

General Disclaimer

One or more of the Following Statements may affect this Document

- This document has been reproduced from the best copy furnished by the organizational source. It is being released in the interest of making available as much information as possible.
- This document may contain data, which exceeds the sheet parameters. It was furnished in this condition by the organizational source and is the best copy available.
- This document may contain tone-on-tone or color graphs, charts and/or pictures, which have been reproduced in black and white.
- This document is paginated as submitted by the original source.
- Portions of this document are not fully legible due to the historical nature of some of the material. However, it is the best reproduction available from the original submission.

IITRI



Report No. IITRI-U6002-63
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

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

FACILITY FORM 602

N69-29596

(ACCESSION NUMBER)		(THRU)	
37			
(PAGES)		(CODE)	
NASA-CR-102203		18	
(NASA CR OR TMX OR AD NUMBER)		(CATEGORY)	

Report No. IITRI-U6002-63
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE
THERMAL-CONTROL COATINGS

November 1, 1967 through February 29, 1968

Contract No. NAS8-5379
Funded Under Code 124-09-18-05-04-25-8-004-028-2510
IITRI Project U6002

Prepared by

G. A. Zerlaut

G. Noble

of

IIT RESEARCH INSTITUTE
Technology Center
Chicago, Illinois 60616

to

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

Copy No. _____

April 15, 1968

IIT RESEARCH INSTITUTE

Table of Contents

	Page
Foreword	ii
I. INTRODUCTION	1
II. ZINC ORTHOTITANATE STUDIES: REACTIVE ENCAPSULATION	3
A. Space Solar-Simulation Parameters Employed	3
B. Zinc Orthotitanate Paints - Materials Preparation	4
C. Results of Space-Simulation Testing	5
III. EPR OF ZINC ORTHOTITANATE	19
A. Introduction	19
B. Irradiation	19
1. ZnO (SP500)	20
2. ZnO (Potassium Silicate-Treated)	20
C. Spectrometer Sensitivity	21
D. EPR Measurements	22
1. Characteristics of the Spectrum	22
E. Interpretation of EPR Spectra	22
1. Powder-Like Shapes	22
2. Qualitative Interpretation	26
3. Interpretation of Integrated Line	26
F. Comparison of Resonances	27
G. Zinc Orthotitanate: Zn_2TiO_4	30
IV. SUMMARY AND CONCLUSIONS	32
A. Zinc Orthotitanate Coatings	32
B. Solid-State Studies	33
References	34

FOREWORD

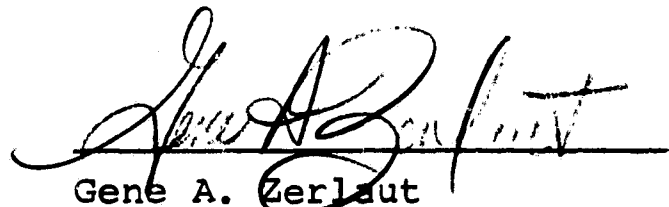
This is Report No. IITRI-U6002-63 (Triannual Report) of IITRI Project U6002, Contract No. NAS8-5379, entitled "Investigation of Environmental Effects on Coatings for Thermal Control of Large Space Vehicles." This report covers the period from November 1, 1967 through February 29, 1968. Previous Triannual 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; February 28, 1967; September 22, 1967 and January 15, 1968.

Major contributors to the program during this period include Gene A. Zerlaut, project leader; William C. Courtnry, consultation on vacuum problems; Robert Boutin, coating and specimen formulations; George Kimura, vacuum technology and space simulation tests; Dr. Gordon Noble, solid-state studies on zinc orthotitanate; Frederick O. Rogers, general paint technology and zinc orthotitanate studies; and Henry DeYoung, reflectance measurements and space simulation tests. The work reported herein was performed under the technical direction of the Research Projects Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

Prior to March 15, 1966, this contract was funded under Codes 124-09-05-26-04, 124-09-05-00-14, 933-50-01-00-00 and 908-20-02-01-47.

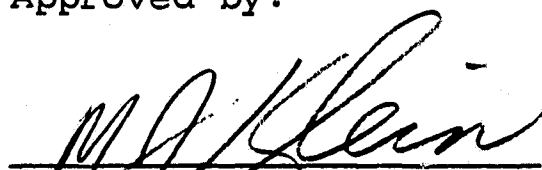
Respectfully submitted, .

IIT RESEARCH INSTITUTE



Gene A. Zerlaut
Manager
Polymer Chemistry Research

Approved by:



M. J. Klein
Director
Chemistry Research

IIT RESEARCH INSTITUTE

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

I. INTRODUCTION

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

The relative emphasis on each major task has varied during the course of the program according to the urgency of the various problems elucidated by our investigations as well as the availability of both funds and personnel.

The work reported in the last Triannual Report (IITRI-U6002-51) consisted of: (1) a review of continued studies on Owens-Illinois 650-resin paints pigmented with silicate-treated zinc oxide and experimental zinc orthotitanate; (2) a discussion of models for sensitized photodegradation; and, (3) electron spin resonance examination of selected zinc orthotitanate powders.

A zinc oxide-pigmented methyl silicone coating was prepared that possessed the greatest stability to ultraviolet irradiation that has been obtained with a white coating to-date. The paint, designated A-429-1, was pigmented with potassium silicate-treated ZnO that was washed with 3% sodium acid phosphate prior to incorporation into the paint.

IIT RESEARCH INSTITUTE

Although a "stable" zinc orthotitanate has been prepared by carrying out the synthesis at a temperature of 1050°C, followed by recalcination of the ZnO-extracted material at 1050°C, the consequential necessity for de-aggregation and the extreme hardness of the resultant pigment are problems that have not been resolved (ref. 1). The intense grinding required to de-aggregate and disperse the high-temperature product results in the creation of "instability" in the pigment -- instability that is originally precluded by the lower surface free energy that is obtained by the high-temperature reaction employed.

The concept of reactive encapsulation using sodium acid phosphate, a procedure that was successfully employed with ZnO, was employed as a possible means of securing a "stable" material at a lower reaction temperature -- thus avoiding the necessity for severe grinding because of the consequently softer, less-aggregated pigment. The experimental treatment with acid phosphate was partially successful. Both phosphate treatment and recalcination improved stability.

A simplified model for reactive encapsulation of zinc oxide was discussed. The barrier mechanism presented itself most prominently. When the surface is treated with potassium silicate, it was proposed that the O_2^- is displaced by silicate which is bound much more tightly because of the higher charge. When the electron hole pair is produced in the boundary, no oxygen is therefore present for photodesorption. A similar mechanism was suggested for the protective tendency exhibited

by the phosphate ion with a deficiency of electrons as a result of the acidity of the acid phosphate, raising the energy required for conduction electron formation.

This report is devoted to the discussion of further research on zinc orthotitanate. The first section (Section II) deals with the formulation and testing of acid phosphate-treated zinc orthotitanate; the second section (Section III) deals with additional studies on the electron spin resonance spectra of decorated zinc orthotitanates.

Two other areas of research that received extensive attention during this report period were: (1) a literature search and the formulation and testing of Owens-Illinois 650 paints pigmented with promising new classes of pigments, and (2) the design of a combined-irradiation-source (protons, electrons and ultraviolet) attachment for the IRIF II space-simulation facility. Both of these studies will be discussed in detail in the next Triannual Report.

II. ZINC ORTHOTITANATE STUDIES: REACTIVE ENCAPSULATION

A. Space Solar-Simulation Parameters Employed

The space-solar-simulation test that was completed during the period covered by this report was performed in IRIF II (IRIF Test 2-1). IRIF II is identical to IRIF I (ref. 2) except that it possesses an improved sample-transfer mechanism. The new transfer mechanism is operated by a cam rather than the rack and pinion employed in IRIF I.

IIT RESEARCH INSTITUTE

A nominal solar factor of four (4X) sun intensities was employed during test 2-1 utilizing a 5000-watt Hanovia mercury-xenon ultraviolet burner. This solar factor was achieved at a lamp-to-sample distance of 48 cm at 4000-watt operation of the power supply.

B. Zinc Orthotitanate Paints - Materials Preparations

The concept of reactive-surface treatment of zinc oxide was adapted to our studies of zinc orthotitanate. All paints prepared from treated pigment were formulated with Owens-Illinois Type 650 "Glass" resin; however, two untreated zinc orthotitanate paints were formulated with potassium silicate (Sylvania Electric's PS7) as the binder.

Experimental

A batch of zinc orthotitanate was prepared by the method, and in the proportions described, in Tri-annual Report No. IITRI-U6002-47 (ref. 3, p. 11). The furnace temperature was 925°C and the reaction time was ca. 16 hr.

A portion of the pigment, without any further modification, was used to make a grind in PS7 potassium silicate to the same formula that is used in IITRI's Z93 thermal-control coating (e.g., at a pigment-binder ratio, PBR, of 4.3) and for the same length of grind.

The Z93-control coating was applied to specimen #1 and the analogous formulation of untreated, unextracted zinc orthotitanate was applied to specimen #2.

The remaining zinc orthotitanate pigment was divided into two portions; one portion was treated directly with a 2% solution of sodium acid phosphate without extracting the residual zinc oxide, and the other portion was extracted with acetic acid to remove the zinc oxide.

The phosphate treatment of the unextracted pigment consisted of slurring 30 g of the pigment for 30 min in 100 ml of a hot (boiling) solution of NaH_2PO_4 . The pigment was then filtered, washed thoroughly and dried for 16 hr at 220°F. Part of this pigment was ground in Owens-Illinois Type 650 "Glass" resin to 33% pigment volume concentration (PVC); this coating was applied to specimen #7. The balance of this portion of the phosphate-treated zinc orthotitanate was heat treated for 20 hr at 650°C, ground in Owens-Illinois Type 650 "Glass" resin at 33% PVC and applied to specimen #8.

