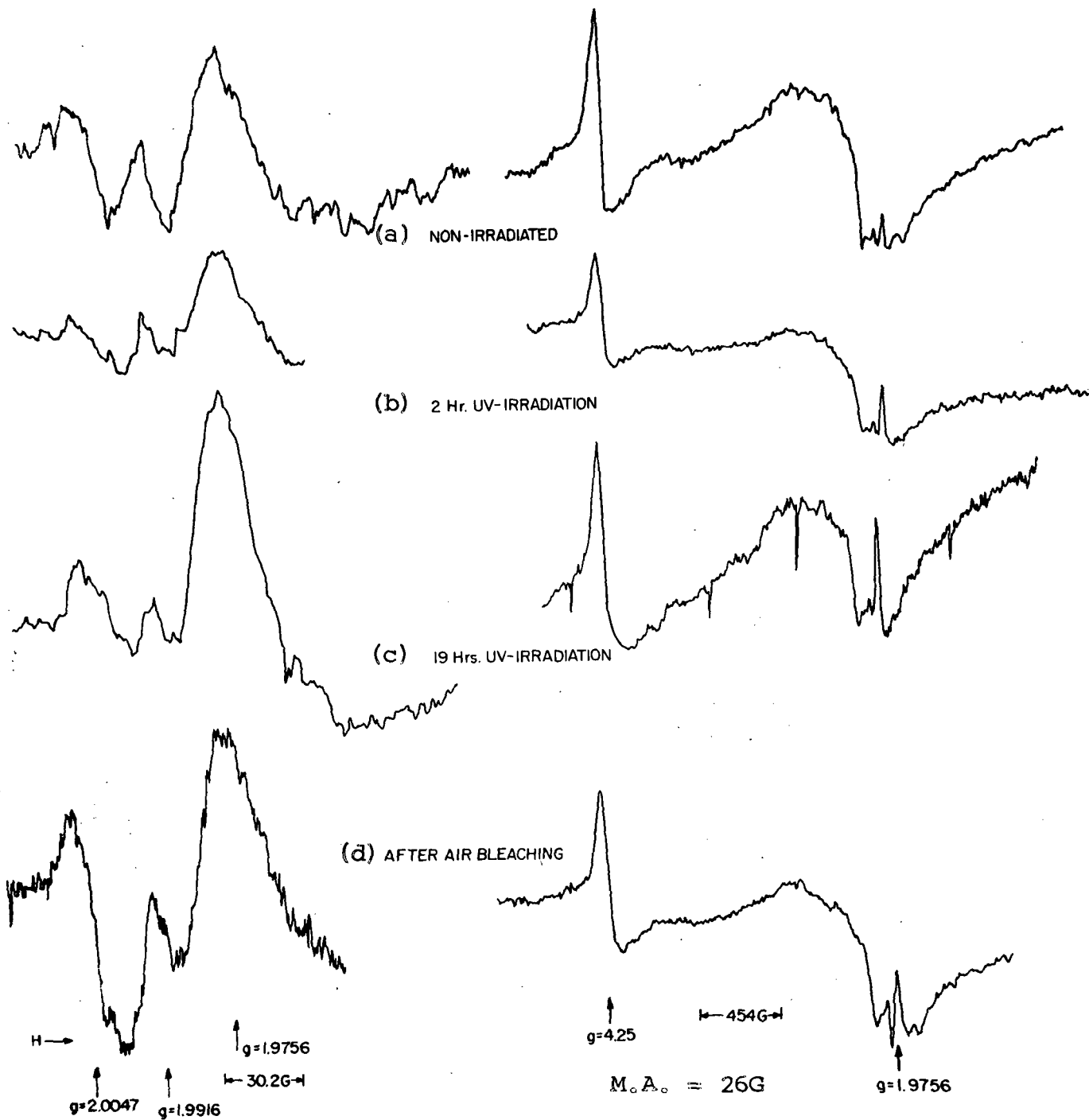


Figure 13 EPR SPECTRUM OF Zn_2TiO_4 WITH EXCESS TiO_2

2.4.5 Discussion of Results

2.4.5.1 ZnO

Unirradiated SP-500 ZnO exhibits only a weak EPR signal at $g = 1.9561$, which is identified by Geisler and Simmons (Ref. 2) as the ultraviolet-sensitive center in non-heat treated ZnO. This signal is increased by ultraviolet irradiation and is oxygen bleachable, thus suggesting that it is associated with the bleachable infrared damage in ZnO. We are reasonably certain that the center itself is not the infrared absorbing species but rather is a localized surface paramagnetic center (trap) that is produced simultaneously with the promotion of electrons to the conduction band. A summary of some of the centers found in ZnO by us and also by others is listed in Table 6. Since the sample that we investigated had not been subjected to high temperature heat-treatment, the center with a mean $g = 1.960$ (which we call "y") and the center whose g components are $g_1 = 1.9556$ and $g_{11} = 1.9569$ were not found in ZnO.

