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Report No. IITRI-U6002-94
(Triannual Report)

DEVELOPMENT OF SPACE-STABLE THERMAL-CONTROL COATINGS

National Aeronautics & Space Administration
George C. Marshall Space Flight Center
Huntsville, Alabama 35812

IIT Research Institute

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May 1 through September 30, 1970

Contract No. NAS8-5379
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IITRI Project U6002

Prepared by

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FOREWORD

This is Report No. IITRI-U6002-94 (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 May 1 through September 30, 1970. Previous Triannual Reports were issued on October 25, 1960; March 5, 1964; July 20, 1964; December 21, 1964; February 23, 1965; July 20, 1965, November 9, 1965; February 21, 1966; July 11, 1966; November 30, 1966; February 28, 1967; September 22, 1967; January 15, 1968; April 15, 1968; October 25, 1968; January 31, 1969; July 11, 1969; November 17, 1969; February 20, 1970; and July 1, 1970.

Major contributors to the program during this period include; Gene A. Zerlaut, Project Leader; Dr. Nicholas A. Ashford, solid state and EPR studies; Mr. John Brzuskiewicz, Zn_2TiO_4 reactive encapsulation studies; Mr. Robert F. Boutin, experimental work with IRIF and CREF; Mr. John E. Gilligan, group responsibility for CREF and analytical studies pertaining to its characterization; and Dr. C. Giori, Owens-Illinois 650 resin studies.

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 was the Project Manager.

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Respectfully submitted,

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Report No. IITRI-U6002-94
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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 major emphasis during the past two years has involved the investigation of new, potentially stable white-pigments - particularly zinc orthotitanate - and on the design, construction and utilization of a combined-radiation environment facility (CREF) that is capable of simultaneously irradiating evacuated specimens with simulated solar-wind protons and extraterrestrial ultraviolet radiation.

The last Triannual Report (IITRI-U6002-90) was devoted in its entirety to the design, construction and operational characteristics of the CREF proton-plus-ultraviolet facility. This report, IITRI-U6002-94, is devoted exclusively to zinc orthotitanate, its surface treatment (reactive encapsulation) and coatings prepared therefrom. Publication of this report has been delayed approximately six weeks in order to re-evaluate certain encapsulation experiments, the results of which required verification prior to disclosure.

The next, and final, Triannual Report (IITRI-U6002-98) is scheduled for publication in January 1971: It will cover the

remaining solid state (EPR) studies on zinc orthotitanate, the results of irradiation of a series of plasma heat-treated zinc orthotitanates and of a series of other pigments such as $ZnSnO_2$, $CaWO_4$ and $ZnZrO_3$ and the results of preliminary studies to modify Owens-Illinois 650 silicone resin.

II. EXPERIMENTAL

A. Materials Preparation

A batch of zinc orthotitanate (Zn_2TiO_4) prepared at 925°C, employing 0.5% excess ZnO, was used as the basic pigment for all the studies reported herein. It is designated Batch B-229. The treatments and coatings prepared from them are presented in the following paragraphs. The phylogeny of all specimen preparations are presented schematically in Figures 1a and 1b.

B-226

Five hundred (500) g of Batch B-229 Zn_2TiO_4 were slurried with 1250 g of 0.001 M potassium ferrocyanide and 1250 g of 0.001 M potassium ferricyanide for 1 hr at room temperature. With continued agitation, the temperature of the slurry was raised to 80°C and held for 30 min. (Thirty minutes was required to raise the temperature to 80°C.) The slurry was then cooled to room temperature (with agitation) and was then vacuum filtered through a Büchner funnel; the resultant powder was dried for 16 hr at 110°C.

B-233

Five hundred (500) g of Batch B-229 were mixed with 267 g of distilled H_2O and 500 ml of PS-7 potassium silicate. The mixture was refluxed with agitation for 8 hr. After refluxing, 666 ml of distilled H_2O was added to the mixture and the mixture was facuum filtered through a Büchner funnel. The filter cake was redispersed in 600 ml of distilled H_2O and refiltered. The moist filter cake was broken up and then dried at 110°C for 16 hr.

B-241

Five hundred (500) g of Batch B-229 Zn_2TiO_4 were mixed with 834 g of a 5% solution of NaH_2PO_4. The slurry was refluxed for 4 hr, vacuum filtered through a Büchner funnel, rinsed with 334 ml distilled H_2O and dried for 16 hr at 110°C.

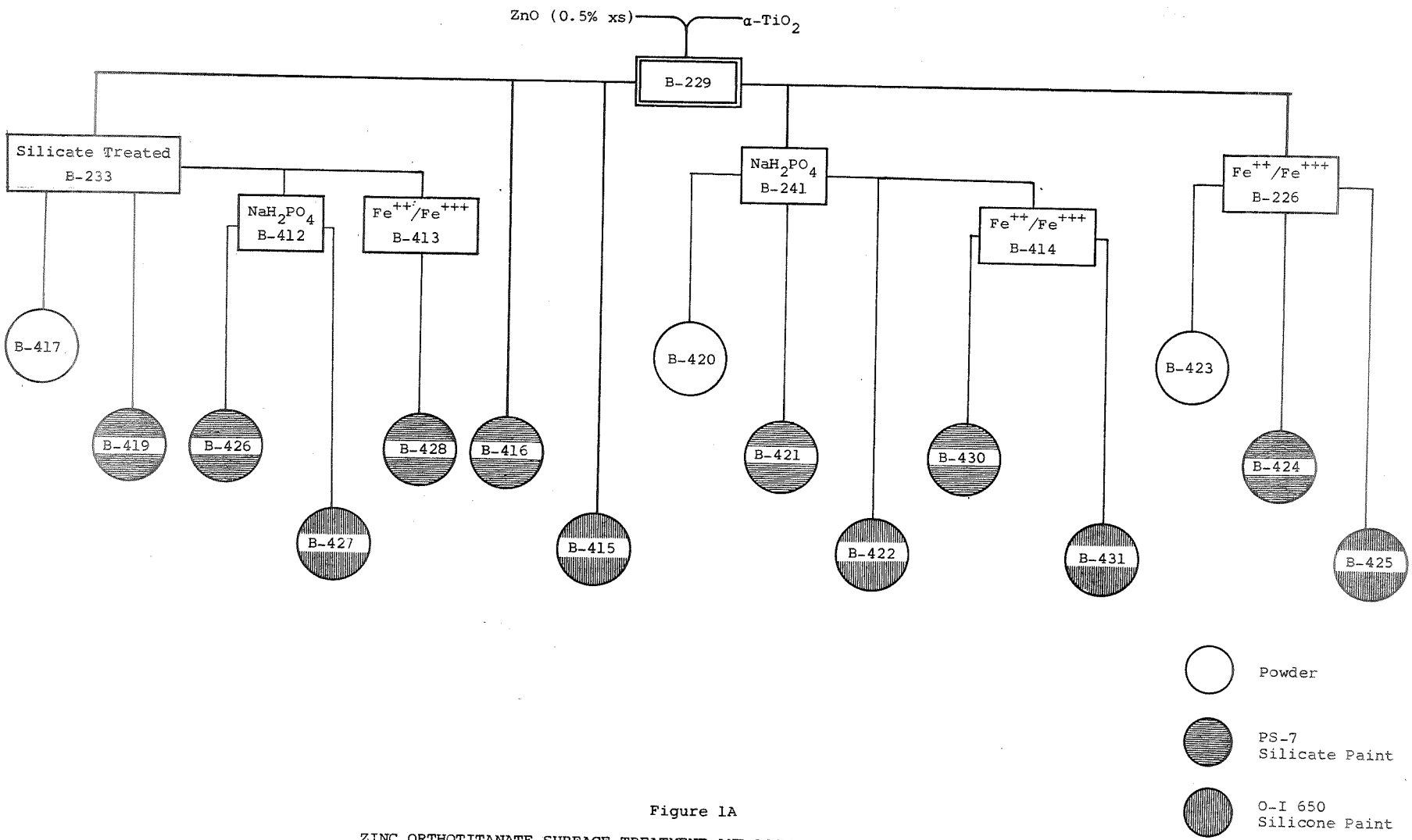


Figure 1A

ZINC ORTHOTITANATE SURFACE TREATMENT AND PAINT COATINGS HISTORY

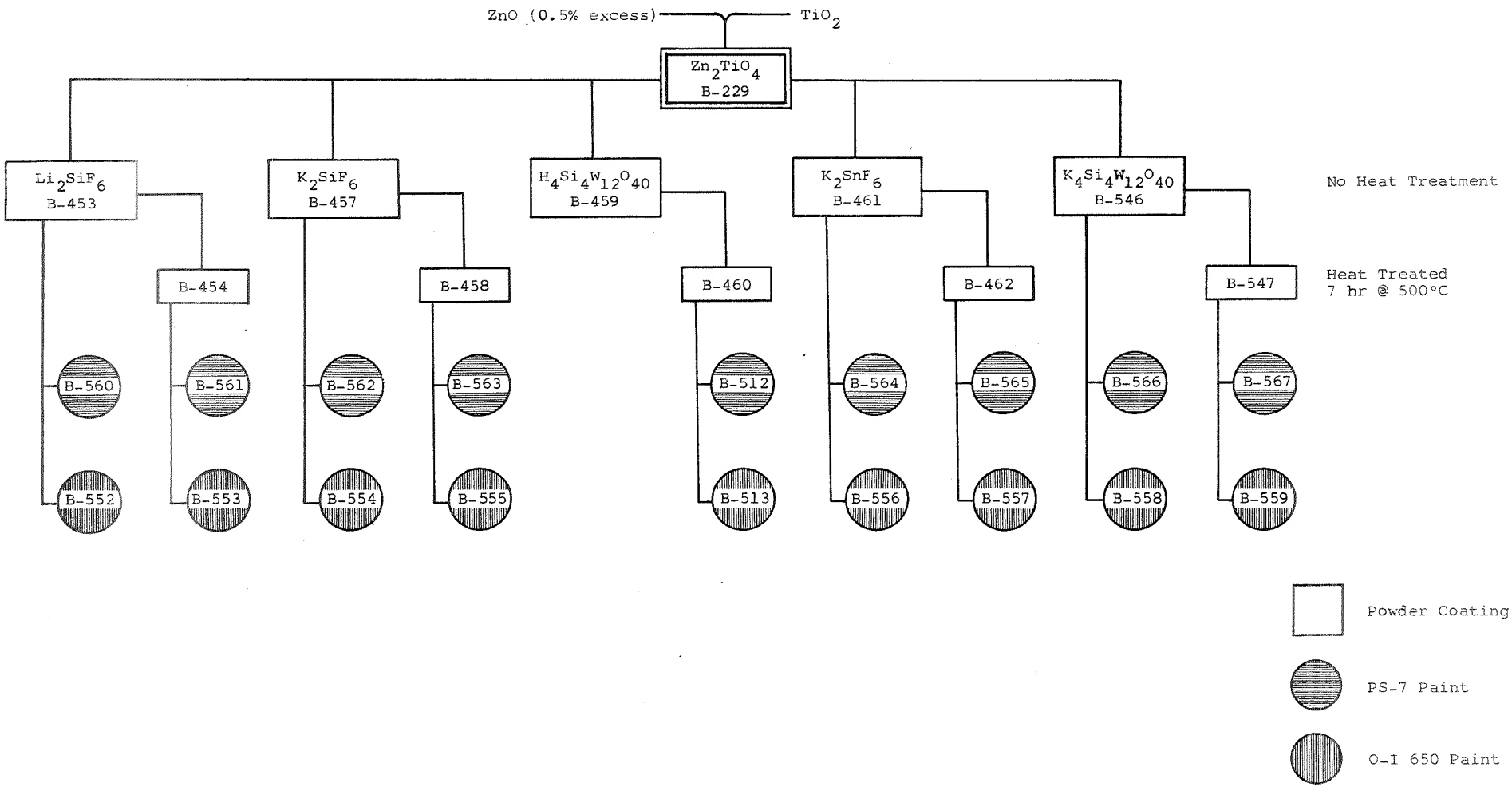


Figure 1B

ZINC ORTHOTITANATE SURFACE TREATMENT AND PAINT COATINGS HISTORY

B-412

One hundred (100) g of Batch B-233 (silicate-treated Zn_2TiO_4) were mixed with 167 g of a 5% solution of NaH_2PO_4. The mixture was refluxed for 4 hr, vacuum filtered through a Büchner funnel, rinsed with 67 ml distilled H_2O and dried for 16 hr at 110°C.

B-413

One hundred (100) g of Batch B-233 (silicate-treated Zn_2TiO_4) were mixed with 250 g of 0.001 M potassium ferrocyanide and 250 g of 0.001 M potassium ferricyanide. The mixture was heated to 80°C with agitation and held for 30 min. After cooling, the mixture was filtered through a Büchner funnel and dried for 16 hr at 110°C.

B-414

One hundred (100) g of Batch B-241 (phosphate-treated Zn_2TiO_4) were mixed with 250 g of 0.001 M potassium ferrocyanide and 250 g of 0.001 M potassium ferricyanide. The mixture was heated at 80°C for 30 min with agitation, cooled and filtered through a Büchner funnel. The resultant filter cake was dried for 16 hr at 110°C.

B-415

Twenty (20) g of Batch B-229 were ground with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin (32% PVC). The mixture was ground for 3 hr in a Mini-mill (000) ball mill. The resultant paint was spray applied on IRIF coupons and baked at 110°C for 16 hr.

B-416

Sixty (60) g of Batch B-229 were ground with 25 ml of PS-7 potassium silicate and 35 ml of distilled H_2O. The mixture was ground for 2 hr in a Mini-mill (000) ball mill. Two sets of IRIF were spray coated with the resultant paint and allowed to air dry for 16 hr. One set was then baked for 16 hr at 110°C and the other set was heat treated for 16 hr at 427°C.

B-417

Fifteen (15) g of Batch B-233 (silicate-treated Zn_2TiO_4) were ground with 35 ml of distilled H_2O for 15 min in a Mini-mill (000) ball mill. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-419

Thirty (30) g of Batch B-233 (silicate-treated Zn_2TiO_4) were ground with 12.5 ml of PS-7 potassium silicate and 12.5 ml of distilled H_2O. The mixture was ground for 1 hr in a Mini-mill (000) ball mill. Two sets of IRIF coupons were spray coated with the resultant and paint and allowed to air dry for 16 hr. One set was then baked for 16 hr at 110°C and the other set was heat treated for 16 hr at 427°C.

B-420

Ten (10) g of Batch B-241 (phosphate-treated Zn_2TiO_4) was mixed with 25 ml of distilled H_2O and ground for 15 min in a Mini-mill (000) ball mill. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-421

Twenty-four (24) g of Batch B-241 (phosphate-treated Zn_2TiO_4) was mixed with 10 ml of PS-7 potassium silicate and 10 ml of distilled H_2O. The mixture was ground for 15 min in a Mini-mill (000) ball mill. Two sets of IRIF coupons were spray coated with the resultant paint and allowed to air dry for 16 hr. One set was then baked for 16 hr at 110°C and the other set was heat treated for 16 hr at 427°C.

B-422

Twenty (20) g of Batch B-241 (phosphate-treated Zn_2TiO_4) were mixed with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground for 3 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on IRIF coupons, air dried for 16 hr, and then baked for 16 hr at 110°C.