The extraction of the residual zinc oxide from the zinc orthotitanate was accomplished by the method outlined in the last Triannual Report, No. IITRI-U6002-59 (ref. 4, p. 11). One part of this extracted pigment was ground in PS7 potassium silicate to the same formula as Z93 (RBR of 4.3) and applied to specimen #3. The balance of the extracted pigment was divided into two portions. One portion was simply heat treated at 650°C and then ground in the Owens-Illinois 650 resin at a PVC of 33%; it was then applied to specimen #6. The other portion was phosphate treated as described above and was then, in turn, divided into two equal portions. One portion was formulated directly into an Owens-Illinois 650-resin paint at 33% PVC and applied to specimen #4. The other portion was heat treated at 650°C and then formulated into an Owens-Illinois 650-resin paint at 33% PVC; it was then applied to specimen #5.

C. Results of Space-Simulation Testing

The results of space-simulation testing in IRIF test 2-1 are given for each of the zinc orthotitanate paints in Table 1. The results are given as an increase in solar absorptance as a function of exposure to ultraviolet in vacuum. The change in hemispherical spectral reflectance is shown for these same zinc orthotitanate paints in Figures 1 through 8. (It should be noted that the spectral data are presented as a function of equal-energy increments.)

Table 1

EFFECT OF UV IRRADIATION IN IRIF-II ON SEVERAL ZINC ORTHOTITANATE
THERMAL-CONTROL SURFACE COATINGS (IRIF-II Test 2-2)

Specimen No.	Description	Exposure* (ESH)	Solar Absorptance			
			α_1	α_2	α_s	$\Delta\alpha_s$
1	Z93 Control	0	.129	.036	.165	--
		70	.135	.033	.168	.003
		600	.148	.032	.180	.015
2	Zn ₂ TiO ₄ /PS7 (Unextracted)	0	.114	.060	.174	--
		70	.120	.055	.176	.002
		600	.146	.059	.205	.031
3	Zn ₂ TiO ₄ /PS7 (Extracted)	0	.107	.079	.186	--
		70	.117	.073	.190	.004
		600	.131	.070	.201	.015
4	Zn ₂ TiO ₄ /O-I 650 (Extracted) (Hot acid phosphate)	0	.113	.092	.205	--
		70	.132	.096	.228	.023
		600	.149	.110	.259	.054
5	Zn ₂ TiO ₄ /O-I 550 (Extracted) (Hot acid phos. + Calcined)	0	.127	.102	.229	--
		70	.132	.103	.235	.006
		600	.138	.114	.252	.023
6	Zn ₂ TiO ₄ /O-I 650 (Extracted) (Calcined)	0	.112	.088	.200	--
		70	.121	.097	.218	.018
		600	.129	.109	.238	.038
7	Zn ₂ TiO ₄ /O-I 650 (Unextracted) (Hot acid phosphate)	0	.130	.096	.236	--
		70	.141	.099	.240	.014
		600	.140	.104	.244	.018
8	Zn ₂ TiO ₄ /O-I 650 (Unextracted) (Hot acid phos. + Calcined)	0	.132	.092	.224	--
		70	.135	.101	.236	.012
		600	.140	.108	.248	.024

*The nominal solar factor was 4X ultraviolet intensities.

Examination of the data presented in Table 1 and in Figure 1 shows that Z93 exhibited a considerably greater $\Delta\alpha_s$ (0.015) in 600 ESH of mercury-xenon irradiation than is normally observed for Z93. More work must be performed with the mercury-xenon source to determine the reasons for the greater damage. However, in the meantime we are assuming that the difference is due to increased energy available in the mercury-xenon source (compared to the A-H6 mercury-argon source) in the region below 225 nm where potassium silicate absorbs ultraviolet.

The potassium silicate-based zinc orthotitanate paints exhibited stabilities that were far superior to the Owens-Illinois 650-resin paints formulated from extracted and unextracted zinc orthotitanate that were prepared by the identical synthesis procedure. In an earlier test (ref. 4, p. 14), an unextracted zinc orthotitanate specimen exhibited an increase in solar absorptance of 0.108 in 550 ESH of AH-6 mercury-argon irradiation. The $\Delta\alpha_s$ of 0.031 exhibited by the specimen pigmented in PS7 potassium silicate indicates that potassium silicate plays a strong role in preventing the bleachable damage exhibited by Zn_2TiO_4 in the Owens-Illinois 650-resin paint. This is made abundantly clear if one examines the character of the spectral damage, which is shown in Figure 2, and compares it to the classical damage exhibited by zinc orthotitanate (ref. 4, p. 14). The spectra of the damaged Zn_2TiO_4 -pigmented Owens-Illinois 650 resin is shown in Figure 3 for the purposes of illustration. Examination of these two spectra show