Table 6

PARAMAGNETIC CENTERS IN ZnO

<u>Center</u>	<u>How Created</u>	<u>Identification of Center</u>
$g = 1.960^*$	(donor-heat created)	Substitutional halogen
$g_1 = 1.9569^*$	Heat created	Electrons in oxygen
$g_{11} = 1.9556^*$		Anion vacancies
$G = 1.9561^{**}$	Ultraviolet created	Shallow surface trap

*Found by Kasai (as well as IITRI and others)

**Found by Geisler and Simmons

In previous reports and publications we have postulated that infrared damage in zinc oxide is due to absorption by electrons trapped in the conduction band (Ref.'s 3-5). The possibility certainly exists that a trap lying a few hundredths of an eV below the conduction band also contributes, but we have claimed that such a trap, would be filled very rapidly and that nearly all of the induced absorption would result from conduction

electrons. The ultraviolet sensitivity of the $g = 1.9561$ center and the fact that it is oxygen bleachable, together with our strong conviction that the EPR of conduction (free) electrons would be extremely difficult to detect at 77°K , make it apparent that this signal is associated with the shallow trap. Thus, the effect of O_2 bleaching is to remove electrons from the conduction band and, consistent with earlier models, and to re-oxidize the localized surface trap at $g = 1.9561$, with the ultimate formation of negatively charged oxygen species at the surface.

2.4.5.2 TiO₂

The EPR spectra of the FF anatase which was partially converted to rutile seems to be unaffected by ultraviolet irradiation, and the EPR centers found in both irradiated and unirradiated materials resemble those found in the unirradiated precursor anatase (cf Figure 15, Ref. 5). These findings, if verified, would rule out any important effect of residual TiO_2 in zinc orthotitanate - at least insofar as Ti^{+3} species (in TiO_2) might contribute to damage at 0.9 microns. An x-ray diffraction pattern of this sample indicated the presence of both forms. Anatase appeared to be predominant, but the rutile form was present to the extent of 30-40%.

2.4.5.3 Metastable Species

In the studies in which we are engaged metastable species are probably unimportant. The term metastable implies that the species is very short-lived, especially at room temperature. Hence it is very important to correlate ultraviolet-induced magnetic resonance changes with the stable optical changes. To achieve the high level of sensitivity required, EPR measurements are normally made at 77°K or lower. Consequently, if an EPR signal which is observable at 77°K disappears upon warming the sample, then it is almost certainly not related to any optical damage which persists unaltered through the same temperature change.

Zinc orthotitanate, like ZnO and TiO₂, is a large band gap semiconductor; very likely its band structure resembles that of TiO₂ more than that of ZnO. The upward curvature of the valence and conduction bands near the surface would lead us to suspect that any given type of defect would have different properties depending upon its distance from the surface compared to the band curvature. Oxygen bleaching experiments (Ref. 4) have in fact conclusively shown that in both TiO₂ and in Zn₂TiO₄ the visible-near infrared damage is only partly bleachable, yet the EPR spectra suggest that the same species; in this case Ti⁺³, are responsible for both the bleachable and unbleachable optical absorption, surface and bulk Ti⁺³, respectively.

It has now been demonstrated that a form of Ti⁺³ which is metastable can be produced by irradiation at 77°K; and that a different Ti⁺³ species is produced only after extensive irradiation at room temperature. This confirmation of metastable species clarifies some of the EPR results previously reported (Ref. 1); long-time room temperature irradiation-produced Ti⁺³ is the species which must be correlated with reflectance damage. In essence we have distinguished centers which are not optically significant from those which may be. In previous 77°K irradiation studies (Ref. 1) we found no essential EPR difference between Zn₂TiO₄ powder and Owens-Illinois paint made from it, yet a great deal of difference in the reflectance spectra was noted. At that time, however, we were looking only at metastable states, and it is now clear that these studies must be repeated using longer-time room-temperature irradiation to produce the stable EPR centers. Indeed, in the Li₂SiF₆-treated pigment no stable Ti⁺³ was detected, while metastable species were observed.