B-423

Fifteen (15) g of Batch B-226 (Fe^{++}/Fe^{+++}-treated Zn_2TiO_4) were mixed with 35 ml distilled H_2O and ground for 20 min in a Mini-mill (000) ball mill. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-424

Thirty (30) g of Batch B-226 (Fe^{++}/Fe^{+++}-treated Zn_2TiO_4) were ground with 12.5 ml PS-7 potassium silicate and 12.5 ml distilled H_2O. The mixture was ground for 1 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on two sets of IRIF coupons and allowed to air dry for 16 hr. One set was baked for 16 hr at 110°C and the other set was heat treated for 16 hr at 427°C.

B-425

Twenty (20) g of Batch B-226 (Fe^{++}/Fe^{+++}-treated Zn_2TiO_4) were ground with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground for 3 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on IRIF coupons, air dried for 16 hr, and then baked for 16 hr at 110°C.

B-426

Thirty (30) g of Batch B-412 (phosphate- and silicate-treated Zn_2TiO_4) were mixed with 12.5 ml of PS-7 potassium silicate and 12.5 ml distilled H_2O. The mixture was ground for 1 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on two sets of IRIF coupons and allowed to air dry for 16 hr. One set was then baked for 16 hr at 110°C and the other was heat treated for 16 hr at 427°C.

B-427

Twenty (20) g of Batch B-412 (phosphate- and silicate-treated Zn_2TiO_4) were mixed with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground for 3 hr in

a Mini-mill (000) ball mill. The resultant paint was spray coated on IRIF coupons, air dried for 16 hr, then baked for 16 hr at 110°C.

B-428

Thirty (30) g of Batch B-413 (Fe^{++}/Fe^{+++}-silicate treated Zn_2TiO_4) were mixed with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground for 1 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on two sets of IRIF coupons and air dried for 16 hr. One set was then baked for 16 hr at 110°C and the other was heat treated for 16 hr at 427°C.

B-430

Thirty (30) g of Batch B-414 (Fe^{++}/Fe^{+++}-phosphate treated Zn_2TiO_4) were mixed with 12.5 ml PS-7 potassium silicate and 12.5 ml distilled H_2O. The mixture was ground for 1 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on two sets of IRIF coupons and air dried for 16 hr. One set was then baked for 16 hr at 110°C and the other set was heat treated for 16 hr at 427°C.

B-431

Twenty (20) g of Batch B-414 (Fe^{++}/Fe^{+++}-phosphate treated Zn_2TiO_4) were mixed with 34 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground for 3 hr in a Mini-mill (000) ball mill. The resultant paint was spray coated on IRIF coupons, air dried for 16 hr, and then baked for 16 hr at 110°C.

B-453

Five (5) g of lithium silicofluoride ($Li_2SiF_6 \cdot 2H_2O$) were dissolved in 1000 ml distilled H_2O. One hundred (100) g of B-229 (Zn_2TiO_4) were added to the solution and the mixture was refluxed for 6 hr with agitation. On cooling, the mixture was filtered through a Büchner funnel, rinsed 4 times with 600 ml

quantities of distilled H_2O, and dried for 16 hr at 110°C. Five (5) g of the dry pigment were dispersed in forty-five (45) ml of distilled H_2O by hand shaking and the resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-454

Approximately fifty (50) g of Batch B-453 were placed in a porcelain crucible and heat treated for 7 hr at 500°C. Five (5) g of the pigment were dispersed in forty-five (45) ml of distilled H_2O by hand shaking and the resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-457

Five (5) g of potassium silicofluoride (K_2SiF_6) were dissolved in 1000 ml distilled H_2O. One hundred (100) g of B-229 (Zn_2TiO_4) were added to the solution and the mixture was refluxed for 6 hr with agitation. On cooling, the mixture was filtered through a Büchner funnel, rinsed 4 times with 600 ml quantities of distilled H_2O, and dried for 16 hr at 110°C. Five (5) g of the dry pigment were dispersed in forty-five (45) ml distilled H_2O by hand shaking and the resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-458

Approximately 50 g of Batch B-457 were placed in a porcelain crucible and heat treated for 7 hr at 500°C. Five (5) g of the pigment were dispersed in forty-five (45) ml of distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-459

Five (5) g of silicotungstic acid ($H_4Si_4W_{12}O_{40}$) were dissolved in 1000 ml distilled H_2O. One hundred (100) g of B-229 (Zn_2TiO_4) were added to the solution and the mixture was refluxed for 6 hr with agitation. On cooling, the mixture was filtered through a Büchner funnel, rinsed 4 times with 600 ml

quantities of distilled H_2O and dried for 16 hr at 110°C. Five (5) g of the pigment were dispersed in forty-five (45) ml of distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-460

Approximately fifty (50) g of Batch B-459 were placed in a porcelain crucible and heat treated for 7 hr at 500°C. Five (5) g of the pigment were dispersed in forty-five (45) ml distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-461

Five (5) g of potassium hexafluorostannate ($K_2SnF_6 \cdot xH_2O$) were dissolved in 1000 ml distilled H_2O. One hundred (100) g of B-229 (Zn_2TiO_4) were added to the solution and the mixture was refluxed for 6 hr with agitation. On cooling, the mixture was filtered through a Büchner funnel, rinsed 4 times with 600 ml quantities of distilled H_2O, and dried for 16 hr at 110°C. Five (5) g of the pigment were dispersed in forty-five (45) ml distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-462

Approximately 50 g of Batch B-461 were placed in a porcelain crucible and heat treated for 7 hr at 500°C. Five (5) g of the pigment were dispersed in forty-five (45) ml distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-546

Five (5) g of potassium silicotungstate ($K_4Si_4W_{12}O_{40} \cdot 18H_2O$) were dissolved in 1000 ml distilled H_2O. One hundred (100) g of B-229 (Zn_2TiO_4) were added to the solution and the mixture was refiltered through a Büchner funnel, rinsed 4 times with 600 ml quantities of distilled H_2O, and dried for 16 hr at 110°C. Five

(5) g of the dry pigment were dispersed in forty-five (45) ml of distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

B-547

Approximately 50 g of Batch B-546 were placed in a porcelain crucible and heat treated for 7 hr at 500°C. Five (5) g of the pigment were dispersed in forty-five (45) ml distilled H_2O by hand shaking. The resultant slurry was "wet" sprayed on "hot" IRIF coupons.

* * * *

The following paints were prepared in identical fashion. The procedure used in their preparation was as follows: Five (5) g of the pigment being studied were mixed with 8.5 g of a 28% ethanol solution of Owens-Illinois 650 resin. The mixture was ground by means of a mortar and pestle. The resultant paint was sprayed on IRIF coupons and baked for 17 hr at 110°C. The pigments studied are tabulated below.

Coating No.	Pigment Batch No.	Pigment Description
B-552	B-453	Li_2SiF_6 treated Zn_2TiO_4
B-553	B-454	Heat treated B-453
B-554	B-457	K_2SiF_6 treated Zn_2TiO_4
B-555	B-458	Heat treated B-457
B-556	B-461	K_2SnF_6 treated Zn_2TiO_4
B-557	B-462	Heat treated B-461
B-558	B-546	$K_4SiW_{12}O_{40}$ treated Zn_2TiO_4
B-559	B-547	Heat treated B-546

* * * *

The following paints were prepared in identical fashion. The procedure used in their preparation was as follows: Seven

and one-half (7.5) g of the pigment being studied were mixed with 3.1 ml PS-7 potassium silicate and 3.1 ml distilled H_2O. The mixture was ground by means of a mortar and pestle. The resultant paint was sprayed on IRIF coupons and baked for 16 hr at 110°C. The pigments studied are tabulated below.

Coating No.	Pigment Batch No.	Pigment Description
B-560	B-453	Li_2SiF_6 treated Zn_2TiO_4
B-561	B-454	Heat treated B-453
B-562	B-457	K_2SiF_6 treated Zn_2TiO_4
B-563	B-458	Heat treated B-457
B-564	B-461	K_2SnF_6 treated Zn_2TiO_4
B-565	B-462	Heat treated B-461
B-566	B-546	$K_4SiW_{12}O_{40}$ treated Zn_2TiO_4
B-567	B-547	Heat treated B-546

B. Ultraviolet Irradiation

The pigment and paint specimens whose preparatory procedures were presented in the preceeding section were irradiated for a minimum of 1000 equivalent sun-hours (ESH) of ultraviolet in the IRIF-I space simulation chamber. Nominal test parameters for the eight tests performed (IRIF-I Tests I-28 through I-35) are presented in Table 1. All irradiations were performed at six (6) equivalent ultraviolet acceleration factors, at nominal substrate temperatures of 10°C or less, and at pressures of less than 7×10^{-7} torr.

Specimen identifications and the applicable IRIF-I test designations are presented in Tables 2 and 3 for reference.

Table 1

IRIF-I TEST PARAMETERS

Test	Irradiation Pressure Initial	Irradiation Pressure Final	Flux (Solar Factor)	Fluence (ESH)	Nominal Specimen Temperature °C
I-28	2.8×10^{-7}	2.4×10^{-7}	6	970	8
I-29	3.0×10^{-7}	1.6×10^{-7}	6	2000	9
I-30	2.6×10^{-7}	2.1×10^{-7}	6	1010	10
I-31	7.0×10^{-7}	5.7×10^{-7}	6	1010	11
I-32	1.2×10^{-7}	1.1×10^{-7}	6	1010	10
I-33	1.3×10^{-7}	1.3×10^{-7}	6	1010	9
I-34	1.3×10^{-7}	1.3×10^{-7}	6	1000	8
I-35	6.0×10^{-7}	1.3×10^{-7}	6	1200	7

Table 2

SCHEDULE OF IRRADIATION OF Zn_2TiO_4 POWDERS

Batch No.	Pigment Treatment: Reactant	Pigment Treatment: Heat Treatment	IRIF-I Test No. (Coupon Nos.) I-28	I-30	I-31	I-34
B-229	Control	---	LL-10		LL-35	
B-417	PS7	---	LL-31			
B-420	NaH_2PO_4	---	LL-32			
B-423	Fe-CN	---	LL-33			
SRI-9-20	Plasma	---		LL-49		
SRI-3-5	Plasma	---		LL-50		
SRI-3-3	Plasma	---		LL-51		
B-453	Li_2SiF_6	---			LL-53	
B-457	K_2SiF_6	---			LL-54	
B-459	$H_2Si_4W_{12}O_{40}$	---			LL-55	
B-461	K_2SnF_6	---			LL-56	
B-454	Li_2SiF_6	7 hr/500°C			LL-57	
B-458	K_2SiF_6	7 hr/500°C			LL-58	
B-460	$H_4Si_4W_{12}O_{40}$	7 hr/500°C			LL-59	
B-462	K_2SnF_6	7 hr/500°C			LL-60	
B-546	$K_4Si_4W_{12}O_{40}$	---				LL-32
B-547	$K_4Si_4W_{12}O_{40}$	7 hr/500°C				LL-35

Table 3

SCHEDULE OF IRRADIATION OF Zn_2TiO_4 PAINTS

Code	Pigment Treatment	Paint (hr/°C)[1]	I-28	I-29	I-30	I-33	I-34	I35
B-416A	None	PS7[2]	LL-34					
B-416B	None	PS7 (16/427)[1]	LL-35					
B-415B	None	OI[3] (16/110)	LL-49					
B-422	NaH_2PO_4	OI (16/110)	LL-50					
B-425	Fe-CN	OI (16/110)	LL-51					
B-427	PS7/NaH_2PO_4	OI (16/110)	LL-52					
B-431	NaH_2PO_4/Fe-CN	OI (16/110)	LL-53					
B-419A	PS7	PS7		LL-36				
B-419B	PS7	PS7 (16/427)		LL-37				
B-421A	NaH_2PO_4	PS7		LL-38				
B-421B	NaH_2PO_4	PS7 (16/427)		LL-39				
B-424A	Fe-CN	PS7		LL-40				
B-424B	Fe-CN	PS7 (16/427)		LL-41				
B-426A	PS7/NaH_2PO_4	PS7		LL-42				
B-426B	PS7/NaH_2PO_4	PS7 (16/427)		LL-43				
B-428A	PS7/Fe-CN	PS7		LL-44				
B-428B	PS7/Fe-CN	PS7 (16/427)		LL-45				
B-430A	NaH_2PO_4/Fe-CN	PS7		LL-46				
B-430B	NaH_2PO_4/Fe-CN	PS7 (16/427)		LL-47				
SRI-9-20	Plasma	OI			LL-61			
SRI-3-3	Plasma	OI			LL-62			
SRI-3-5	Plasma	OI			LL-63			
Nimbus	KKK	PS7				B-517		
B-574	None	RTV602[4]					LL-68	
B-561	B-454 (HT)[5]	PS7						LL-37
B-563	B-458 (HT)	PS7						LL-39
B-565	B-462 (HT)	PS7						LL-42
B-567	B-547 (HT)	PS7						LL-44
B-553	B-454 (HT)	OI						LL-46
B-555	B-458 (HT)	OI						LL-52
B-557	B-462 (HT)	OI						LL-63
B-559	B-547 (HT)	OI						LL-65

[1]Paint heat treatment.

[2]Potassium silicate paint.

[3]Owens-Illinois 650 silicone resin.

[4]General Electric RTV-602.

[5]Pigment heat treated for 7 hr at 500°C.

III. RESULTS

A. Introduction

The complete history of all reactive-encapsulation studies performed in 1970 are presented schematically in Figures 1a and 1b (see pp. 4 and 5). The exact experimental procedures employed in the preparation of each batch were also presented in the previous section. The open circles and squares in Figures 1a and 1b represent surface-treated (reactively encapsulated) powders that were irradiated in the IRIF-I and/or employed as pigment material for silicate and silicone paints. The first row of "filled" circles represent PS-7 potassium silicate-based inorganic paints and the second row of filled circles (the last row) represents silicone paints prepared from Owens-Illinois 650 Glass Resin.

B. Data

1. Control Powders

The results of irradiation of the zinc orthotitanate control powder (Batch B-229) and control powders of silicated, phosphated and iron cyanide-treated zinc orthotitanate are presented in Table 4 and Figures 2 through 5.

The spectral damage sustained by the control zinc orthotitanate (B-229) and the silicated powder (B-417) compare favorably with previous results (Ref. 1). See specifically Batches B-244 and B-250, IRIF-II Tests II-17a and II-19, listed in Table 1 of Reference 1.) The phosphated powder (B-420) was more seriously damaged in these tests than in previous studies (e.g., sample B-245, Table 2, Reference 1).