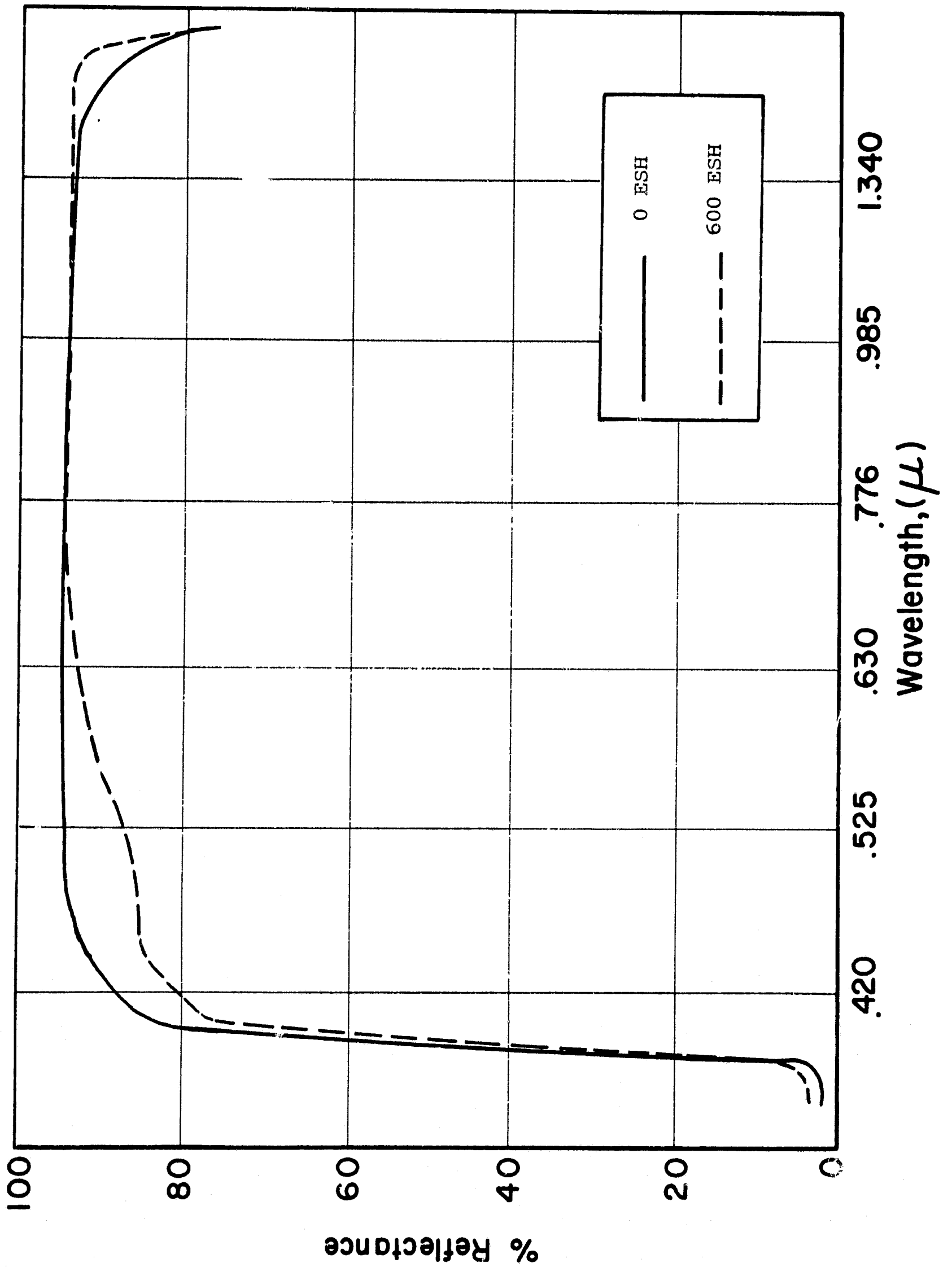


Figure 1: REFLECTANCE OF Z93 IRRADIATED FOR 600 ESH IN IRIF II

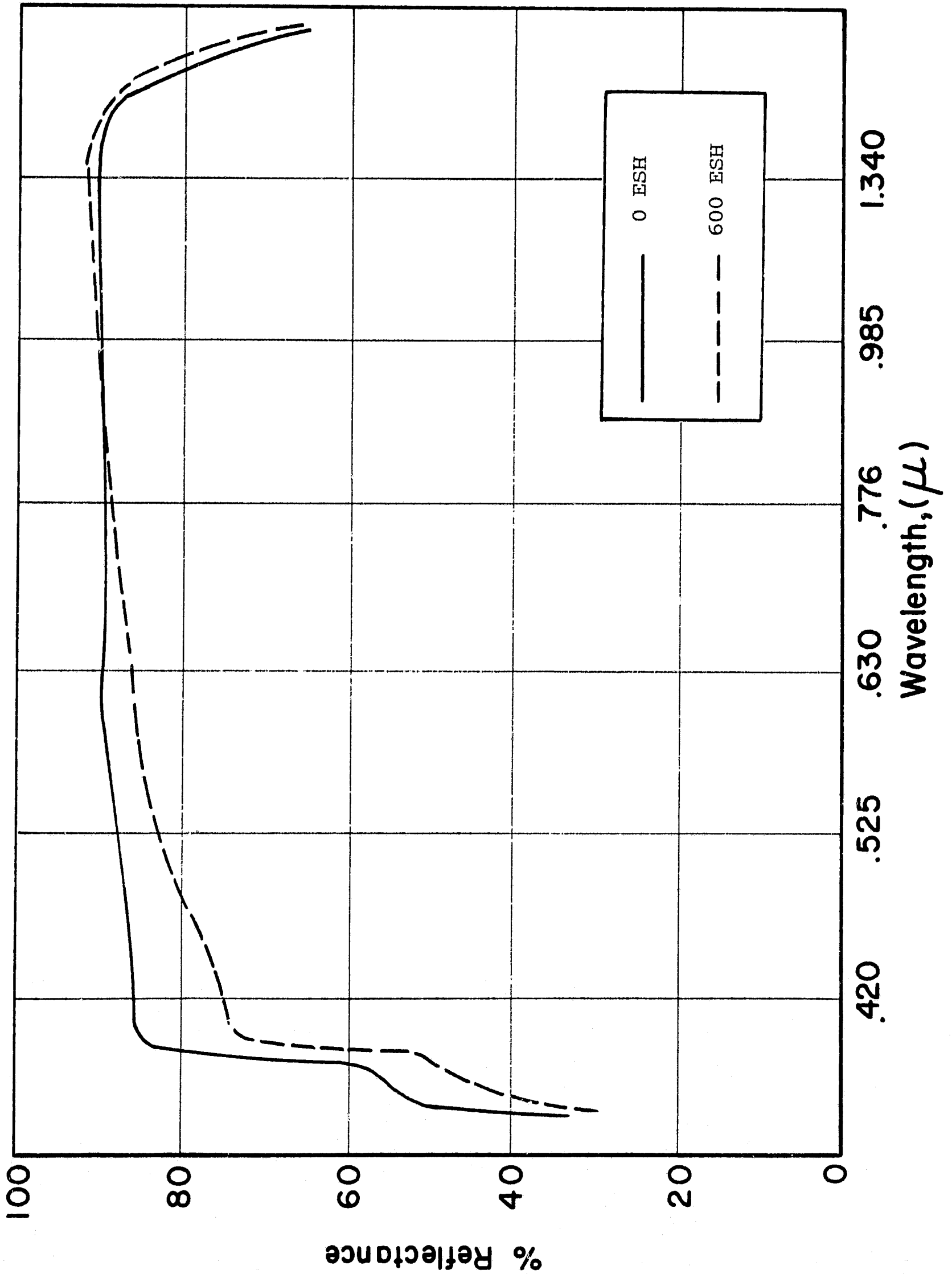


Figure 2: REFLECTANCE OF $Zn_2TiO_4/PS7$ PAINT IRRADIATED FOR 600 ESH IN IRIF II
(Unextracted Pigment)

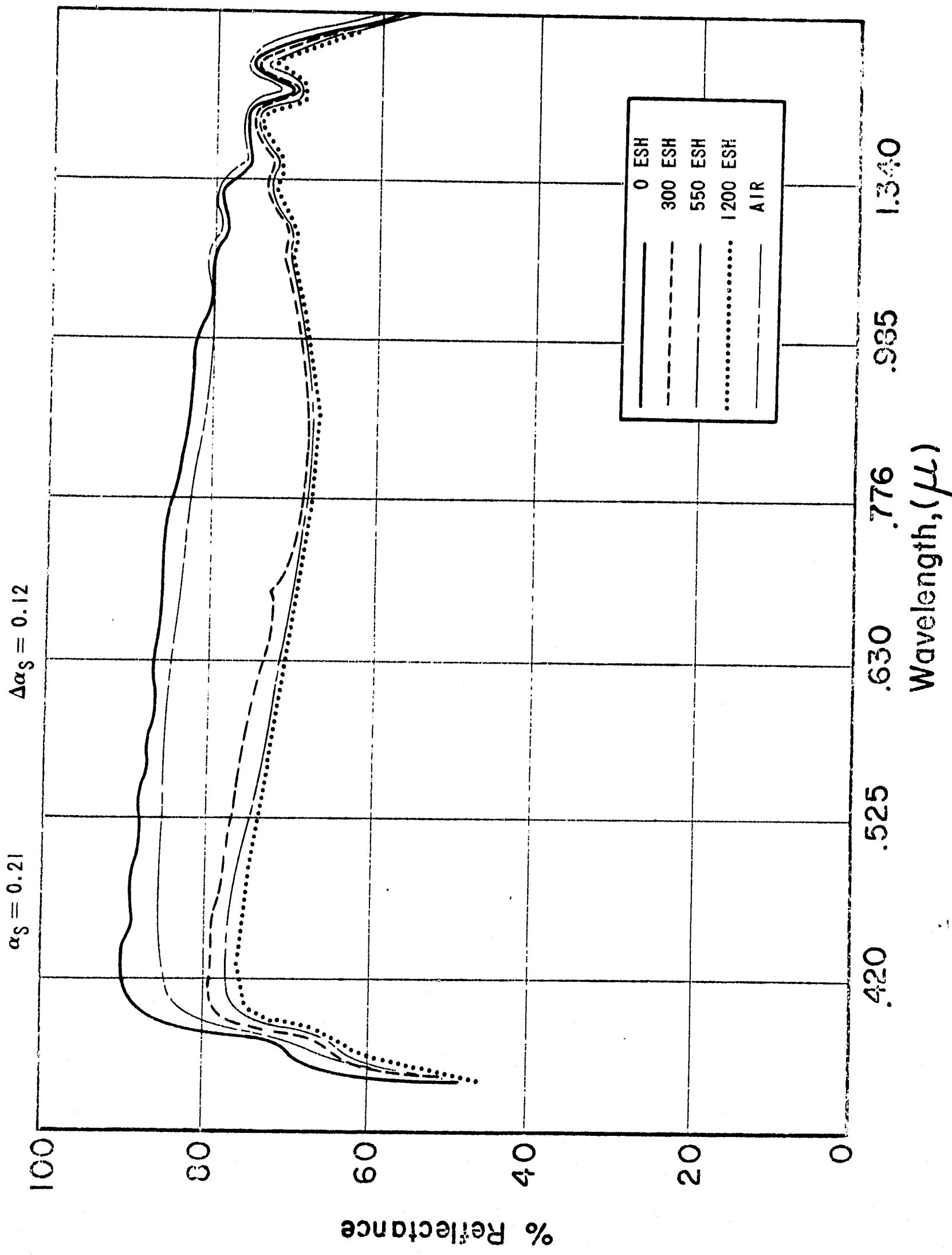


Figure 3 EFFECT OF UV IRRADIATION ON A ZINC ORTHOTITANATE-PIGMENTED
 0-1 650 PAINT (BATCH A-378A) ADAPTED FROM IITRI-U6002-59 p. 15

that the "fast" bleachable absorption band that centers roughly at 800 nm is completely missing in the analagous potassium silicate paint.

Of even more interest is the still increased stability exhibited by the potassium silicate paint pigmented with extracted zinc orthotitanate; the $\Delta\alpha_s$ was apparently halved to 0.015 by extraction. The spectral damage is presented graphically in Figure 4. Again, the characteristic broad absorption band that forms in "non-silicated" (untreated) zinc orthotitanate is completely absent.

Reaction of the extracted zinc orthotitanate with 2% sodium acid phosphate also resulted in a sharp reduction in damage on irradiation. Specimen #4 (Table 1) exhibited a $\Delta\alpha_s$ of 0.05 in 600 ESH compared to the $\Delta\alpha_s$ of 0.07 exhibited by a similar specimen irradiated for only 300 ESH in IRIF test No. 14 (ref. 4, p. 14): This specimen was prepared from zinc orthotitanate that was only slurried for 15 min in a 1% solution of sodium acid phosphate at room temperature. The spectral reflectance of specimen #4 is presented in Figure 5. (The peak in reflectance of this and following spectral curves at about 390 nm is believed to be due to fluorescence -- although its origins are unknown at this time.)

Heat treatment of the extracted pigment that was subsequently reacted with sodium acid phosphate resulted in a paint with a $\Delta\alpha_s$ of 0.023, less than one-half that of the specimen prepared from the same pigment that was not heat