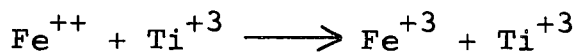
2.4.5.4 ZnO in Untreated Zn₂TiO₄ (B-229)

The ZnO remaining in Zn₂TiO₄ (B-229) after high-temperature (925°C) reaction exhibits not only the ultraviolet-sensitive center, but also the heat-created center reported by Kasai (Ref. 7). These two centers comprise what we have called y' (Ref.'s 1 and 6).

The ultraviolet sensitivity and effect of air bleaching is observed in the low-field side of the signal in the right hand part of Figure 11. We believe that the permanent non-bleachable damage at 363 nm may be associated with the high field component of y' . Note that the center we called y found in high temperature (2400°C) plasma-annealed material at $g = 1.960$, is not found in our non-plasma-annealed materials.

2.4.5.5 Zn₂TiO₄ (B-229)

The signal at $g = 4.25$ is most likely due to Fe^{+++} (Ref. 8). The observation that irradiation of the material increases the intensity of this signal suggests that the Fe^{++} form of iron may be contributing electrons which cause permanent Ti^{+3} damage according to



The presence of iron in orthotitanate may produce another complicating feature in that Fe^{++} is known to absorb at 875 nm (Ref. 9). These findings need to be more fully investigated.

2.4.5.6 Li₂SiF₆ Treated Zn₂TiO₄ (B-454)

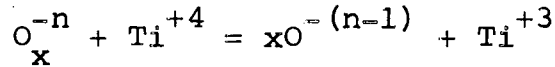
The Li_2SiF_6 -treated B-229 exhibits a less intense signal at $g = 4.25$ (less Fe^{+++}) than its (untreated) precursor (B-229) and also exhibits no ZnO-type centers. This supports our earlier thesis (Ref. 3) that the surface treatment provides either an electron scavenging effect or prevents primary ionization processes from occurring by providing an electron-rich surface. Stable Ti^{+3} was not found in these materials and the optical reflectance showed no damage at ~ 0.9 microns.

2.4.5.7 Zn₂TiO₄ with Excess TiO₂

Here the creation of partially-bleachable Ti^{+3} is apparent and is corroborating evidence for a Ti^{+3} species being responsible for the damage at 0.9 microns.

2.4.5.8 Preliminary Model for Damage in Zn₂TiO₄

A model of the optical damage in Zn₂TiO₄ at 0.9 microns is not a simple one because part of the optical damage is oxygen stable and part (the long wavelength side) is oxygen-bleachable. A model suggested earlier was based on the equation:



where O_x^{-n} stands for O_2^- , O^- , O^{-2} .

As we stated earlier Ti^{+3} defects on or near the surface will behave differently than those closer to the interior of a particle. Thus a different donor-acceptor scheme will be important for each. The table below lists a few of the more likely donors and acceptors active in the zinc orthotitanate photolysis scheme.

Table 7

LIKELY DONORS AND ACCEPTORS IN Zn₂TiO₄ PHOTOLYSIS

Donors	Acceptors
$Cl^- = Cl \cdot + e^-$	$Ti^{+4} + e^- = Ti^{+3}$
$O_x^{-n} = xO^{-(n-1)} + e^-$	$O_2 + e^- = O_2^-$
$Fe^{++} = Fe^{+++} + e^-$	$Fe^{+++} + e^- = Fe^{++}$

However complex the solid-state and surface chemistry of this material is, it is obvious that gaseous oxygen plays an important role as a "shuttle" for electrons - and this role can be drastically affected by surface treatment or plasma-treatment alteration, causing a suppression or enhancement of primary ionization processes. The remaining efforts on the current program will be devoted to further development of this model.

3. GENERAL COATINGS INVESTIGATIONS

3.1 Introductory Remarks

Thermal control surfaces for spacecraft are very likely to be only as reliable as the protective means taken to assure and maintain their cleanliness while in storage, because all surfaces and surface coatings, even the most stable, are susceptible to contamination. During the period after application of a paint to a spacecraft surface up to the time of vehicle launch, external surfaces will be exposed to numerous environments, - human handling and storage to name but two. The types of contamination are legion; the effects, however, are of two general kinds. The first is due to the fact that contamination contributes optical absorption initially and as it degrades, thus increasing α_s . The second, and by far the more important, effect is the potential acceleration of ultraviolet damage in the paint. The effect of ultraviolet radiation on an oil-contaminated white paint, for example, is to accelerate the normal degradation rate of solar absorptance. We are convinced that the reported poor - and often ten-times erratic, performance in space of many white coatings has been the direct result of contamination. We are equally convinced that the timely application of a protective coating to all exposed, critical thermal control surfaces, to be removed immediately prior to launch, should be made standard procedure. From the time that a coating is applied until the time of launch, the opportunities for contamination are virtually limitless. Since the effects of contamination are never desirable, the primary thrust of any R&D effort should be towards protection - at least until more fundamental studies of contaminants and their effects can isolate and correct the source conditions.