2. New Reactively Encapsulated Powders

Five (5) new materials were employed as reactive encapsulants for zinc orthotitanate. They are: lithium hexafluorosilicate (Li_2SiF_6); potassium hexafluorosilicate (K_2SiF_6); potassium hexafluorostannate (K_2SnF_6); silicotungstic acid ($H_4Si_4W_{12}O_{40}$);

Table 4

EFFECT OF IRRADIATION ON
THE SPECTRAL REFLECTANCE OF CHEMICALLY TREATED Zn_2TiO_4 POWDERS

Batch No.	Chemical	Hr. @ Temp., °C	Exposure (ESH)	362-nm Shoulder Reflectance	Reflectance Decrease, ΔR_λ (λ = nm), %				
					362	400	700	950	2400
B-229	None	(Control)	970	62.0	2.0	4.0	4.0	4.5	2.8
B-229	None	(Control)	1010	51.5	0.0	3.6	4.0	5.8	3.2
B-417	PS7	---	970	50.5	4.5	8.0	1.5	1.0	1.5
B-420	NaH_2PO_4	---	970	91.5	7.0	7.5	6.0	5.0	1.5
B-423	Fe-CN	---	970	52.5	2.6	7.0	5.4	6.2	3.3

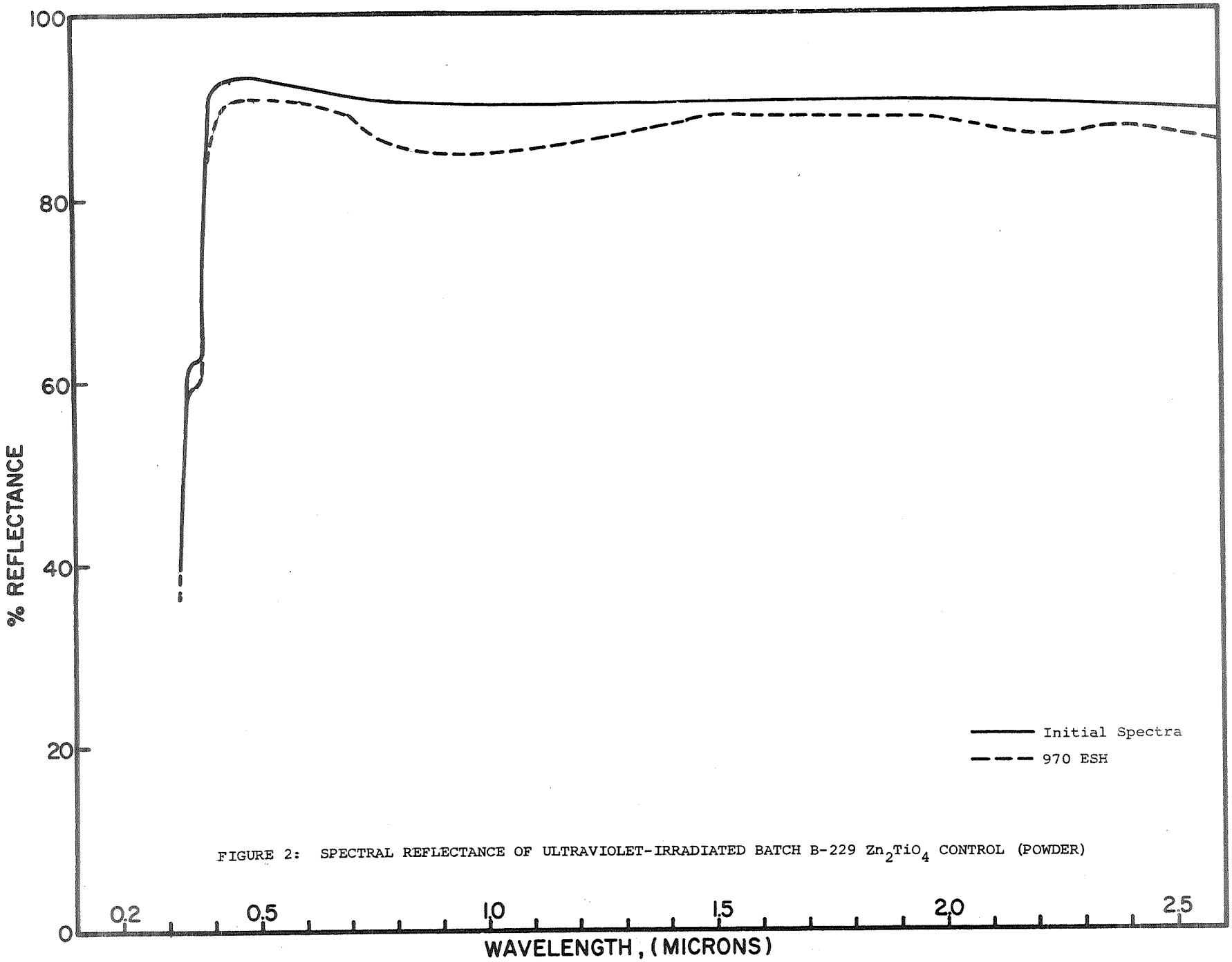


FIGURE 2: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-229 Zn_2TiO_4 CONTROL (POWDER)

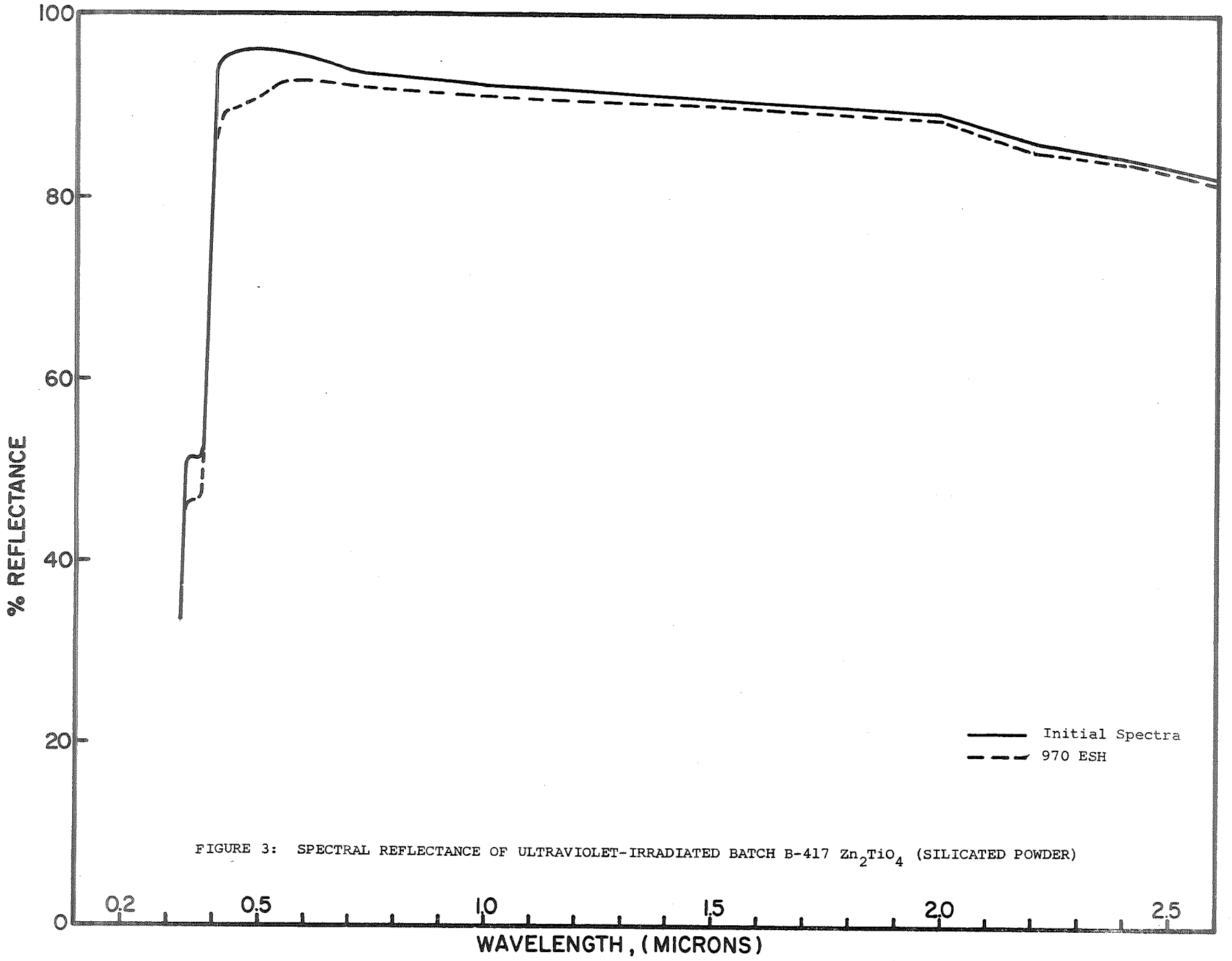


FIGURE 3: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-417 Zn_2TiO_4 (SILICATED POWDER)

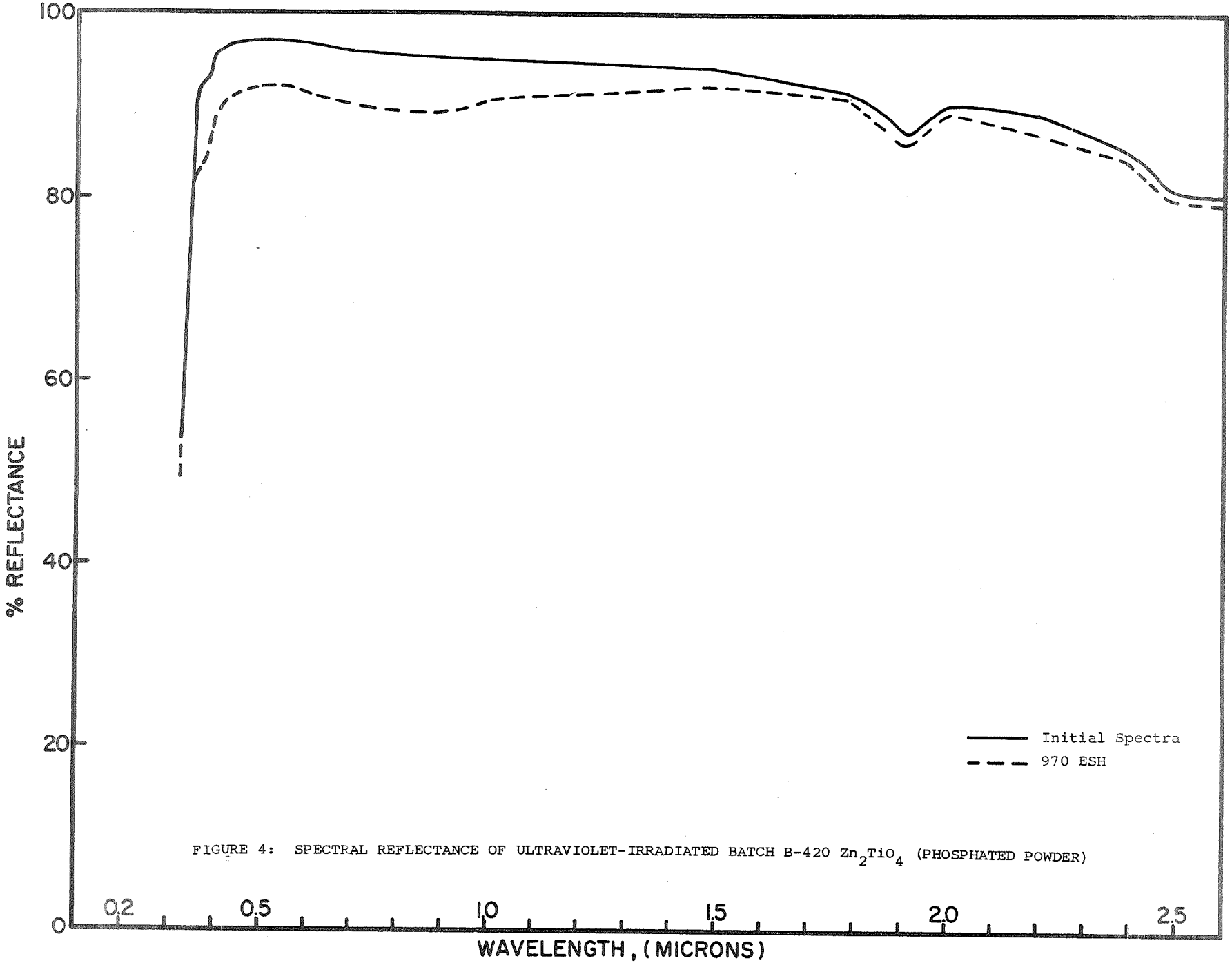


FIGURE 4: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-420 Zn_2TiO_4 (PHOSPHATED POWDER)

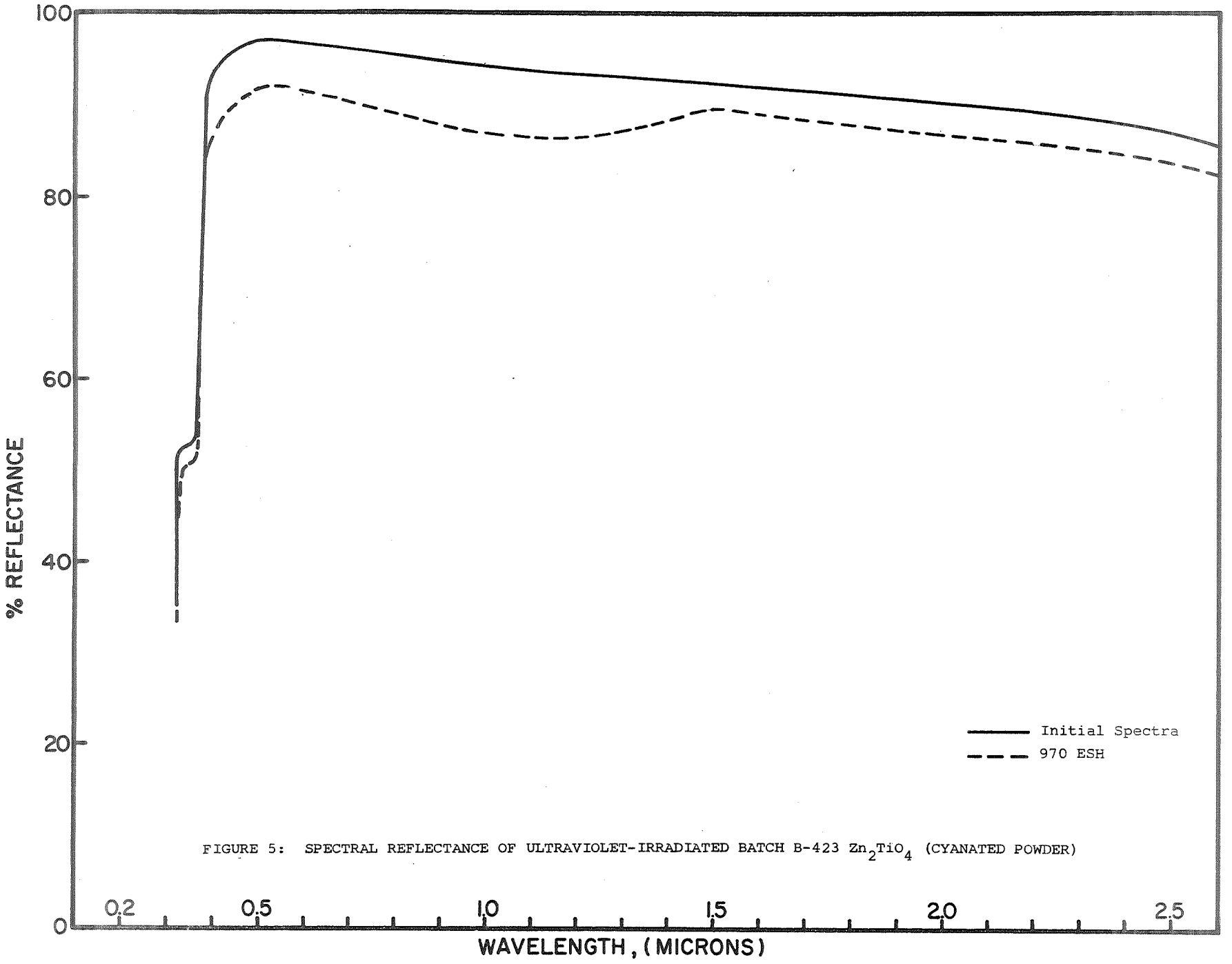


FIGURE 5: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-423 Zn_2TiO_4 (CYANATED POWDER)

and, potassium silicotungstate ($K_4Si_4W_{12}O_{40}$). The reflectance changes induced by ultraviolet irradiation in vacuum of the Zn_2TiO_4 powders treated with these reactants are presented in Table 5 and Figures 6 through 15.