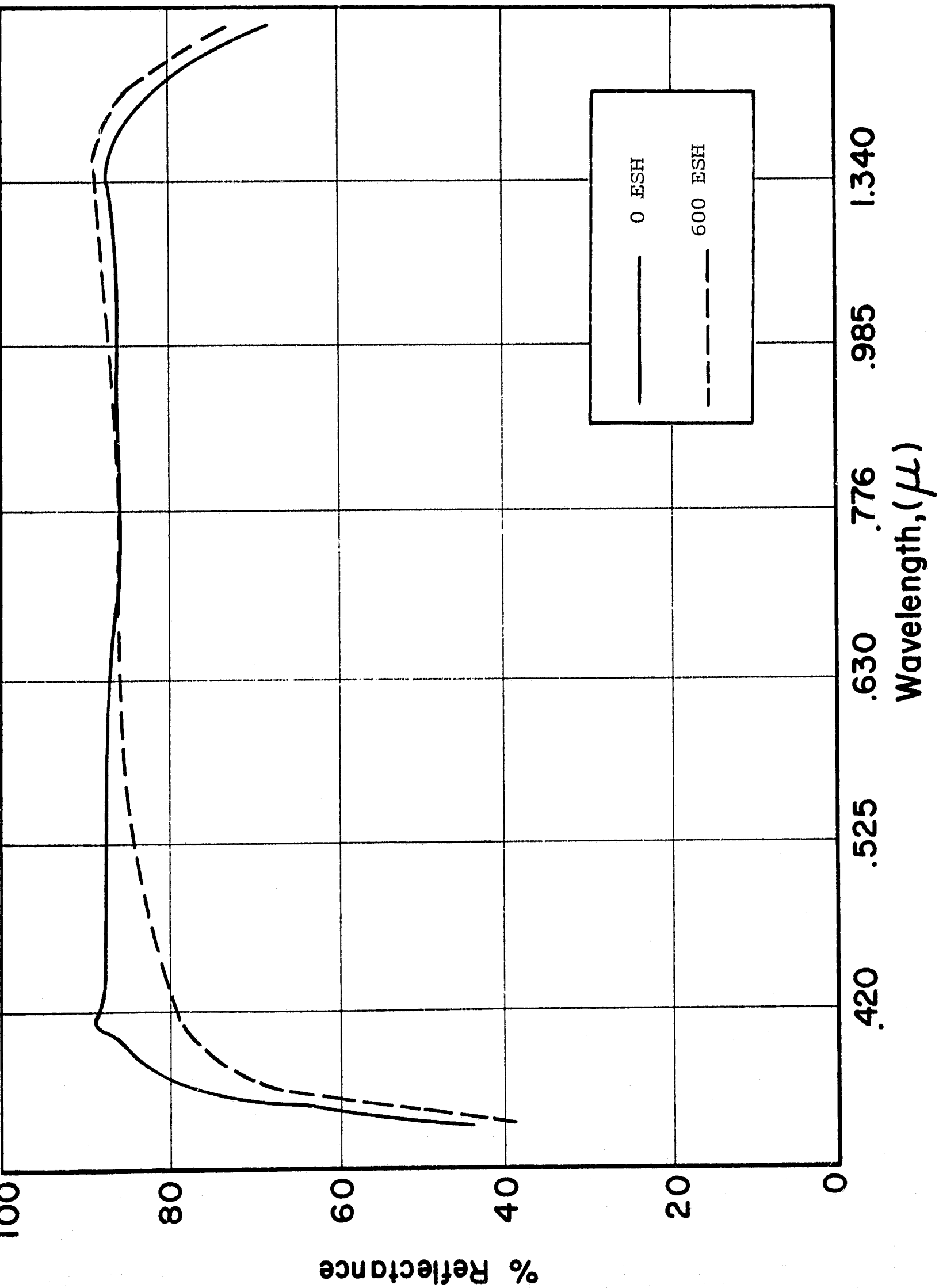


Figure 4: REFLECTANCE OF Zn_2TiO_4/PS_7 PAINT IRRADIATED FOR 600 ESH IN IRIF II.
(Extracted Pigment)

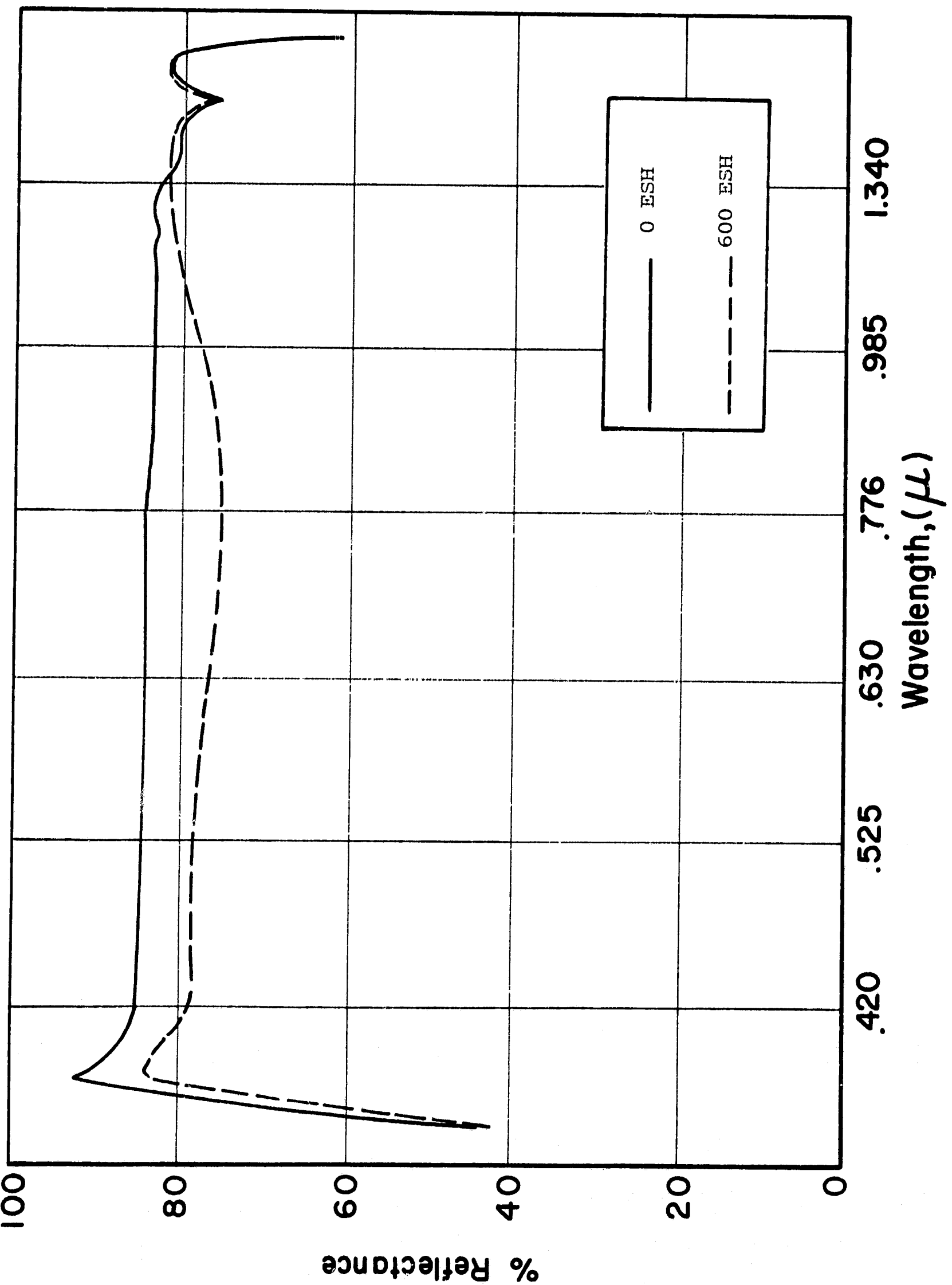


Figure 5: REFLECTANCE OF $Zn_2TiO_4/O-I$ 650 PAINT IRRADIATED IN IRIF II
 (Extracted pigment; Reacted with 2% NaH_2PO_4)

treated. This compares very favorably with the specimen irradiated in IRIF test 14 (ref. 4, p. 14) that was reacted with 1% sodium acid phosphate at room temperature. The spectral reflectance of specimen #5 is presented in Figure 6.

Specimen #6 (Table 1) exhibited a $\Delta\alpha_s$ of 0.038 in 600 ESH of mercury-xenon irradiation compared to a $\Delta\alpha_s$ of 0.028 in 550 ESH of A-H6 irradiation exhibited by an identical specimen that was irradiated in IRIF Test 14. Thus, it appears that this test was more severe than is generally the case for mercury-argon (A-H6) space-simulation tests of similar exposure. The spectral data for the specimen #6 is presented in Figure 7. The 800-nm absorption band, although not intense, is clearly indicated in the damage spectra. The slight band at about 390 nm indicates that not all of the residual ZnO was extracted from the initial reaction product.

The Owens-Illinois 650-resin paint (specimen #7) prepared from unextracted zinc orthotitanate that was subsequently reacted with hot 2% sodium acid phosphate exhibited the highest stability ($\Delta\alpha_s$ of 0.018) of any of the zinc orthotitanate-pigmented Owens-Illinois 650-resin paints examined to date (Figure 8). Indeed, the same pigment when calcined, and prepared into a paint, also exhibited excellent stability (specimen #8). While specimen 8 was no less stable than its "extracted" counterpart (specimen 5), specimen 7 exhibited considerably greater stability than its "unextracted" analog (specimen #4). It is thus obvious that the role of residual zinc oxide, or its absence, cannot be determined from the data available. The spectral data for specimen #8 are plotted in Figure 9.