Accordingly, the studies conducted under this program have sought to develop protective coatings for various, representative thermal control surfaces. We have chosen four representative surfaces: S-13G, Z-93, polished aluminum and suprasil quartz. While largely arbitrary these choices cover a large spectrum of

actually used materials - from the silicones to the inorganic paint systems and from the metals to the dielectric surfaces. The ideal coating would be an universal one; it would be water-based, impermeable, adherent to all surfaces yet easily stripped even after long periods of outdoor exposure, and, of course, would leave no contamination.

3.2 Strippable Pre-Launch Protective Coatings

3.2.1 Test Results

Currently, the most promising strippable coating is Potter Paint's "Peel-astic" No. ZM-11-CC. This coating is a modified polyvinyl chloride type designed for spraying without thinning (lacquer thinner is the recommended cleaning solution). It is slightly pigmented (white). The price is \$2.45 per gallon in 55 gallon drums.

Potter Paint's formula strips well from S-13G in the range of 4-7 mils dry thickness and from Z93 in the range of 6-11 mils. These thickness tolerances are critical and must be carefully determined for each protected material before field use. No visual contamination was evident after stripping from the four substrates: S-13G, Z93, polished aluminum and suprasil quartz.

Another likely candidate is DeSoto's 843L001-910L731 which has stripped cleanly from S-13G, polished aluminum and suprasil quartz. It could not be used over Z93, however, because, like most other coatings, it adheres to it too strongly.

Because of its excellent stripping characteristics Potter Paint's No. ZM-11-CC, "Peel-astic" was applied to a series of Z93 and S-13G coupons for ultraviolet testing. The protective coating was removed from the Z93 and the S-13G surfaces just prior to installation in the IRIF. At that time the coatings had been in contact with their respective substrates a total of 37 days. Half of the coupons had been subjected to 7 days in the Atlas Weatherometer during this period of contact. Spectral reflectance values at three visible wavelengths before and after

501 ESH of ultraviolet radiation are listed in Table 8. Visible wavelengths are selected because contamination effects generally appear in the visible portion of the spectrum.

It is obvious the strippable coating left considerable contamination on the Z-93 surface; it definitely was not apparent on visual examination. Oddly enough the weatherometer treatment seemed to alleviate the poor results. Possibly the weatherometer spray leached out some of the contaminants.

The S-13G series shows hardly any difference between the controls and the test coupons. This tentatively indicates that Potter Paint's product ZM-11-CC is a satisfactory protective coating for three of the four substrates, Z93 being the exception.

We much prefer, however, that a single protective coating be applicable to all four surfaces. We thus reviewed all of the test results to date in order to select a coating which might be acceptable for use with Z93. The B.F. Goodrich combination of 60% by volume of Hycar 2679 and 40% Hycar 2600x138, referred to as "Goodrich No. 8," is a water soluble material having excellent stripping qualities over all the test surfaces, except polished aluminum. In initial screening tests Goodrich No. 8, when peeled off the vapor deposited aluminum substrates, tended to lift the aluminum. We have since raised serious doubts as to the quality of the vapor-deposited aluminum film.

Reflectance scans were made of freshly peeled surfaces of Z93 and S-13G which had been in contact with Goodrich No. 8 for five months. They indicated that initial reflectances are unaffected.

3.2.2 Summary

During the four month period ending September 5, 1971, IRIF coupons were prepared and tested to ascertain whether Potter Paint's strippable coating No. Zm-11-CC, "Peel-astic," does not leave a residue on S-13G that would affect its reflectance. As indicated in Table 8 Peel-astic leaves a residue only on Z93,