3. Paints Prepared from Control Pigments

The results of irradiation of potassium silicate and Owens-Illinois 650 silicone paints prepared from silicated, phosphated and iron cyanate-treated Zn_2TiO_4 powders are presented in Table 6 and Figures 16 through 23.

Figures 16 through 19 present data on paints prepared from the untreated, precursor control-pigment, Batch B-229. These data were not obtained in the previous studies (Ref. 1). However, Batch B-422 (Figure 20) is similar to Batch B-247 which was irradiated previously and which was discussed in Table 2 of Reference 1. The present preparation (B-422) sustained considerably greater damage than the paint irradiated in Tests I-25 and II-19. On the other hand, no comparison can be made between the damage sustained by B-425 in test I-28 and B-252 in test II-17 (see Table 2, Reference 1). The silicone paints B-427 and B-431 were pigmented from treated pigment that was not prepared previously.

4. Potassium Silicate Paints

Data for air-dried and heat-treated potassium silicate paints based upon treated zinc orthotitanate pigments are presented in Table 7. Reflectance curves are presented for the air-dried paints only (Figures 24 through 29).

The PS-7 paints prepared from silicated Zn_2TiO_4 (Batches B-419A and B) exhibit ultraviolet damage effects as a function of heat treating the paint for 16 hr at 427°C that are the reverse of those observed in the previous studies (Batches B-224A and B, Table 1, Reference 1). Heat treating improved the stability of the silicate paint in the 400- to 500-nm wavelength region in the

Table 5

EFFECT OF 1010 ESH OF UV IRRADIATION ON
THE SPECTRAL REFLECTANCE OF CHEMICALLY-TREATED Zn_2TiO_4 POWDERS

Batch No.	Chemical	Hr. @ Temp., °C	362-nm Shoulder Reflectance	Reflectance Decrease, ΔR_λ (λ = nm), %				
				362	400	700	950	2400
B-453	Li_2SiF_6	---	82.5	8.0	7.2	3.0	2.5	1.0
B-454	Li_2SiF_6	7 @ 500	72.0	1.0	2.8	1.0	1.7	1.7
B-457	K_2SiF_6	---	82.0	5.0	5.3	3.1	3.0	1.8
B-458	K_2SiF_6	7 @ 500	73.0	2.7	3.0	1.6	2.2	1.8
B-459	$H_4Si_4W_{12}O_{40}$	---	49.6	0.6	4.0	11.8	11.5	3.8
B-460	$H_4Si_4W_{12}O_{40}$	7 @ 500	59.0	1.3	2.0	1.6	2.0	1.5
B-461	K_2SnF_6	---	77.5	8.0	6.5	1.0	1.5	1.5
B-462	K_2SnF_6	7 @ 500	77.0	9.0	6.0	1.3	2.5	1.7
B-546	$K_4Si_4W_{12}O_{40}$	---	50.9	0.8	4.2	5.0	4.8	1.5
B-547	$K_4Si_4W_{12}O_{40}$	7 @ 500	52.5	0.5	3.3	2.1	2.1	1.3

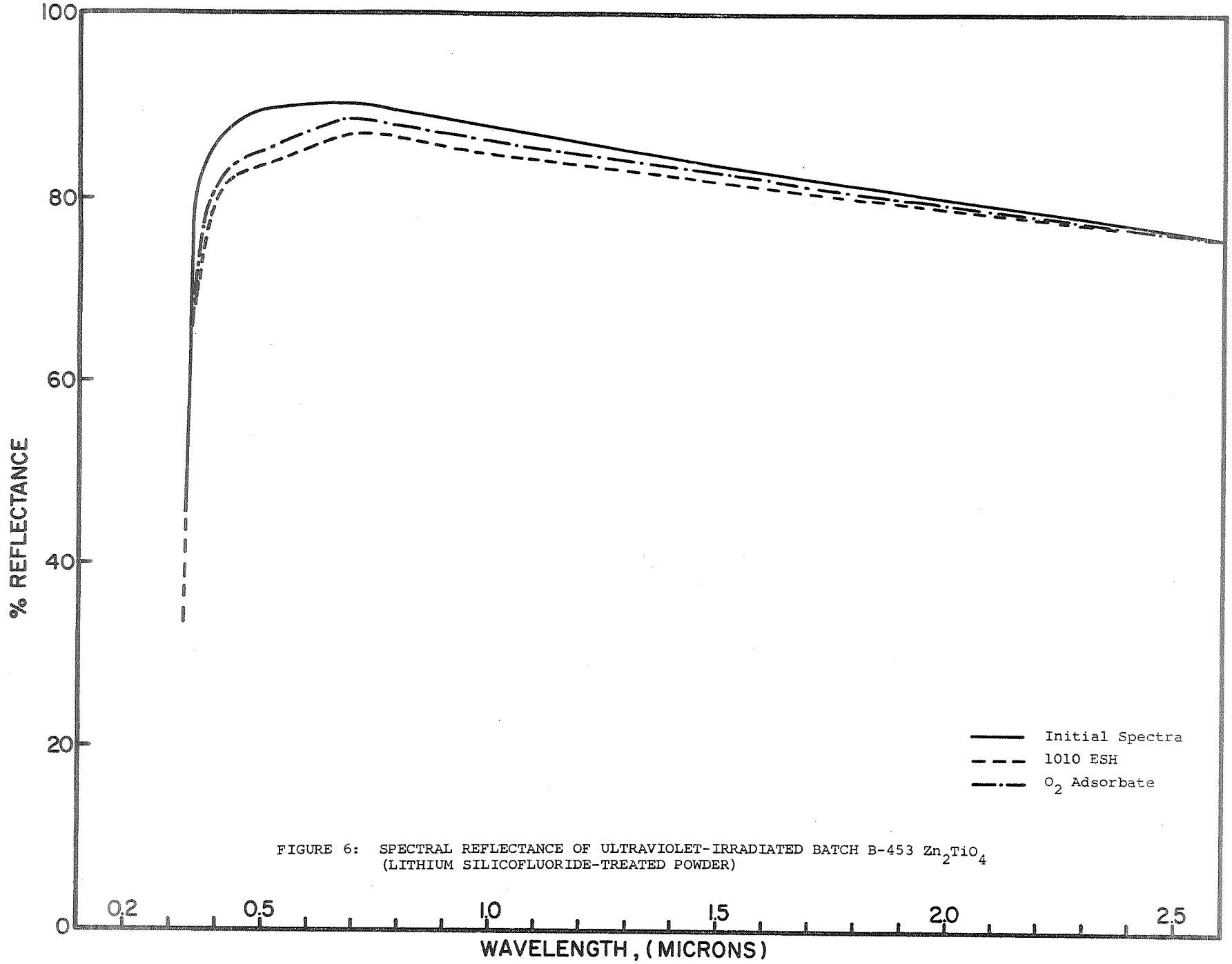


FIGURE 6: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-453 Zn_2TiO_4 (LITHIUM SILICOFLUORIDE-TREATED POWDER)

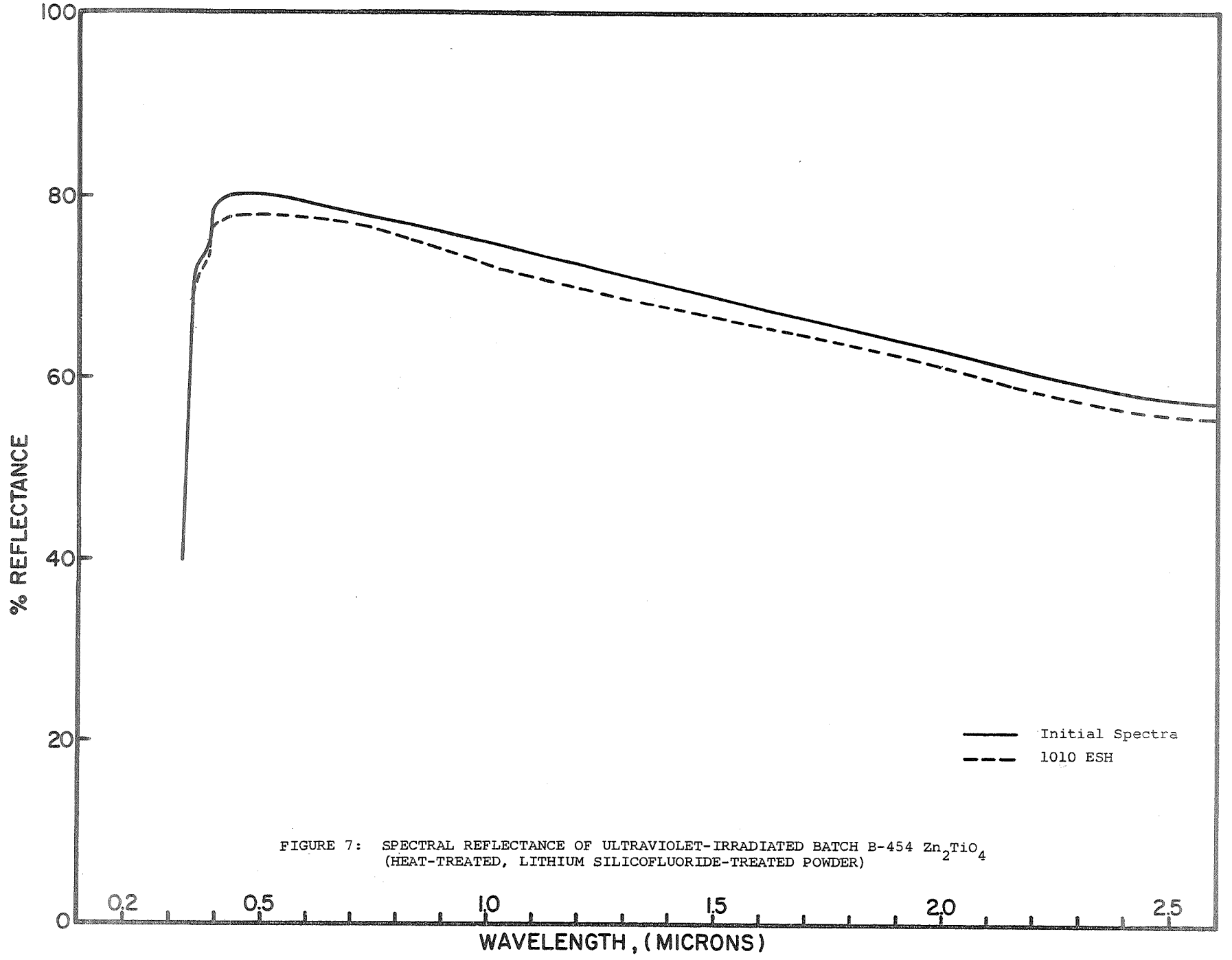


FIGURE 7: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-454 Zn_2TiO_4 (HEAT-TREATED, LITHIUM SILICOFLUORIDE-TREATED POWDER)

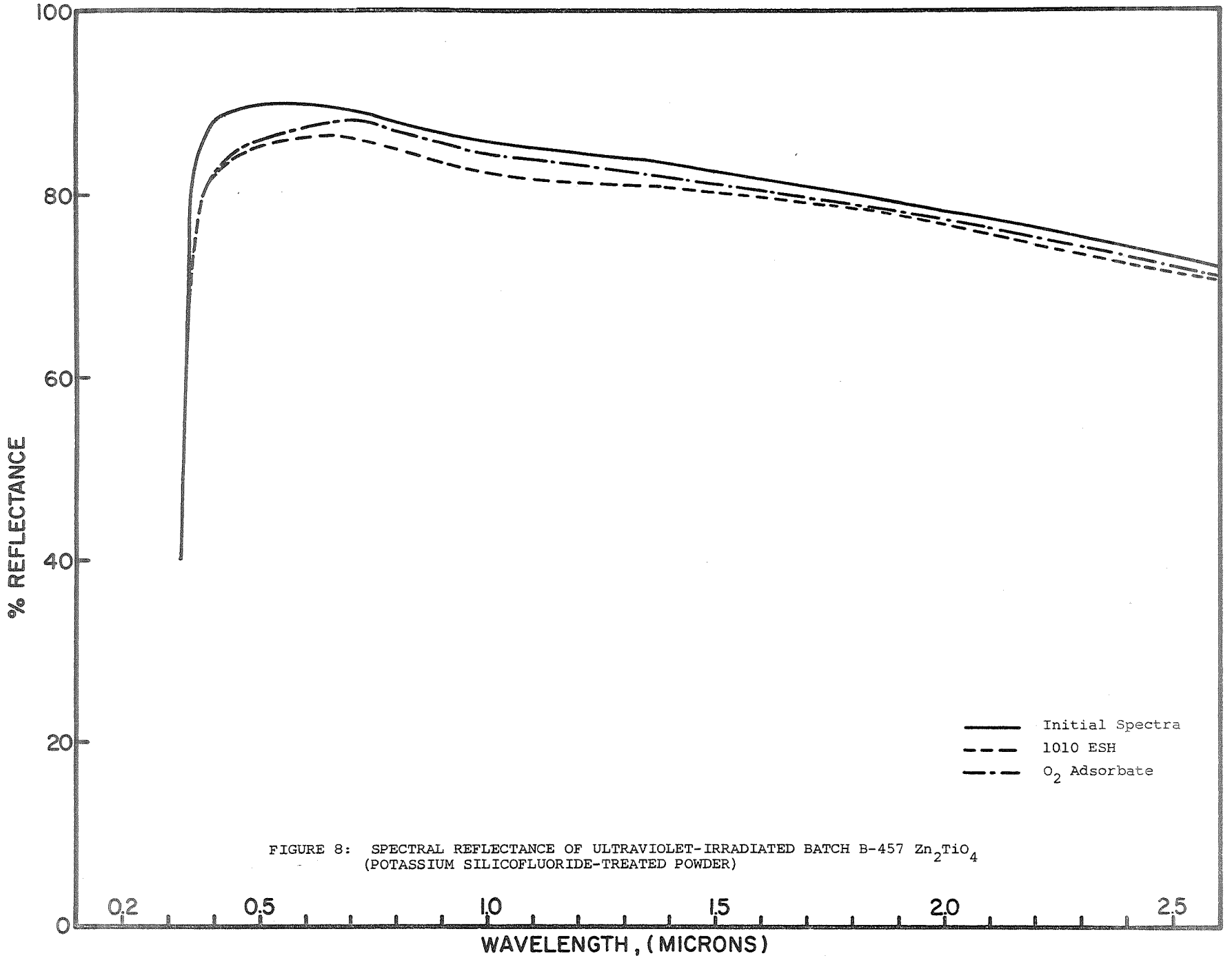


FIGURE 8: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-457 Zn_2TiO_4 (POTASSIUM SILICOFLUORIDE-TREATED POWDER)