IIT RESEARCH INSTITUTE

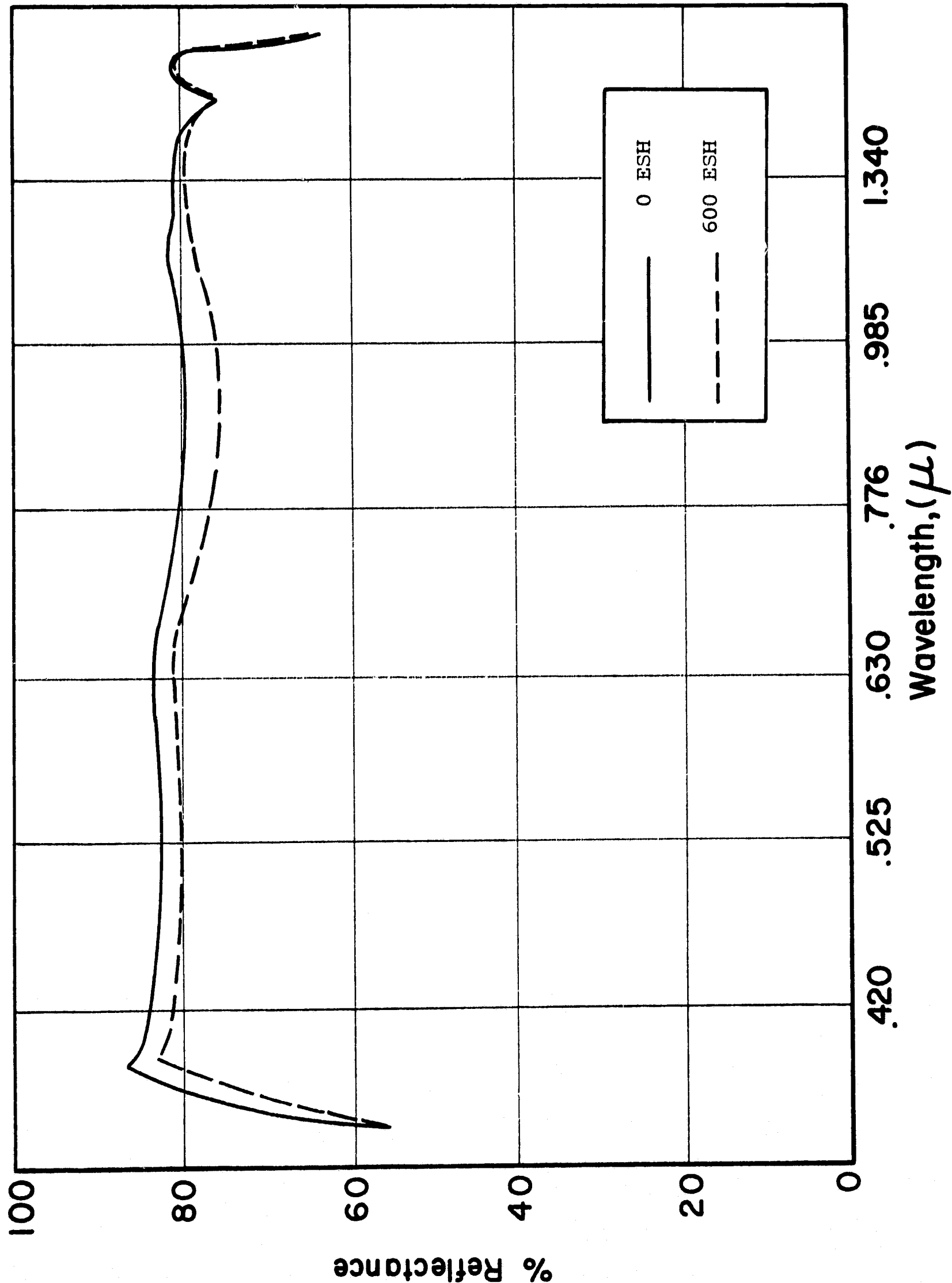


Figure 6: REFLECTANCE OF Zn₂TiO₄/O-I 650 PAINT IRRADIATED IN IRIF II
 (Extracted Pigment; Reacted with 2% NaH₂PO₄; Calcined)

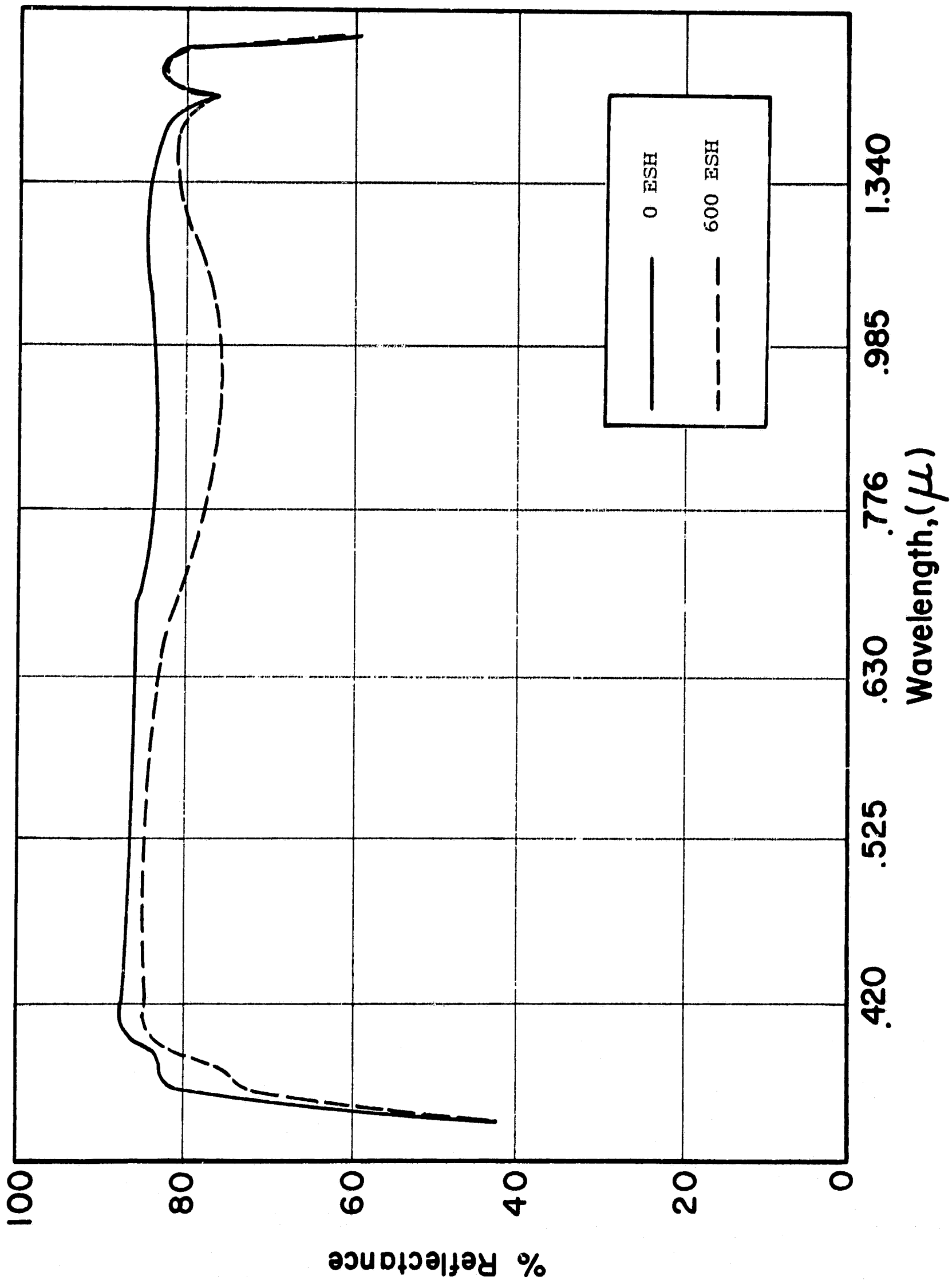


Figure 7: REFLECTANCE OF $Zn_2TiO_4/O-I$ 650 PAINT IRRADIATED IN IRIF II
(Extracted Pigment; Calcined)

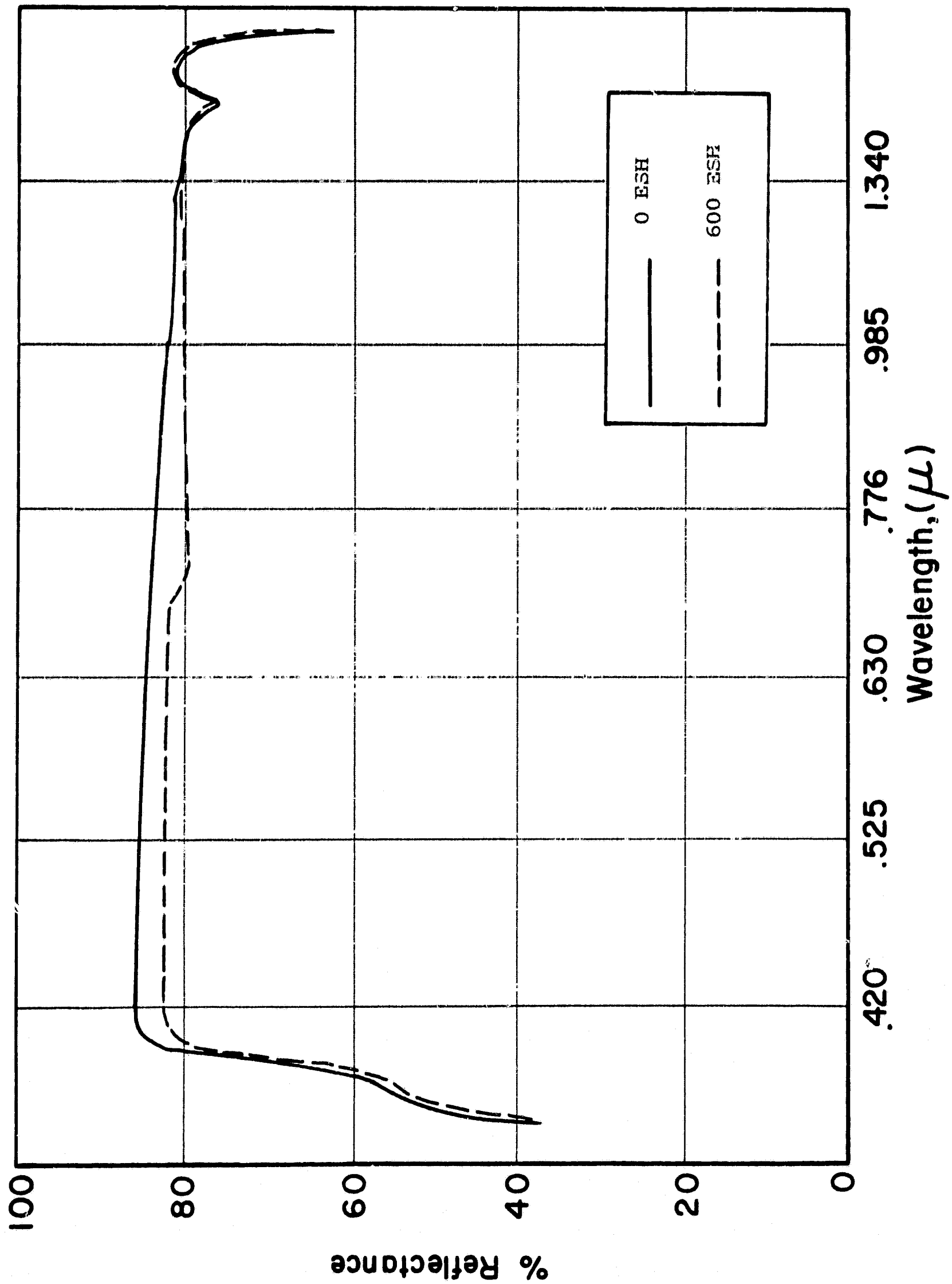


Figure 8: REFLECTANCE OF $Zn_2TiO_4/O-I$ 650 PAINT IRRADIATED IN IRIF II

(Unextracted; Reacted with 2% NaH_2PO_4)