Table 8

EFFECTS OF POTTER PAINTS ON
 "PEELASTIC" STRIPPABLE COATING ULTRAVIOLET
 STABILITY OF S-13G* AND Z-93*

Test Coatings	Spectral Reflectance Values					
	400 nm		500 nm		600 nm	
	Before	After	Before	After	Before	After
<u>Z-93</u>						
a**	73.0	68.0	94.0	93.0	95.5	95.0
b**	68.5	68.5	93.4	93.0	95.0	95.0
c**	60.0	47.0	81.0	73.0	87.0	84.0
d**	63.0	55.0	81.0	79.0	87.0	86.0
e**	66.0	50.0	89.5	79.0	93.0	89.0
f**	40.5	37.0	90.0	87.0	93.0	92.5
<u>S-13G</u>						
a	66.5	----	91.0	----	91.8	----
b	66.0	65.0	90.1	88.8	91.3	91.3
c	57.0	55.0	93.0	92.0	95.0	95.0
d	75.0	66.5	93.1	90.0	94.0	91.8
e	50.0	50.0	93.5	93.0	94.5	94.5
f	76.0	71.0	93.9	92.0	93.9	92.9

*Strippable coating was removed immediately prior to IRIF ultraviolet test.

**a,b controls, no strippable coatings applied

c,d coatings to which strippable coating was applied for 5 weeks before UV testing

e,f same as c,d, except includes 1 week in Atlas Weatherometer

which, even though not apparent to the unaided eye, caused serious damage to its reflectance. S-13G was not affected.

The results of all tests to date indicate that Potter Paint's Peel-astic would be satisfactory over three of the four substrates being used in these tests, viz., Suprasil Quartz, Polished Aluminum and S-13G. The most promising protective coating for Z93 is B.F. Goodrich's formula No. 8, which is water dispersible.

Until recently we believed the Goodrich formula might prove satisfactory over all four substrates. Unfortunately it does not consistently wet the S-13G surface. In many cases numerous craters would form which left holes in the film.

Since the Goodrich No. 8 natural is transparent, a red iron oxide shading base has been prepared to give it a slight redish cast. This should assure complete coverage and removal. The base was prepared by pebble milling, a synthetic red iron oxide, Pfizer's R-2199, in Hycar 2679, a constituent of the Goodrich formula. Test coupons now being prepared will incorporate the tinted version in order to detect any detrimental effects on the reflectance of "protected" substrates.

Potter's Peel-astic has an off-white pigmentation which we believe offers sufficient contrast to S-13G that addition of a shading base is not necessary.

On the basis of tests already completed we tentatively have a coating for Z-93 and another for S-13G, either one of which can also be applied over Suprasil Quartz or polished aluminum.

3.3 S-13G Outgassing

Quite recently we submitted a series of "S-13G" paint samples to the Goddard Space Flight Center (GSFC) of the National Aeronautics and Space Administration to obtain quantitative data on outgassing. All of the paint samples submitted were prepared according to the standard S-13G formulation. The only difference in the samples was the polymer pre-treatment. Each sample was

prepared in film form and was sprayed with a very thin layer of G.E. SS-4044 primer to simulate a paint film as it would exist on (or be stripped from) a hardware surface.

The NASA-GSFC outgassing test consists of an exposure of the sample for 24 hrs to a temperature of 125°C at a pressure of less than 10^{-6} torr. The sample is weighed before and after the test to determine total weight loss (TWL). The volatile condensible material (VCM) weight loss is determined from the amount of material collected on a collector plate operated at 25°C, compared to the original film weight. We are indebted to Dr. John Park and to Dr. Ben Seidenberg of NASA-GSFC for performing these tests. Their cooperation is appreciated.

The data are shown in Table 9. The difference between TWL and VCM is obviously not consistent; in the case of standard S-13G and the pot distilled batches the ratio of TWL/VCM is ~ 3 and in the molecularly distilled batches it ranges from ~ 12 to ~ 3 . NASA-GSFC has established 1.0% as the maximum allowable TWL limit. These data show that, while all specimens pass the TWL test, standard (unmodified) S-13G and S-13G paints prepared from pot distilled RTV 602 (e.g., C6227 Lots 5, 6 and 7) do not pass the VCM test. The best performer is NASA-GSFC's Batch No. 11. Except for batches No.'s MS-6 and MS-8 the paints prepared from molecularly distilled RTV 602 passed the VCM test. From the data in Table 9 it is obvious that the better product is obtained when higher temperatures at longer times are employed in the distillation. The results, however, can be partly understood on the basis of the quantity of material processed. In the pot distillations performed under IITRI project C6227 (Ref. 14) the batch size was 20 lb; in the NASA-GSFC distillation process technique, it is probably of the order of one pound; and in the molecular distillation process it is a very thin film ($\sim 1/16$ ") which gets heated. The volatiles must travel very different path lengths in each case. Since the "vapor pressure" of the volatile