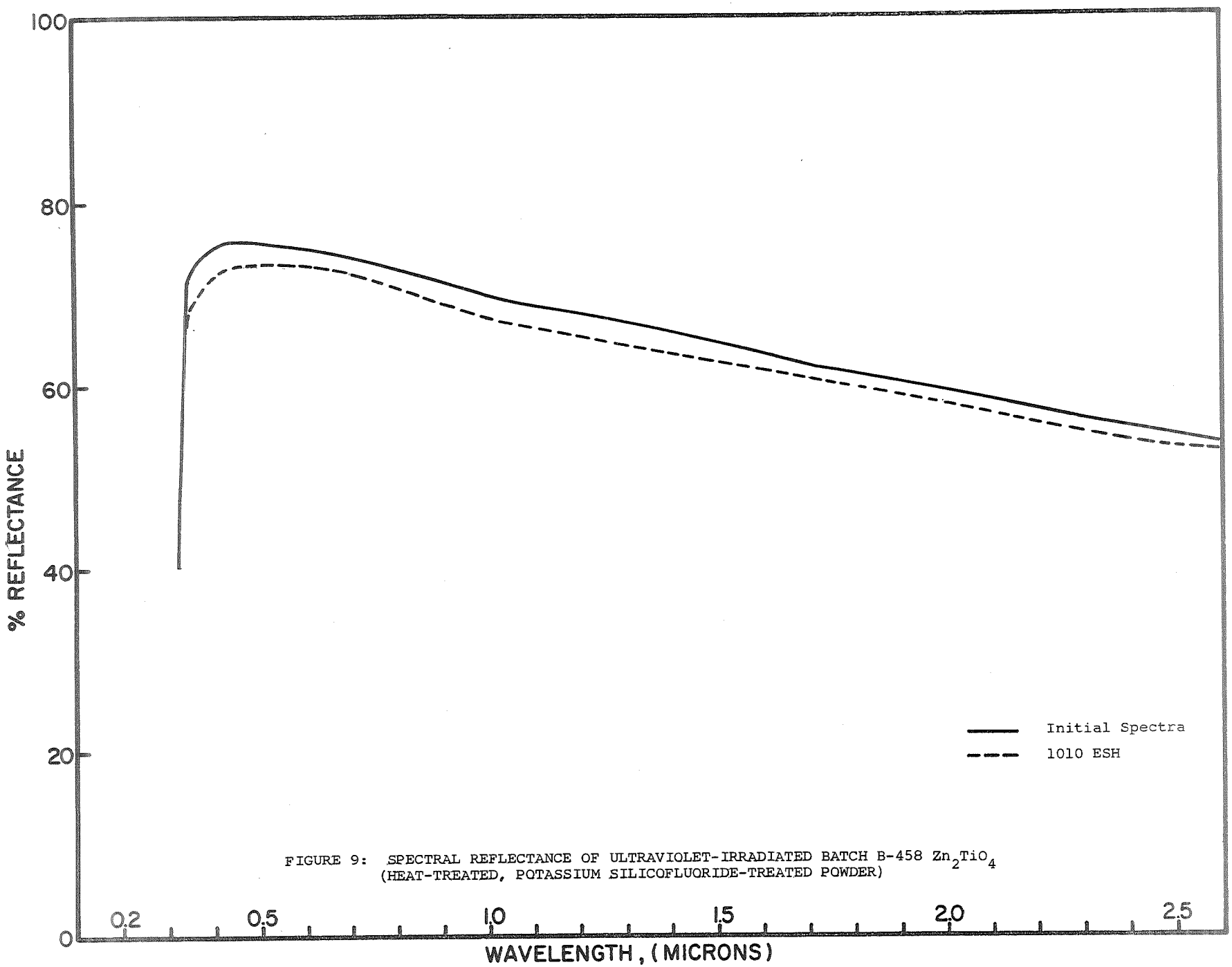


FIGURE 9: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-458 Zn_2TiO_4
(HEAT-TREATED, POTASSIUM SILICOFLUORIDE-TREATED POWDER)

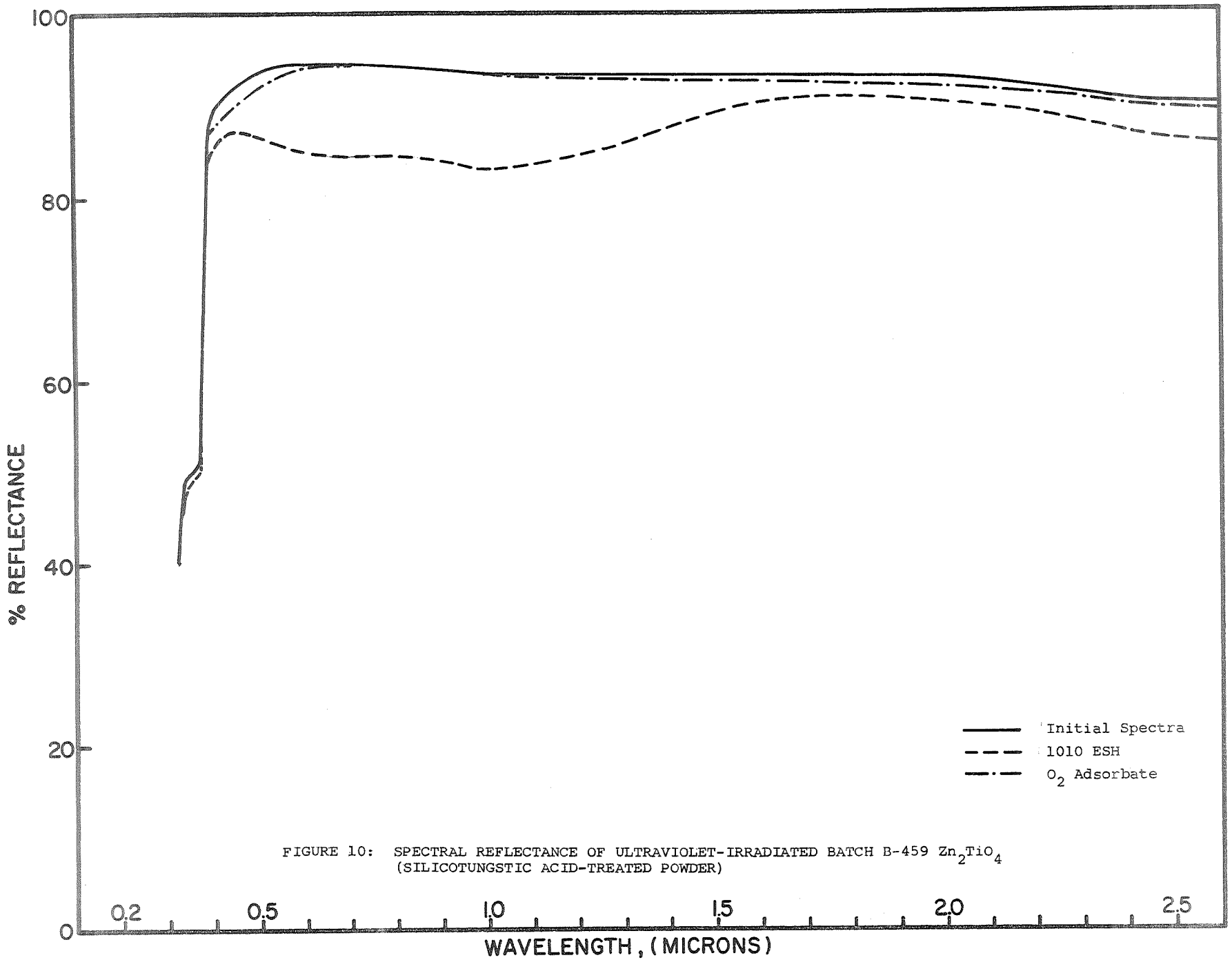


FIGURE 10: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-459 Zn_2TiO_4 (SILICOTUNGSTIC ACID-TREATED POWDER)

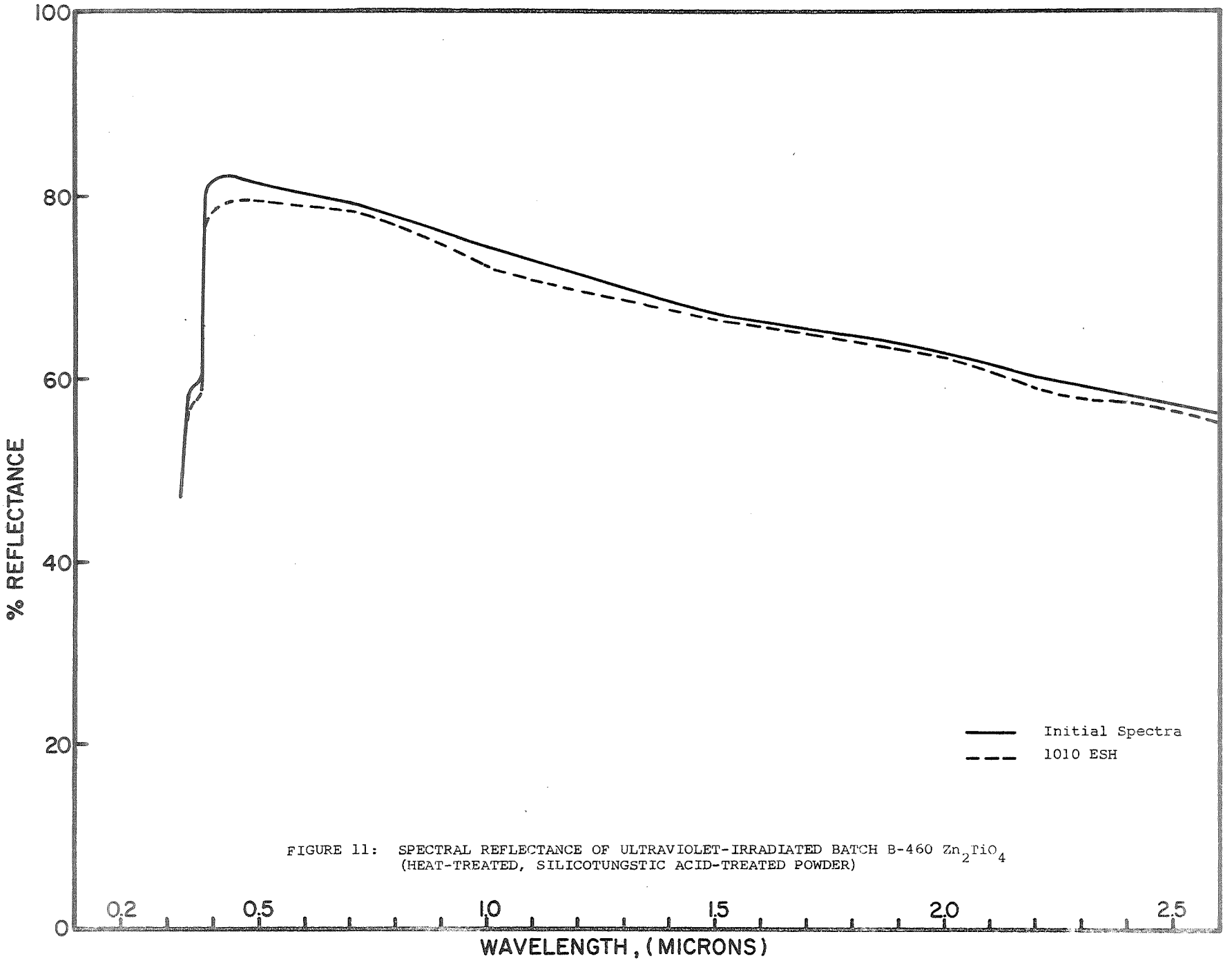


FIGURE 11: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-460 Zn_2TiO_4 (HEAT-TREATED, SILICOTUNGSTIC ACID-TREATED POWDER)

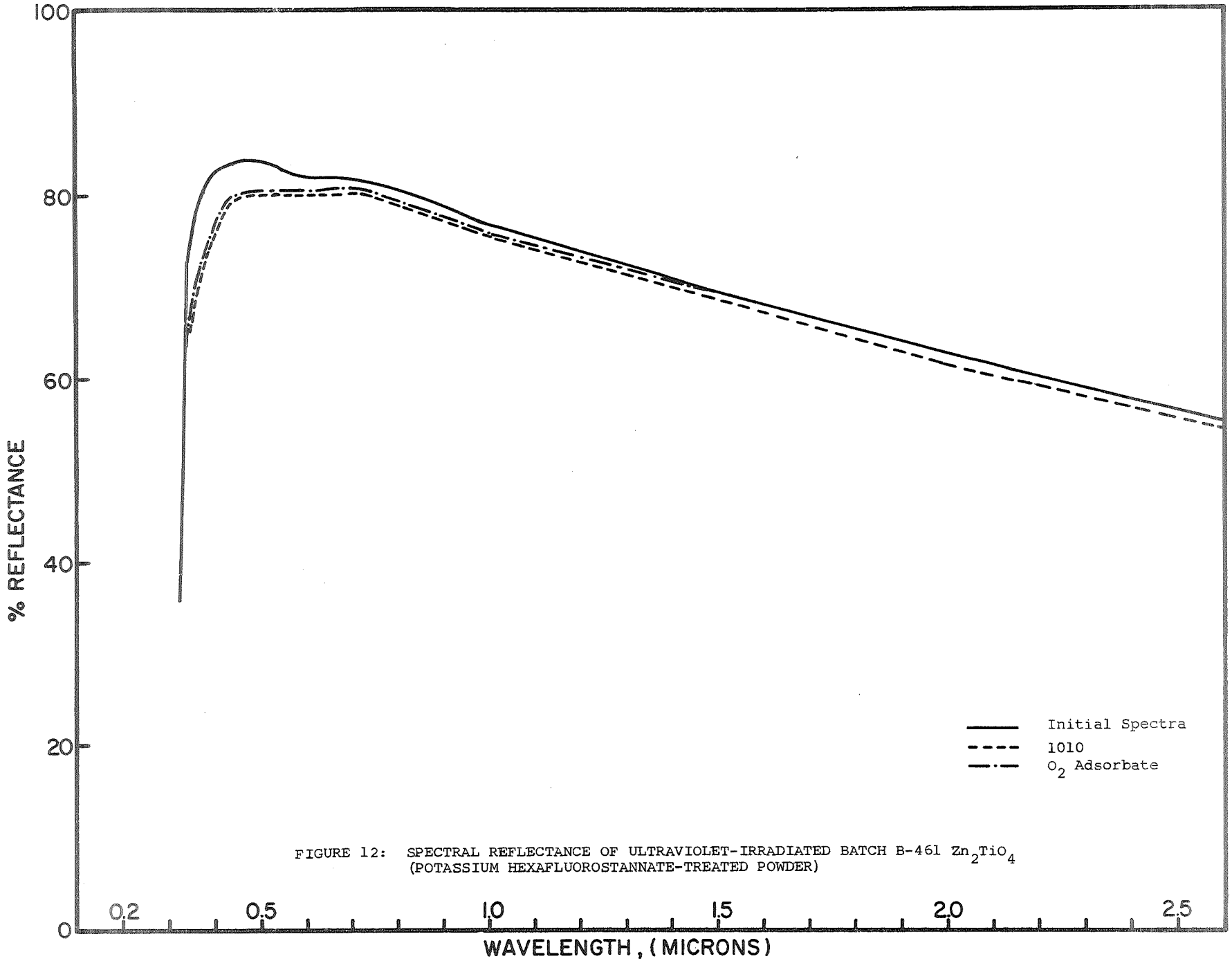


FIGURE 12: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-461 Zn_2TiO_4 (POTASSIUM HEXAFLUOROSTANNATE-TREATED POWDER)