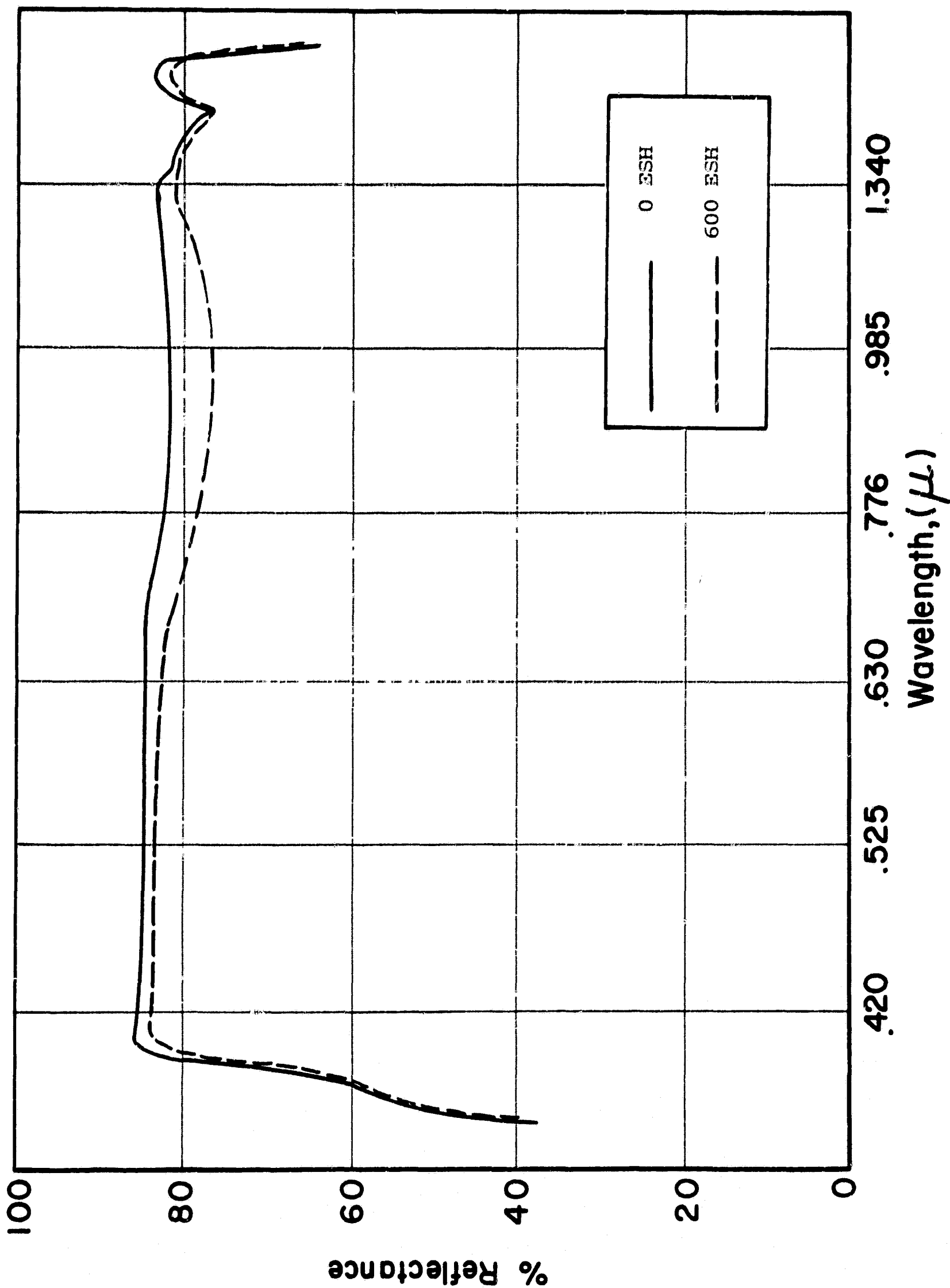


Figure 9: REFLECTANCE OF Zn₂TiO₄/O-I 650 PAINT IRRADIATED IN IRIF II
(Unextracted; Reacted with 2% NaH₂PO₄ Calcined)

III. EPR OF ZINC ORTHOTITANATE

A. Introduction

In the last report the electron paramagnetic resonance in zinc orthotitanate was presented. This resonance was produced by the calcining involved in the production of zinc titanate but surface treatment with sodium acid phosphate removed it. Since it was also found that no resonance was observed in SP500 ZnO or in TiO_2 , the resonance probably was in intrinsic defect and not an impurity.

The principal purpose of the experiments to be reported on here is to look for correlations between defects produced in ZnO, TiO_2 and Zn_2TiO_4 materials. Single crystal information is not available for any of the zinc titanates and therefore we must again spend considerable time to carefully consider the interpretation of EPR spectra obtained on powdered materials. The primary purpose has been to review the preparation of defect centers in the materials of interest and to demonstrate the sensitivity required so that these can be observed accurately. This will be used to identify the species and to provide a reference for further use in optical generation of defects. All sample tubes were evacuated with a mechanical pump while being heated to about $300^\circ C$ before irradiation.

B. Irradiation

The same samples as reported previously (ref. 4) were irradiated at $78^\circ K$ in the "hot cell" using cobalt 60. The irradiation dose was 78 hours using about 500 curies as source.

IIT RESEARCH INSTITUTE

All samples are being studied but we will report on only the ZnO and silicate-treated ZnO at this time. After irradiation the samples were stored in liquid nitrogen.

1. ZnO (SP500)

This material seemed to have about the same dielectric properties after irradiation as previously. The top of the tube "blew off" when it was warmed slightly. There was the possibility of a leak in the tube but the probable explanation is gases desorbed by the irradiation. This seems appealing but one should estimate the surface areas and tube volumes accurately. The ZnO showed a resonance to be described later.

2. ZnO (Potassium Silicate-Treated)

This material showed a distinct change in dielectric properties. Samples always cause a shift in the resonant frequency of the cavity and sometimes make an abnormal change in the Q and mismatch. The sensitivity can be seriously affected if the Q falls below 3,000 or the cavity reflection coefficient rises above 10%. This sample did produce these effects when inserted in the spectrometer. There was little evidence of loss due to conductivity but considerable evidence for a change in the dielectric constant, or for a small departure from the usual unity for the magnetic permeability. Nevertheless, experimental conditions could be adapted to the sample and a very weak resonance was observed. This was outside the range of field values used to observe the resonance in ZnO and the resonance was qualitatively different in shape and other properties. Thus, it served the purpose of showing

IIT RESEARCH INSTITUTE

that even under adverse conditions the resonance in SP500 could have been observed if it were in the silicate-treated material. The resonance in the silicate-treated ZnO is not being presented since it cannot be analyzed because the signal to noise ratio is so low that only a subjective judgement is possible.

C. Spectrometer Sensitivity

Our primary interest is in defects on the surface. This requires the ultimate in sensitivity if we are to obtain accurate data. The spectrometer is assembled from commercial components. During this contract period it has been improved to reduce noise. An additional tuned amplifier was added to the detector circuit to operate at the field modulation frequency and this reduced the "sideband beating noise" which appears to be significant when the signal is about equal to noise. This narrow band feature is not included in many commercial instruments. The measurements on ZnO requires a superheterodyne detector because the resonance in SP500 saturates so that more than 1. milliwatt input to the cavity does not increase the signal intensity. On the other hand the small resonance in the silicate-treated ZnO does not saturate at ordinary power levels. The 30 mc intermediate frequency amplifier was aligned and checked to operate under both conditions. The output of the IF amplifier is 50 ohms at 30 mc but the input of the audio circuitry is 300 ohms. The detector circuit coupling these was redesigned for optimum power transfer. This reduced certain stray couplings and, the improved bandwidth allows stable operating periods of

IIT RESEARCH INSTITUTE

several hours without necessity of restabilizing the microwave frequency or adjusting the local oscillator. The net result of these changes is that very small field modulations may be used to display the derivative signals.

D. EPR Measurements

1. Characteristics of the Spectrum

About five informative scans of the SP500 ZnO resonance were made. These scans showed that in the range of from $g = 0.5$ to 4.0 no other significant signal was present. A modulation was found to be small enough that only a change of intensity of the signal occurred if it was reduced except possibly a change in the zero crossover. A significant baseline for the derivative signal was obtained at high and low field. A long tail was observed on the high field side of the resonance. Figure 10 is a tracing of the recorder chart with calibrated field; saturation effects were minimal. The high-field tail is cut off but was observed to its fullest extent using larger modulation and wider scans so that it could be included in the computations. It must be emphasized that the resonance extends over 150 gauss but the modulation is only two gauss and distance between points of maximum slope is about twenty gauss. The change in slope at the inflection point occurs over a range considerably larger than 5 gauss.

E. Interpretation of EPR Spectra

1. Powder-Like Shapes

Figure 11 is a schematic diagram showing the resonance

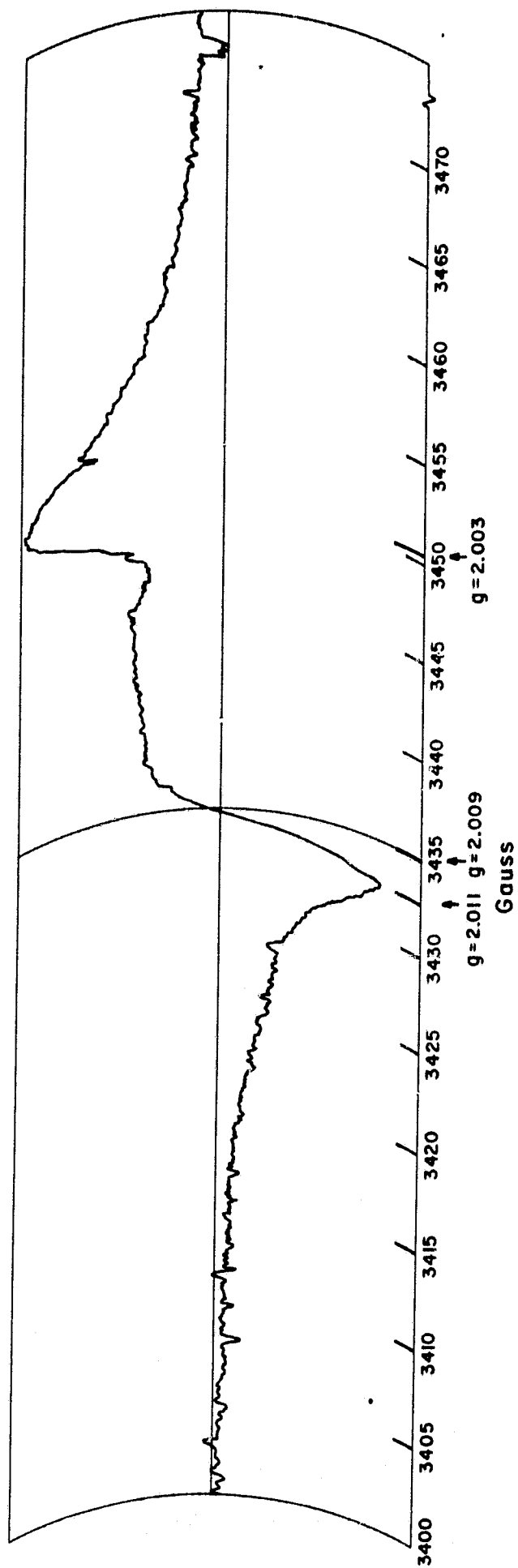


Figure 10
 THE EPR DERIVATIVE SIGNAL OBTAINED ON A SAMPLE OF GAMMA IRRADIATED ZnO at 78°. THE MICROWAVE FREQUENCY WAS 9.658 GHz.