Table 9

RESULTS OF S-13G OUTGASSING TESTS

Sample Description ¹	Temperature/Time °C/hr	Viscosity ² (Centipoises)	Thickness (mils)	Total ³ Weight Loss, %	Volatile ³ Condensibles %
Standard (unmodified)		1000	11	0.767	0.279
C6227-5	145/24	1350	17	0.781	0.244
C6227-6	160/24	1650	11	0.711	0.221
C6227-7	175/24	3350	18	0.808	0.256
GSFC Batch #11	150/24	2400	12	0.360	0.017
M.S. #4	200/315	1500	21	0.427	0.034
M.S. #5	160/2.3	1250	23	0.484	0.088
M.S. #6	160/1.0	1225	17	0.480	0.120
M.S. #7	{160/0.15 } 210/1.0	1450	14	0.409	0.060
M.S. #8	140/0.5	1225	18	0.480	0.110

Notes:

¹The descriptions pertain to the RTV 602 silicone - whether and how modified.

²The viscosity is that of the silicone polymer.

³The value given is the average of two determinations.

species increases with temperature, the composition of the VCM likewise varies with temperature.

There are many important considerations in the materials outgassing problem, but with regard to possible modifications, these are the two principal ones: first, changes other than reductions in TWL and VCM occur, and second, the relative composition of that which is termed TWL and that which is VCM is important. In regard to the first consideration, it is our conviction that for large quantity production, say, 10 pounds per batch, pot distillation is the least effective technique for outgassing reduction. In the pot distillation of large quantities, higher pot temperatures and longer distillation times result in higher polymer viscosities without significant improvement in VCM. For the process of making S-13G the ideal viscosity of RTV 602 is about 1300-1500 centipoise (cps). Variations of as much as 500 cps units away from this range are readily handled.

The thermal removal of low-outgassing components of RTV 602 inevitably increases its viscosity. The magnitude of the increase in general depends upon many factors, including temperature, temperature history, vacuum level, distillation method and quantity per batch. From a paint technology point of view, as viscosity increases S-13G exhibits increasingly better physical properties - better adhesion, increased film toughness, and less catalyst demand - up to a point! Beyond 2000 cps, the shelf life of the paint is sharply affected, and adhesion also suffers. Viscosities in excess of 2500 are not tolerable; desirable paint properties are seriously deteriorated, and it becomes nearly impossible to meet applicable NASA specifications (NASA 10M01835 and 10M01836).

Outgassing, the second consideration, obviously can originate in both the pigment and the vehicle. In the case of S-13G we believe that the largest component of the TWL, perhaps up to 90%, is due to water from the S-13G pigment; the pigment making process involves several successive aqueous steps, but does not include a

calcination to remove absorbed (or adsorbed) water. The remainder of the outgas products includes low molecular weight components of the polymer, and, depending upon cure conditions, some retained solvent and unreacted catalyst.

Finally, of the two methods tried the more effective for producing large scale (10-100 pounds per batch) quantities of a low outgassing RTV 602 silicone is molecular distillation. The process is much more easily controlled, and thus yields much more reproducible results. If outgassing of water becomes objectionable a calcination step could be added to the process.

3.4 Owens-Illinois 650 Glass Resin Improvement Study

A composition of Owens-Illinois 650 glass resin (O-I 650) was prepared containing 4.8% (by weight) polydimethylsiloxane. The latter was prepared as an internal plasticizer by the method reported in the previous triannual report (Ref. 1). Paints were formulated from standard O-I 650 and from the "modified" O-I 650, using zinc orthotitanate as the pigment at 36.5% PVC. Both of these paints are soft to the finger nail after an air dry. Adhesion to water break-free panels with either paint was not better than to solvent cleaned panels.

Impact testing of paint films air-dried for 2 days indicated that the "standard" paint would sustain a reverse impact of 6 lb; the "modified" paint, less than 2 lb. Baking overnight at 200°F, however, improved the impact resistance of the standard paint film (~12 lb) and dramatically improved that of the "modified" film (>12 lb).

Tests of 41% PVC films indicated a lowered adhesion of both standard and modified films. The "modified" film, however, when baked at 200°F overnight displayed a better gloss (implying less binder demand) than the standard film; and it formed a much tougher film than that of the standard paint. Films baked at 350°F were not improved, and in fact became somewhat brittle.

The addition of an internal plasticizer to O-I 650 glass resin definitely prevents the aging effects which have been a major problem with this material. The need to bake the "modified" paint film at a modest temperature should not be a major deterrent to its use, should it prove out in all other aspects.