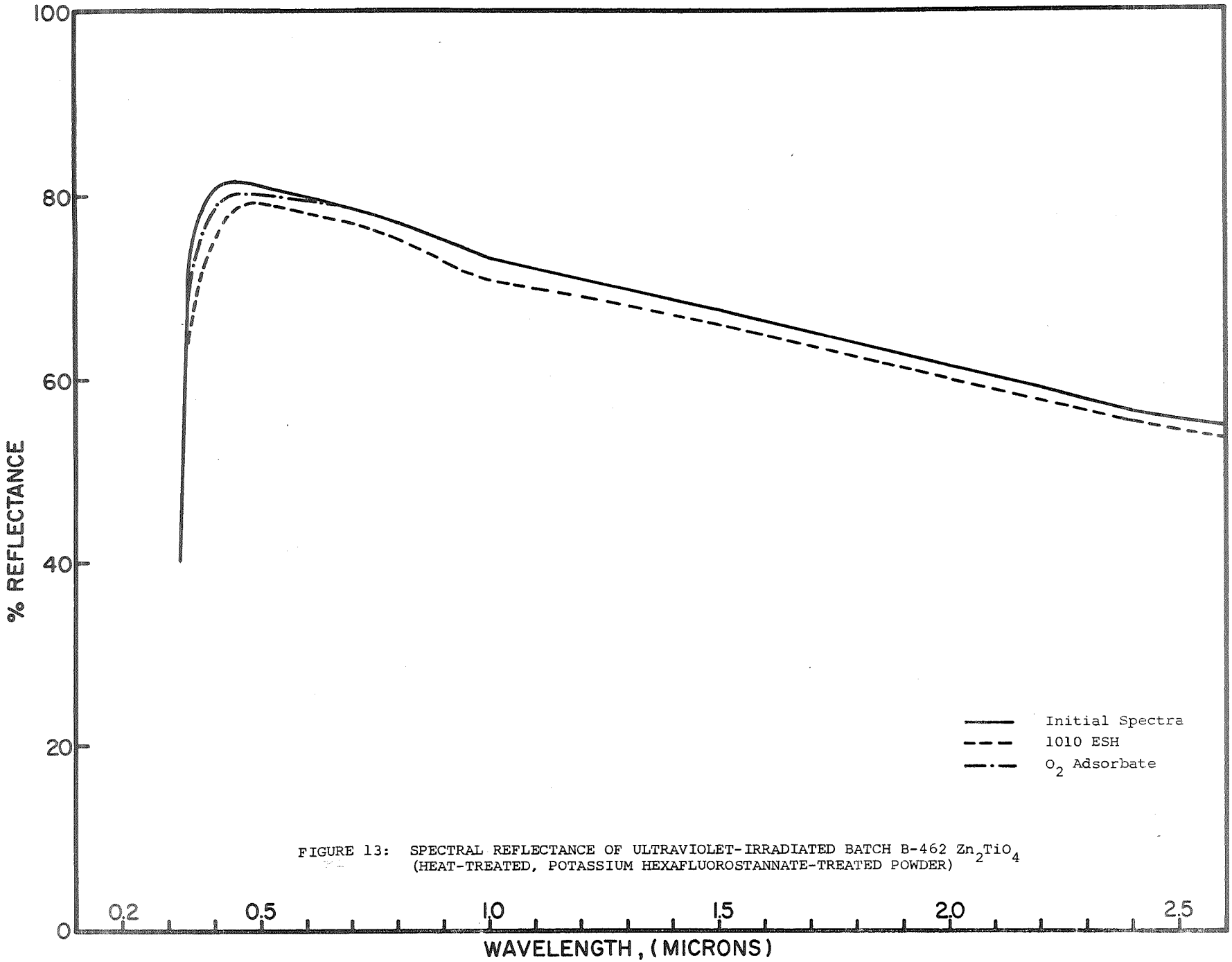


FIGURE 13: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-462 Zn_2TiO_4 (HEAT-TREATED, POTASSIUM HEXAFLUOROSTANNATE-TREATED POWDER)

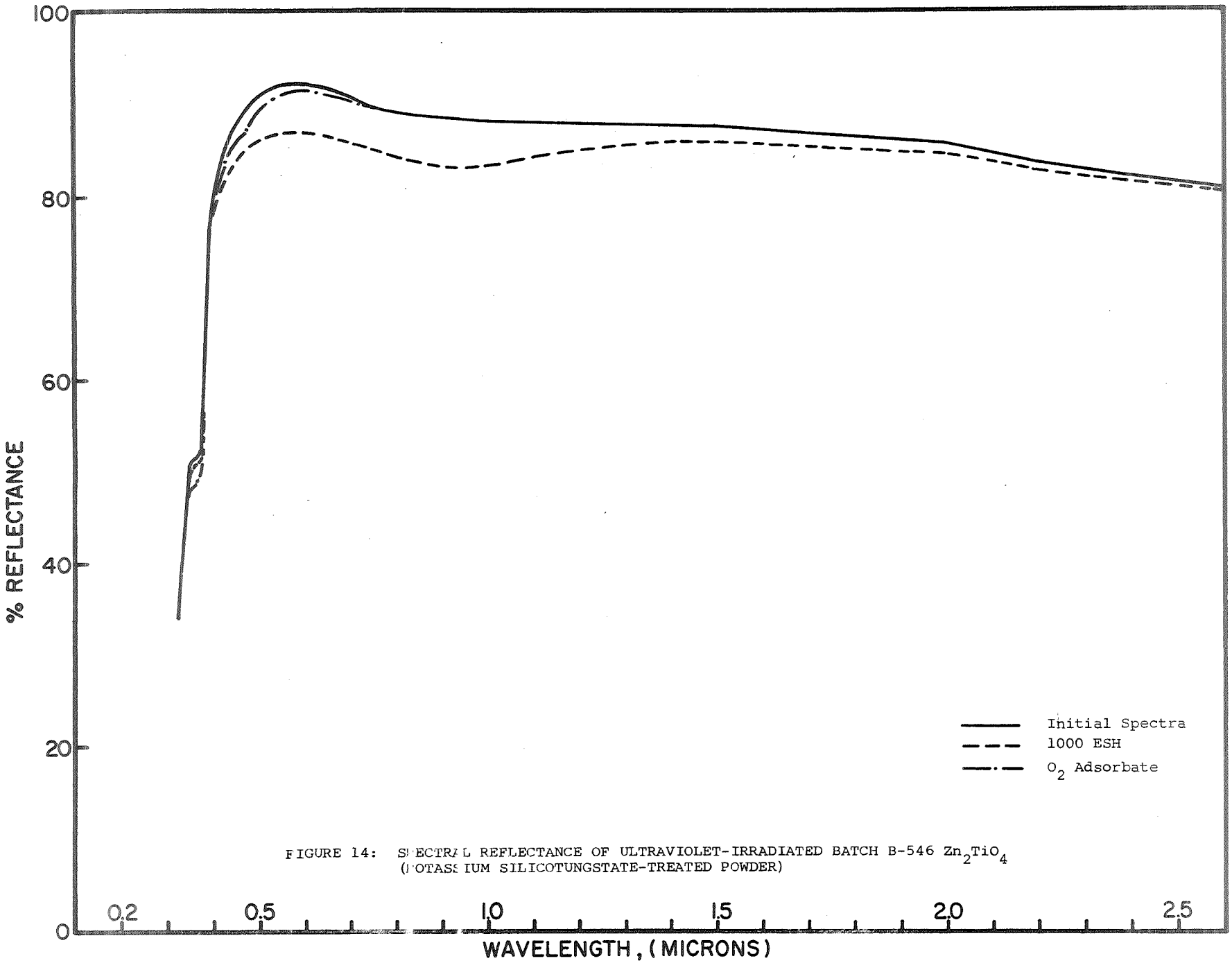


FIGURE 14: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-546 Zn_2TiO_4 (POTASSIUM SILICOTUNGSTATE-TREATED POWDER)

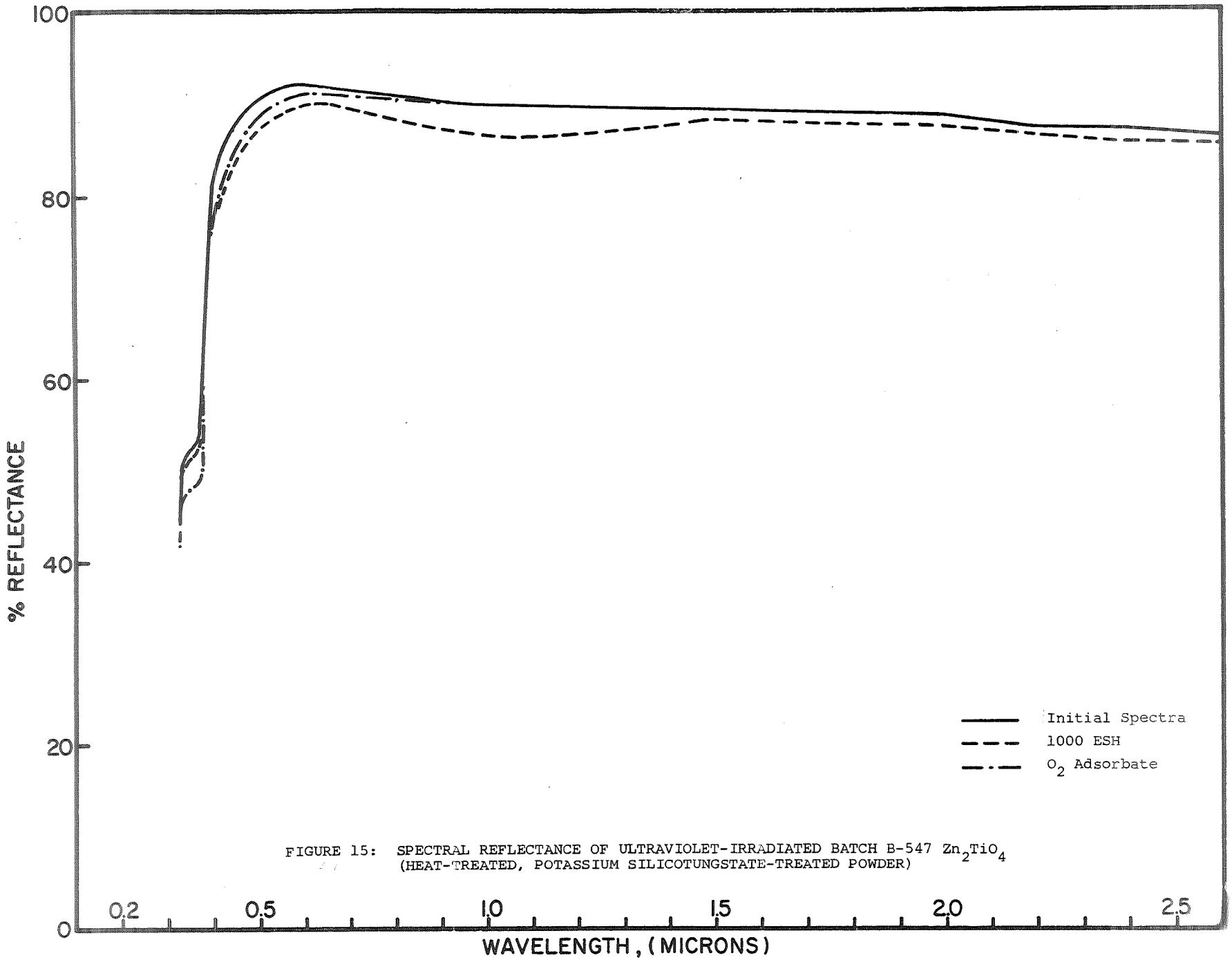


FIGURE 15: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-547 Zn_2TiO_4 (HEAT-TREATED, POTASSIUM SILICOTUNGSTATE-TREATED POWDER)

Table 6

EFFECT OF IRRADIATION ON THE SPECTRAL REFLECTANCE OF Zn_2TiO_4 PAINTS

Batch No.	Paint	Heat Treatment Hr	Heat Treatment Temp. °C	Pigment Treatment Batch No.	Pigment Treatment Chemical	Exposure (ESH)	Reflectance Decrease, ΔR_λ (λ = nm), % 362	425	700	950	2400
B-416A	PS7	--	---	B-229	---	970	4.0	5.0	0.7	1.0	0.8
B-416B	PS7	16	427	B-229	---	970	3.2	3.4	0.8	0.2	0.3
B-415B	OI	16	110	B-229	---	970	1.0	3.5	6.0	7.8	2.8
B-574	RTV	--	---	B-229	---	1000	15.5	40.5	12.0	6.5	0.8
B-422	OI	16	110	B-241	$HPO_4^=$	970	3.0	8.0	15.0	13.0	0.0
B-425	OI	16	110	B-226	Fe-CN	970	1.5	5.8	6.0	7.4	2.0
B-427	OI	16	110	B-412	PS7/$HPO_4^=$	970	2.2	5.2	6.0	6.9	3.9
B-431	OI	16	110	B-414	$HPO_4^=$/Fe-CN	970	4.5	9.5	12.7	12.0	4.0