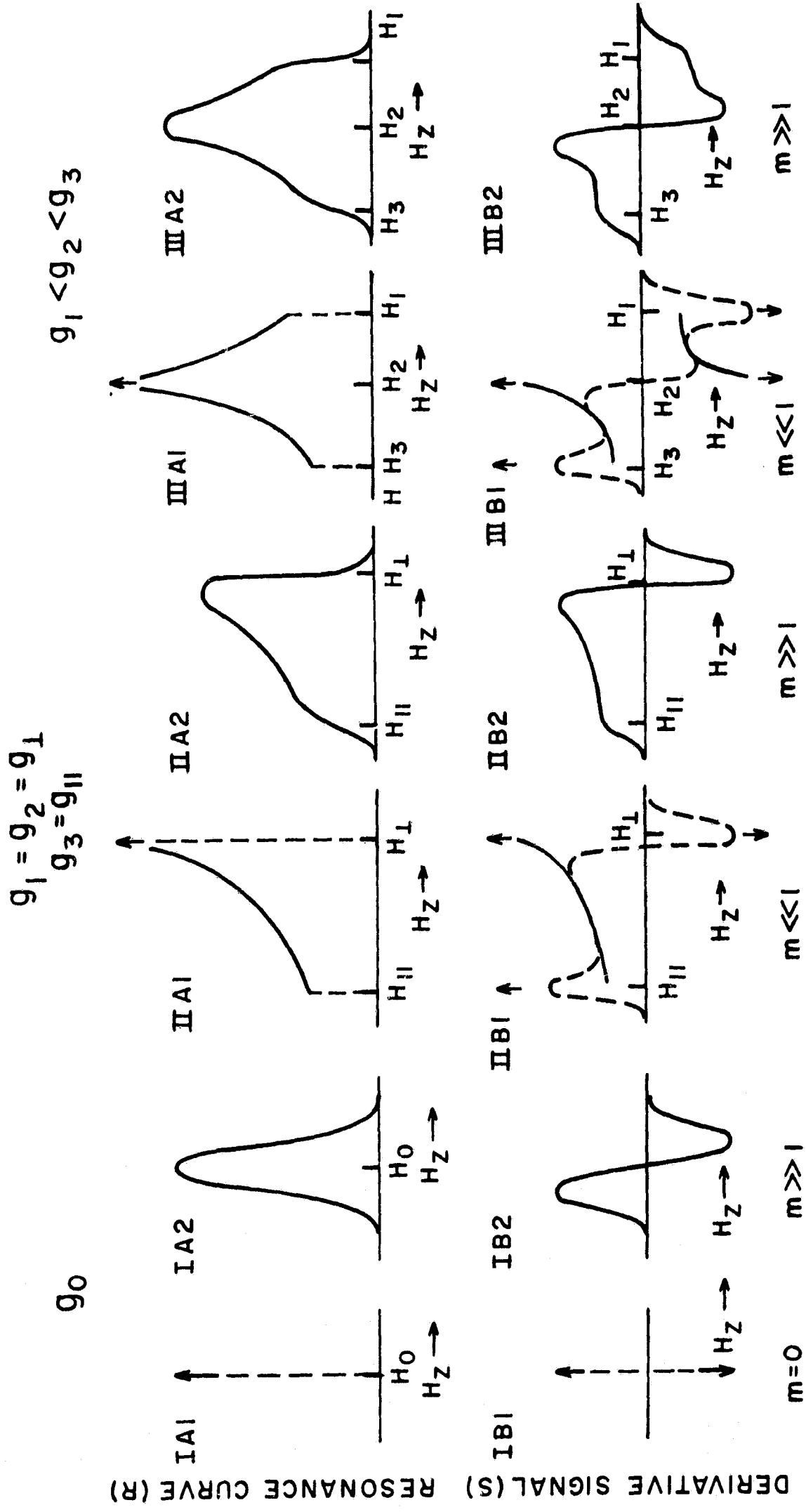


FIGURE 11

THE RESONANCE ABSORPTION CURVES (A) AND DERIVATIVE SIGNALS (B) FOR EPR POWDER SPECTRA. THE MATERIALS HAVE ONE (I), TWO (II), OR THREE (III), PRINCIPAL g VALUES. EACH IS SHOWN FOR SMALL (1) AND LARGE (2) COMPONENT LINE WIDTHS. THE DASHED LINES IN DERIVATIVES FOR SMALL COMPONENT LINE WIDTH INDICATE PORTIONS OF THE SPECTRA WHICH DEPEND ON THE MODULATION USED. ARROWS INDICATE DISTRIBUTIONS WHICH IDEALLY RISE TO INFINITY. m IS THE RATIO OF COMPONENT LINE WIDTH TO DISTRIBUTION WIDTH.

curves and the corresponding derivative signals corresponding to one, two or three g-values. It is based on the discussion by Kneubuhl (ref. 5). The polycrystalline material and orientation-dependent g factors provide the inhomogeneous distribution curve depicted in IIA1 and IIIA1 of Figure 11. If each transition were observed independently as in an experiment using a single crystal at a specific orientation, it would have a line width as shown in curve IA2. When the component broadening is very small the resonance absorption sets in abruptly and for any practical modulation the derivative signal is as in IIA1 or IIIA1. The dashed portions of the curves IIB1 and IIIB1 indicate that the signal is not a true derivative of the absorption and it depends on the modulation amplitude because the modulation is large compared to the width of the field region where the absorption changes rapidly. However the solid portion of the curve is a reliable derivative of the absorption and the shape is independent of the modulation amplitude. On the other hand in the case of large component line widths, IA2, IIA2, IIIA2 the signal is an accurate presentation of the derivative (IB2, IIB2, IIIB2) except at the peak of the resonance. The infinity in the distribution at that point still has an overwhelming influence on the line shape because so many systems are involved. The discontinuity at the ends seems gradual because fewer states are involved. The usual range of amplitudes for the recorder display is about fifty so that the extreme high peaks and low cut offs are lost. This is unavoidable. Using the derivative

patterns it is difficult to distinguish between IIB1 and IIIB2. In the latter case one cannot take the maximum slope points to indicate a g value as used frequently. It is best to obtain the integrals if suitably linear derivative conditions can be obtained for data.

2. Qualitative Interpretation

The qualitative characteristics of the spectrum are almost exactly as shown in Figure 11, part IIB2 (ref. 5). On that basis we would find that the spectrum is for a defect with

$$g_1 = g_2 = 2.011 \text{ and } \underline{g_1} = 2.003$$

Such an interpretation is justified if the line widths are narrow compared to the anisotropic-orientation broadening. A crude \bar{g} would be 2.006. The relative intensities of the peaks cast doubt on this recognition of similarity. An alternative interpretation of the derivative will be presented next.

3. Interpretation of Integrated Line

Under the conditions where the data were obtained it seems that we have a true derivative of a line shape. We observe all parts of the line and the inflection points are relatively independent of the modulation although the point of zero slope has a possible modulation dependence. The long tail would seem to indicate broadening either due to anisotropic or homogeneous effects, yet the slope near the peak changes extremely rapidly. We assume that the resonance absorption (r) and its derivative

are zero at low and high fields. Our signal (s) is proportional to the true derivative except at the peak. The integration was done using the RUSH computer system as described in the last report (ref. 4). The absorption curve (integral of Figure 10) is given in Figure 12. The result is remarkably close to (Figure 11), Part IIA2. This is a spectrum with g_1 close to 2.0093 but possibly having a considerable second-order shift. The difficulty in obtaining a good presentation of the line near the peak is indicated by the dashed line extrapolation near the peak. The other two g values are above and below g_1 and are nonsymmetrically distributed. However a \bar{g} equal to 1.9995 is obtained from the \bar{g} calculation which properly includes the long tail at high field.

F. Comparison of Resonances

Before attempting to associate the resonance with possible bulk centers we consider oxygen absorbed on ZnO as reported in Lunsford and Jayne (ref. 6). They obtain three g values from derivative curves. A similar treatment of the derivative curve in Figure 10 could be obtained.