3.5 Paint Development

A paint consisting of Z93 pigment (calcined SP500 ZnO) and of Lithium Silicate (Lithcoa's Lithsil #4) was prepared using the standard Z93 formulation. When subjected to ultraviolet radiation in IRIF Test No. I-45, the coating displayed excellent stability and, even though the formulation was not optimized for maximum reflectance, the initial solar absorptance was 0.161. The $\Delta\alpha_s$ was 0.006 in 1100 ESH. Figure 14 shows the reflectance spectra of this paint. Compared to Z93 (Figure 15), the lithium silicate paint exhibits approximately the same amount of binder damage as potassium silicate. The absence of infrared reflectance changes suggests that there is little or no photodesorption of water from lithium silicate. Although the demonstrated stability is of great interest, the paint tends to chalk. Hence, a method of reducing this effect will be necessary.

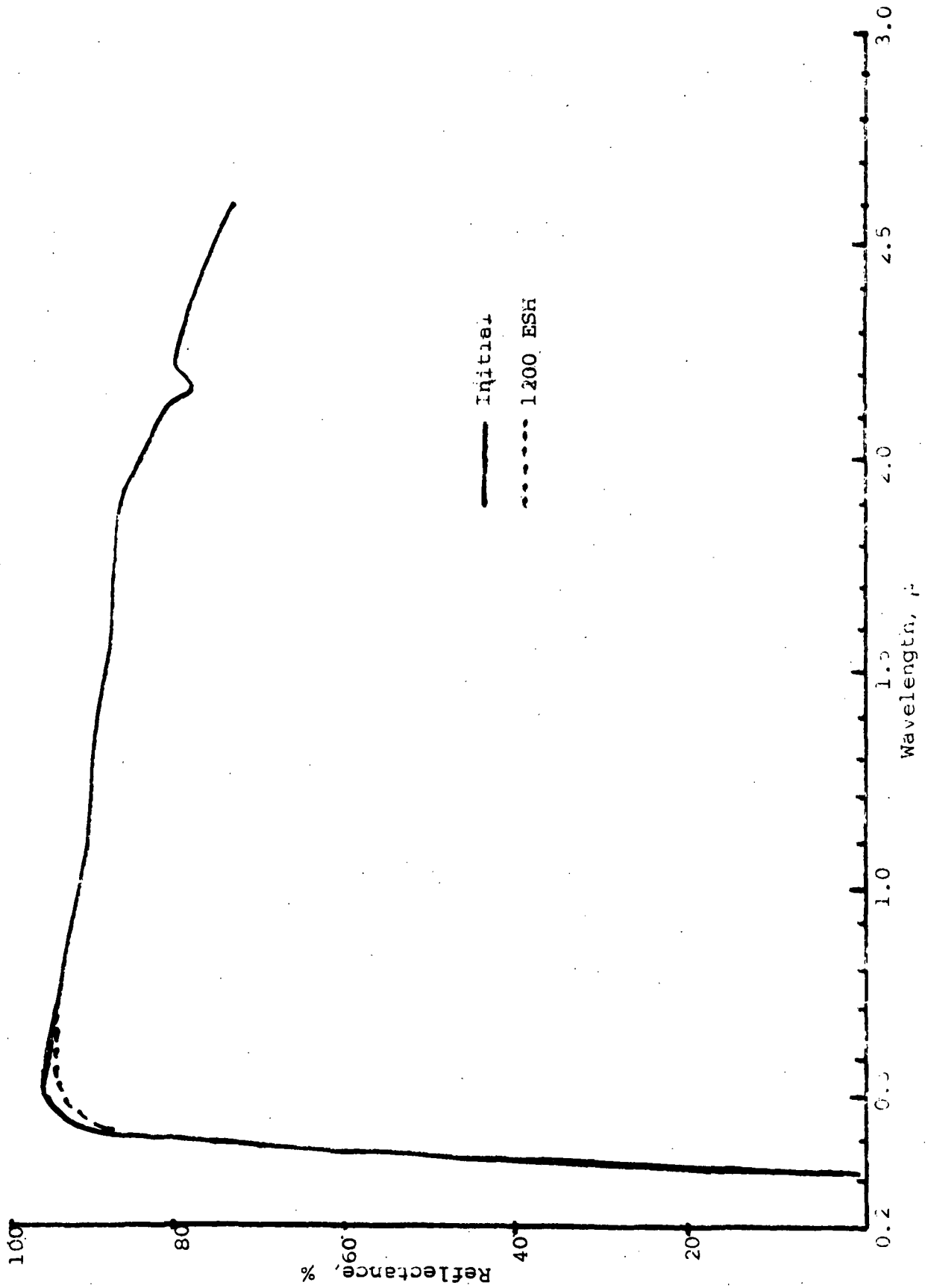


Figure 14 EFFECT OF ULTRAVIOLET RADIATION ON A ZINC OXIDE PIGMENTED LITHIUM SILICATE PAINT

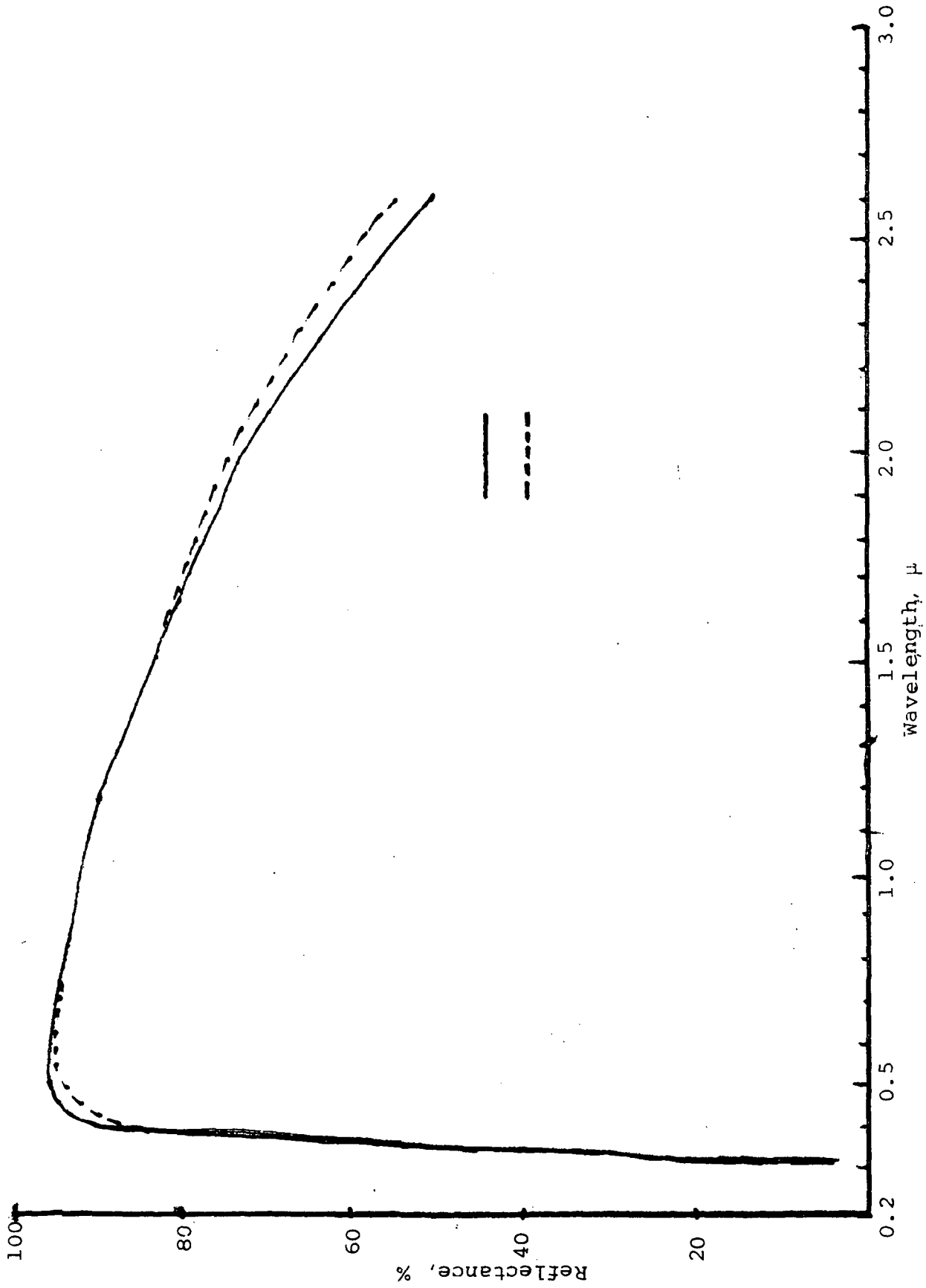


Figure 15 EFFECT OF ULTRAVIOLET RADIATION ON Z-93

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