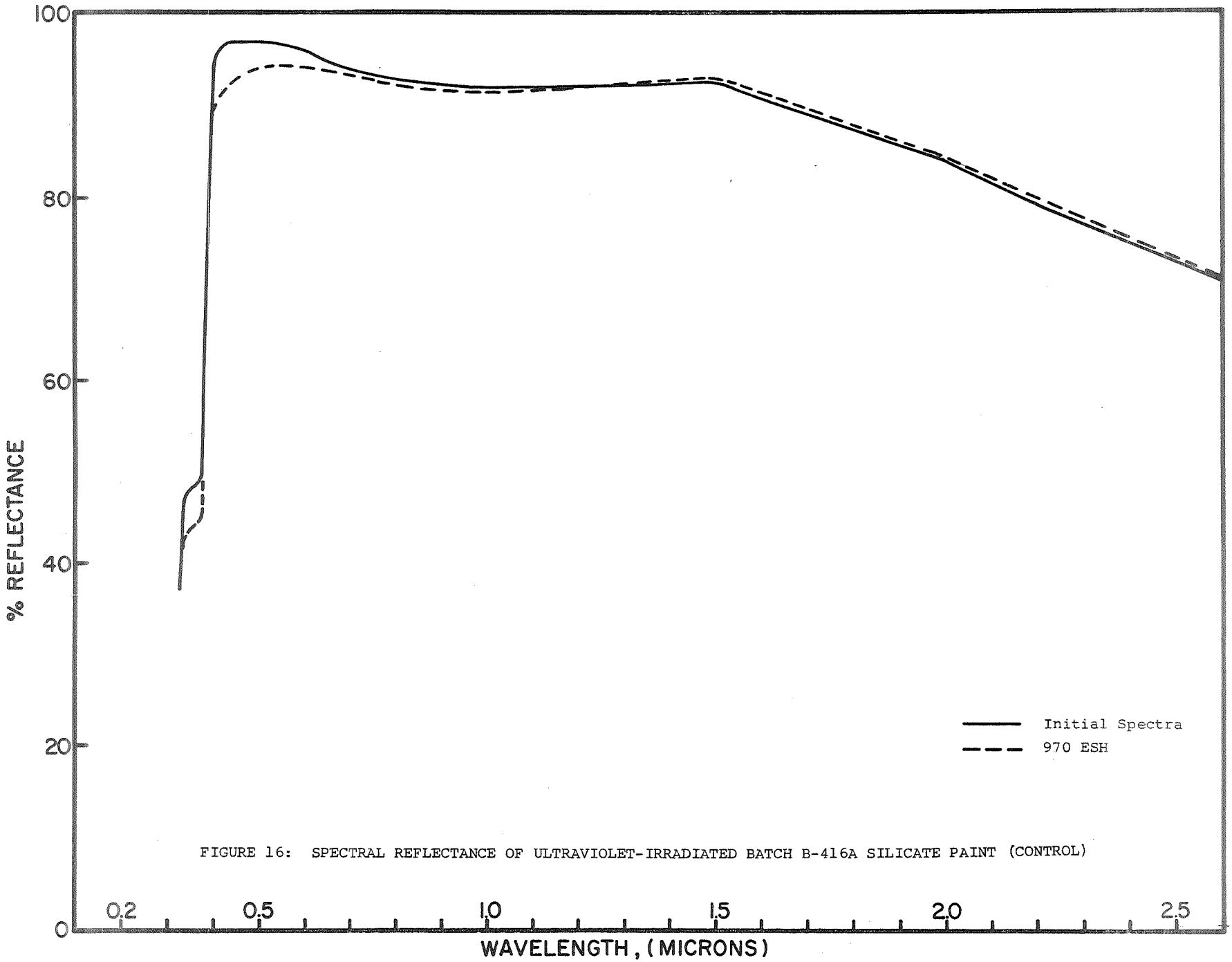


FIGURE 16: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-416A SILICATE PAINT (CONTROL)

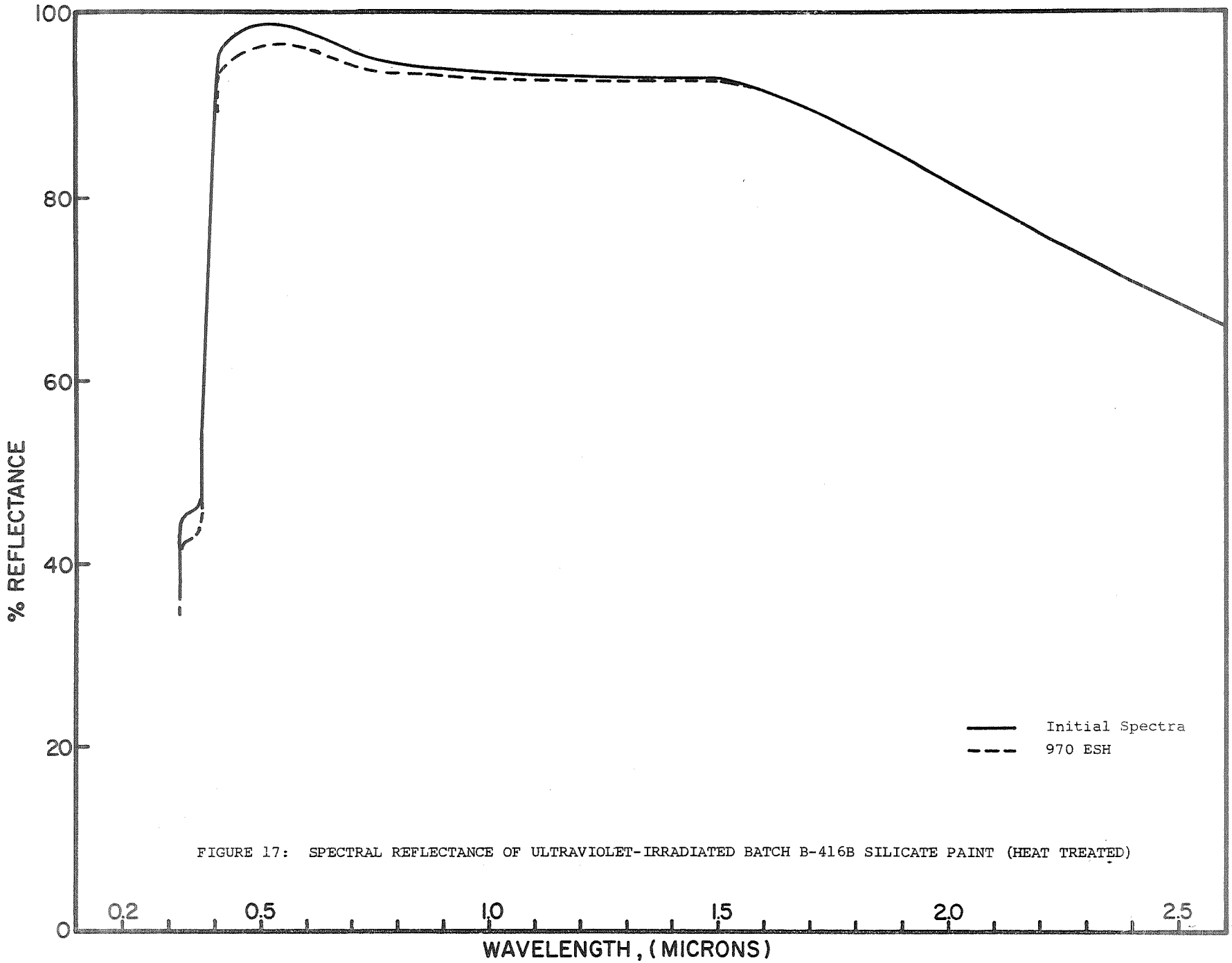


FIGURE 17: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-416B SILICATE PAINT (HEAT TREATED)

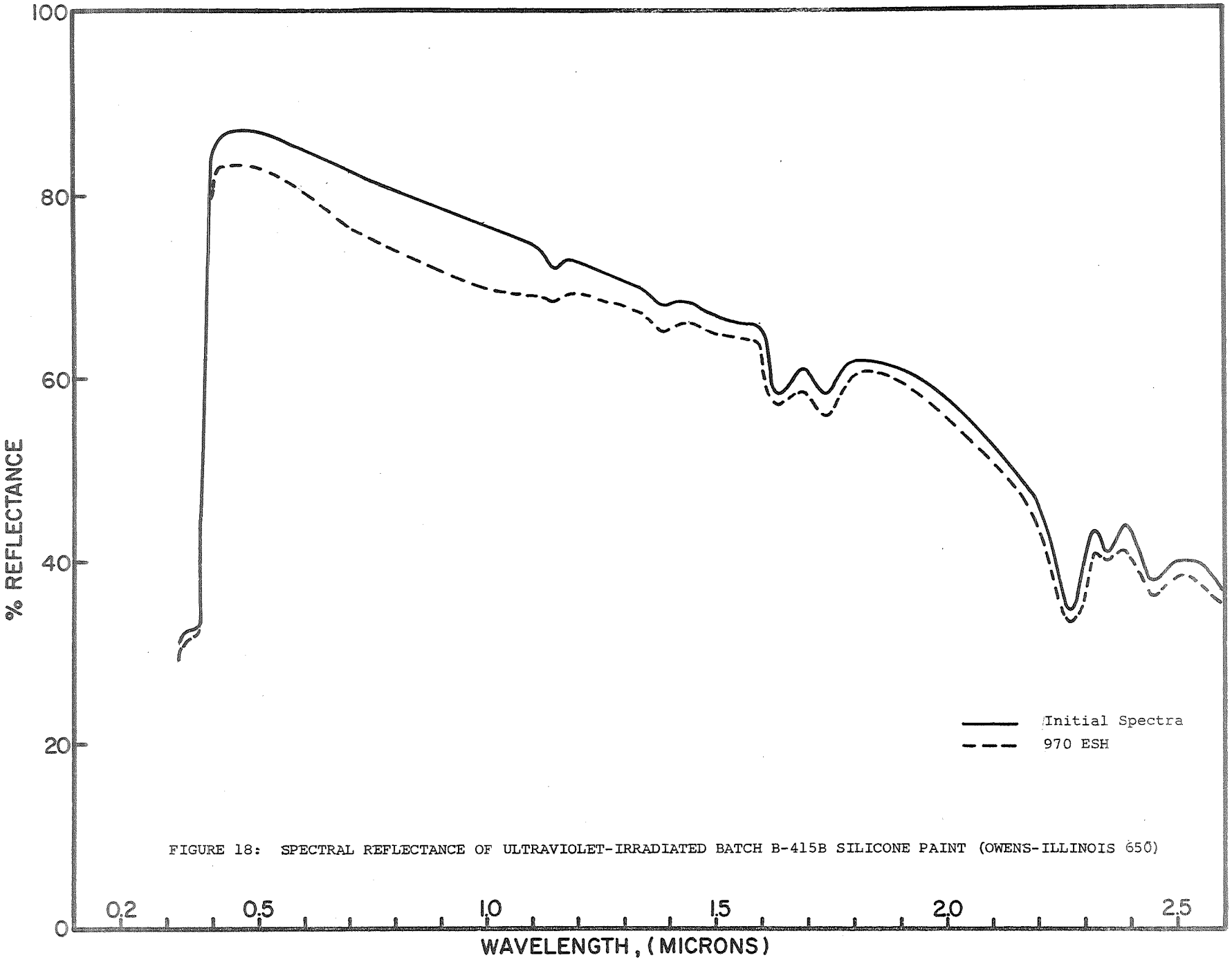


FIGURE 18: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-415B SILICONE PAINT (OWENS-ILLINOIS 650)

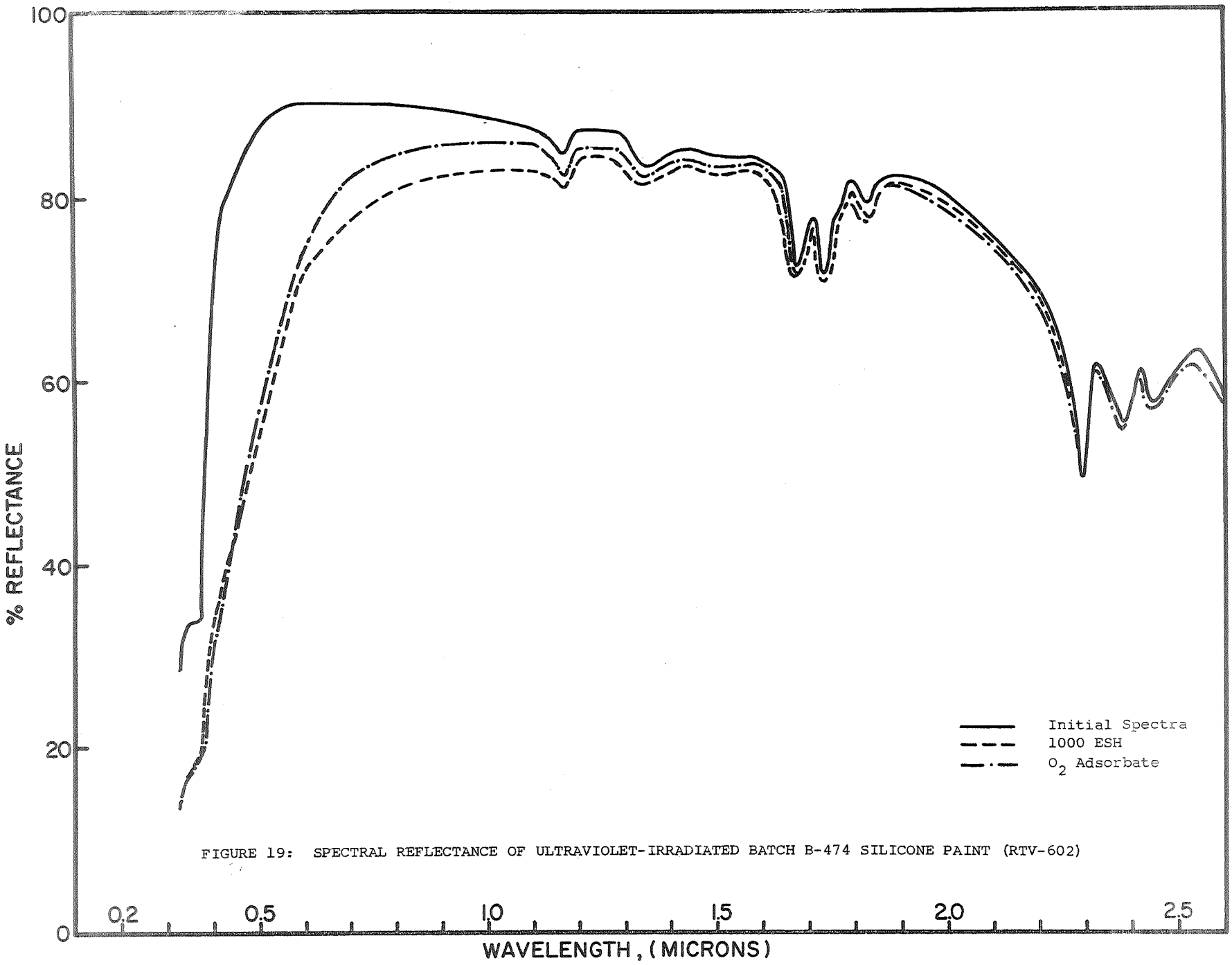


FIGURE 19: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-474 SILICONE PAINT (RTV-602)