Table 2 is a summary of the g values assembled from related experiments described in the literature. Using equivalent interpretive methods the results obtained here correlate with O_2^- on ZnO, as based on the order of g values and almost exact agreement of g_{zz} values. However any qualitative examination of the spectra would not indicate a similarity since the Lunsford and Jayne data have a long tail at low field associated

TABLE 2

THE g VALUES OF MAGNETIC CENTERS RELATED TO OXIDES

	<u>Reference</u>	<u>g_{zz}</u>	<u>g_{xx}</u>	<u>g_{yy}</u>	<u>\bar{g}</u>
SP500 Gamma Irradiated	These Experiments	2.009	2.011	2.003	2.007
O^-					
from OH^-	6	2.002	2.070	2.070	--
from FPO_2	6	2.0012	2.0516	2.0516	--
O_2^-					
in KCL	6	1.9551	2.4359	1.9512	--
on MgO	6	2.0073	2.077	2.0011	--
on ZnO	6	2.0082	2.051	2.0020	2.020
from NaO_2	6	2.000	2.175	2.000	--
O_3^-					
in $KClO_3$	6	2.0025	2.0113	2.0174	--
from NaO_3	6	2.003	2.015	2.015	--
CO^-					
on ZnO	7	2.002	2.005	2.005	--
SP500 UV Irradiated (Metastable)	8	--	--	--	1.957
	9*	--	--	--	1.954
	9*	1.998	1.998	2.001	--

* These values have been estimated approximately

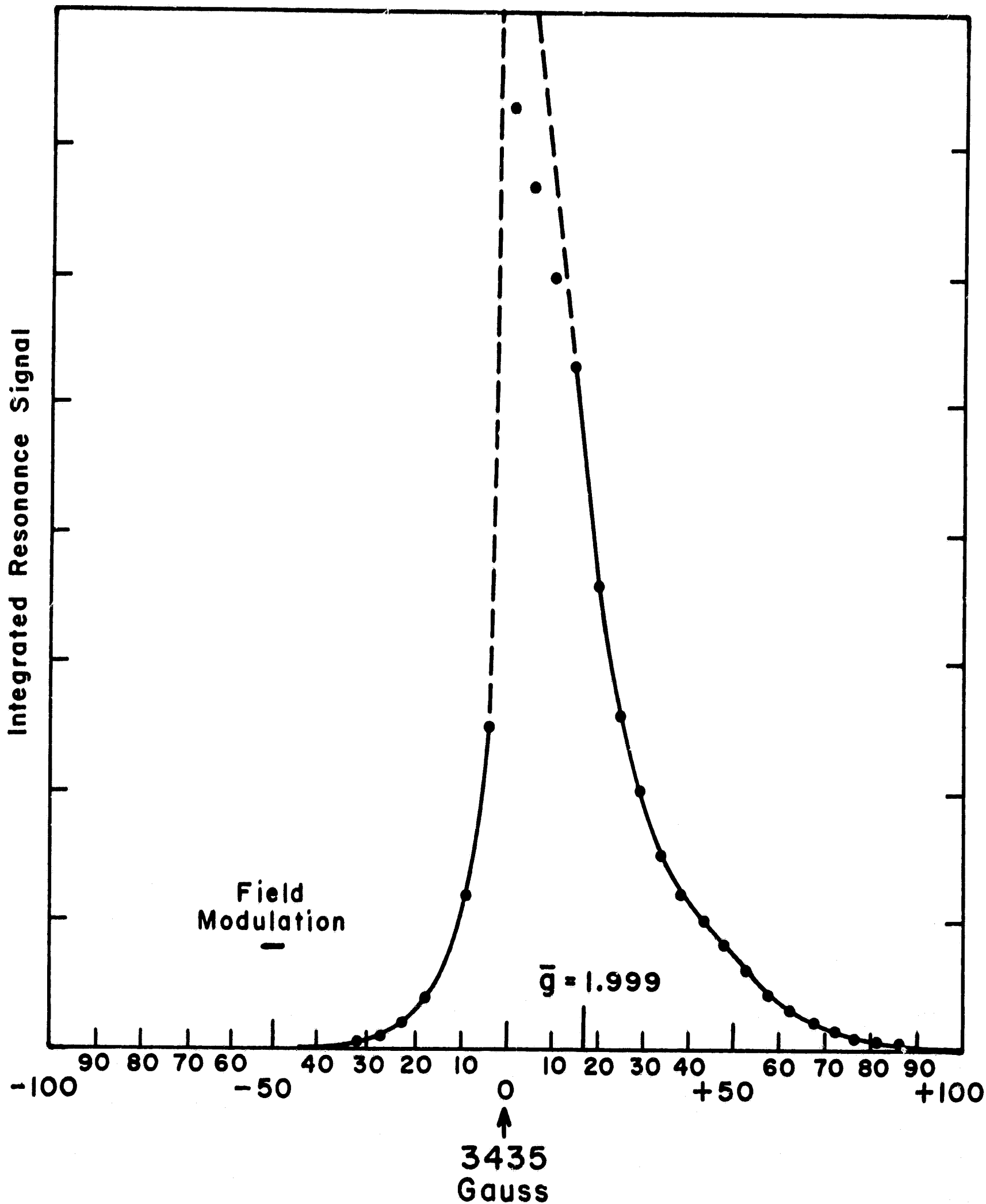


FIGURE 12

THE MAGNETIC RESONANCE ABSORPTION LINE SHAPE OBTAINED BY INTEGRATION OF THE DERIVATIVE SIGNAL.

with the 2.05 g value while we have a long tail at high field and no sharp change in slope at the end. Some of the line shape may result from conditions of observation. A computed \bar{g} value has little significance in this type of spectral interpretation. It should also be noted that principal g tensor components and \bar{g} values differ as O_2^- occurs on ZnO, or MgO, in NaO_2 or in KCL. But the g value associated with the strongest peak does appear remarkably close in both samples.

A possible interpretation of the experiments is that SP500 contains rather large amounts of absorbed oxygen. The concentration is so high that the spins pair and no resonance (paramagnetic or ferromagnetic) is observed. Irradiation removes this (generating a significant volume of gas) and the remaining oxygen shows a resonance. If it is oxygen, the crystalline fields are possibly more symmetrical indicating an interior position. The gas need not be oxygen since the g values do not fit exactly but one notes that only two values are obtained for CO^- and this species would be generated by irradiation. Finally, one would remark that the silicate treatment prevents the absorption of large amounts of O_2^- . These remarks are presented as tentative speculations requiring more careful examination.

G. Zinc Orthotitanate: Zn_2TiO_4

Returning to the zinc orthotitanate we find that the resonance in irradiated ZnO is not related to that in calcined Zn_2TiO_4 by any parameters. These values are compared in Table 3.

TABLE 3
 COMPARISON OF RESONANCES FOR ZnO and Zn₂TiO₄

	<u>Width</u>	<u>\bar{q}</u>	<u>Shape factor</u>
SP500 ZnO	35	1.999	5.4
A319 Zn ₂ TiO ₄	2.1	1.957	14
A371-U Zn ₂ TiO ₄	2.5	1.956	15

IV. SUMMARY AND CONCLUSIONS

A. Zinc Orthotitanate Coatings

The use of reactive encapsulation was shown to be effective in stabilizing zinc orthotitanate against ultraviolet-irradiation-induced damage in vacuum. Both potassium silicate and sodium acid phosphate were observed to reduce degradation. Of the two, "pigmentation" in potassium silicate was the most effective in preventing the creation of the broad, bleachable adsorption band centered at about 800-nm wavelength that is characteristic of untreated zinc orthotitanate. Indeed, an "extracted" zinc orthotitanate-pigmented potassium silicate paint exhibited stability that was equal to a Z93 control specimen in the same test.

Although the data are still insufficient, the studies thus far show that heat treatment, or calcination, and reaction with sodium acid phosphate are important in affecting stability of zinc orthotitanate that is used to pigment the Owens-Illinois "650" resin system. The effect of first silicating, as is done to zinc oxide prior to incorporation into the S-13G paint, and then reacting with acid phosphate has not been attempted to date. We have shown however that the reaction of zinc orthotitanate with 2% sodium acid phosphate for 30 min at 100°C is more effective in reducing degradation than reaction at room temperature with a 1% solution.

B. Solid-State Studies

Radiation damage can produce trapped electrons or holes at the surface or in the interior of the material and the competition between the two processes is very important in powders. Considerable care must be exercised in the interpretation of EPR spectra, but only a few magnetically observable centers appear.

From a powder spectrum one can estimate the g values which would be observed if the magnetic centers could be oriented in a single crystal. These would serve to identify the resonant species. However, particularly in the case of O_2^- the three components of the g values are non-degenerate and depend very strongly on the environment. This has the advantage of providing a tool for investigating the location of trapped charges but it does complicate obtaining model defect centers.

From the study of zinc oxide it seems that the stable traps have a very low symmetry and are probably O_2^- . Not all such species can be desorbed. The more symmetrical species, such as the anion vacancies are not important even under intense irradiation. The silicate treatment of zinc oxide does prevent the formation of a magnetic center by irradiation and this seems to justify associating the magnetic species with the degradation of the pigment.

Having reached these generalization on zinc oxide we find that more work must be done to interpret the magnetic resonances of zinc orthotitanate.

REFERENCES

1. Zerlaut, G. A., Noble, G., and Rogers, F. O., "Development of Space-Stable Thermal-Control Coatings," IIT Research Institute Triannual Report No. IITRI-U6002-55, Contract NAS8-5379, September 22, 1967.
2. Zerlaut, G. A., and Courtney, W. J., "Space-Simulation Facility for In Situ Reflectance Measurements," in Thermophysics of Spacecraft and Planetary Bodies, ed. G. Heller, Progress in Aeronautics and Astronautics, Academic Press, 1968, p. 349.
3. Zerlaut, G. A., and Rogers, F. O., "Development of Space-Stable Thermal-Control Coatings," IIT Research Institute Triannual Report No. IITRI-U6002-47, Contract NAS8-5379, November 30, 1966.
4. Zerlaut, G. A., Noble, G., and Rogers, F. O., "Development of Space-Stable Thermal-Control Coatings," IIT Research Institute Triannual Report No. IITRI-U6002-59, Contract NAS8-5379, January 15, 1968.
5. Kneubuhl, F. K., J. Chem. Phys. 44, 1074 (1966).
6. Lunsford, J. H., and Jayne, J. P., J. Chem. Phys. 44, 1487 (1966).
7. Lunsford, J. H., and Jayne, J. P., J. Chem. Phys. 44, 1492 (1966).
8. Lall, R. B., and Arnett, G. M., J. Phys. Soc. Japan 21, 2743 (1966).
9. Sklensky, A. F., MacMillan, H. F., and Greenberg, S. A., "Solar-Radiation-Induced Damage to Optical Properties of ZnO-type Pigments" Lockheed Missiles and Space Company Report, Contract NAS8-18114, February 1968.