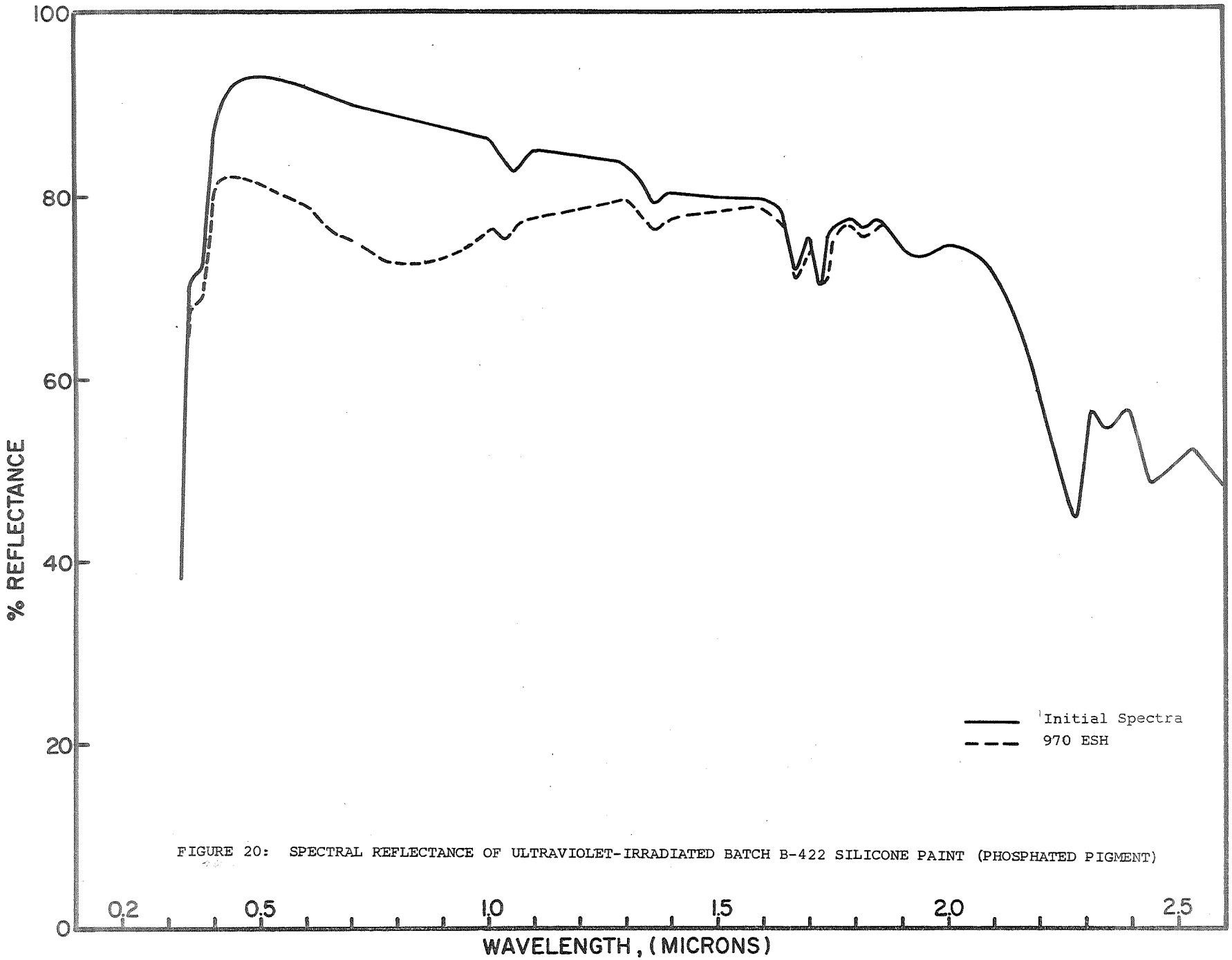


FIGURE 20: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-422 SILICONE PAINT (PHOSPHATED PIGMENT)

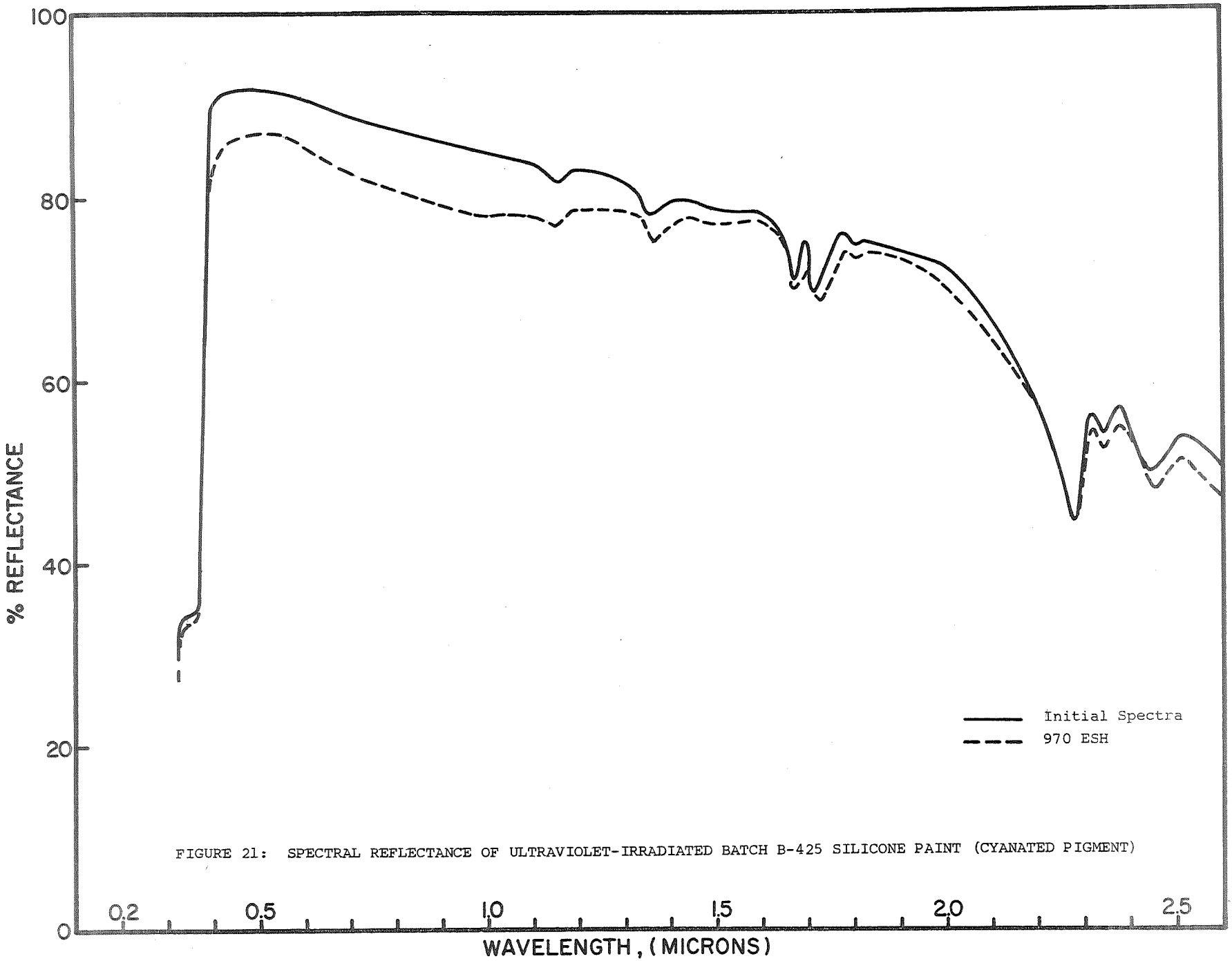


FIGURE 21: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-425 SILICONE PAINT (CYANATED PIGMENT)

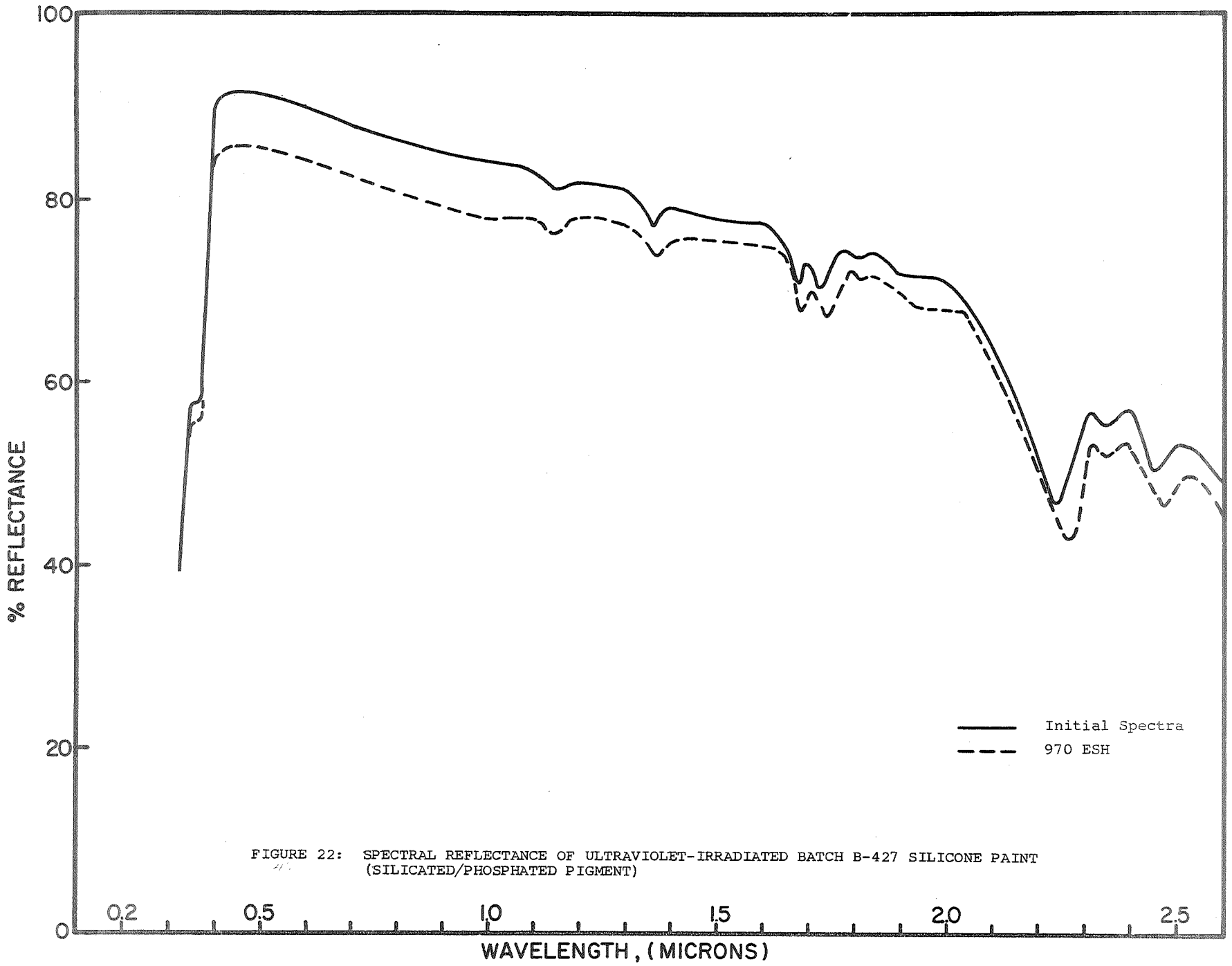


FIGURE 22: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-427 SILICONE PAINT (SILICATED/PHOSPHATED PIGMENT)

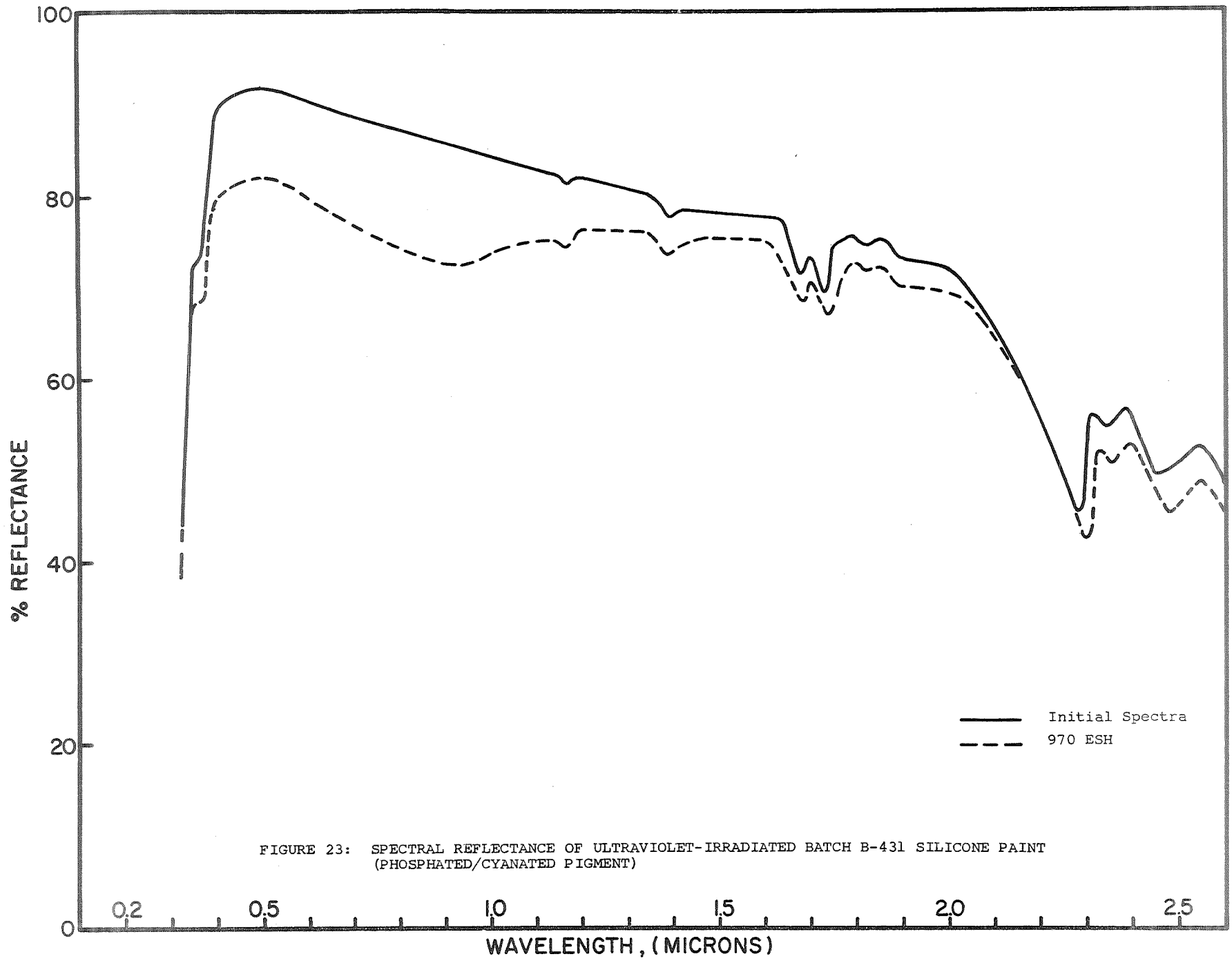


FIGURE 23: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-431 SILICONE PAINT (PHOSPHATED/CYANATED PIGMENT)

Table 7

EFFECT OF IRRADIATION FOR 2000 ESH ON Zn_2TiO_4-POTASSIUM SILICATE PAINTS

Batch No.	Paint	Heat Treatment Hr	Heat Treatment Temp. °C	Pigment Treatment (Chemical)	Reflectance Decrease, ΔR_λ (λ = nm), % 362	425	700	950	2400	α_s	$\Delta\alpha_s$
B-419A	PS7	--	---	PS7	4.0	7.0	1.0	1.0	-1.0	0.136	0.020
B-419B	PS7	16	427	PS7	3.6	5.0	0	0	-1.0	0.133	0.016
B-421A	PS7	--	---	$HPO_4^=$	7.0	5.5	0.2	-0.4	-2.2	0.122	0.010
B-421B	PS7	16	427	$HPO_4^=$	7.0	5.5	0	0	-2.0	0.118	0.013
B-424A	PS7	--	---	Fe-CN	4.2	5.0	1.8	1.0	-2.2	0.154	0.011
B-424B	PS7	16	427	Fe-CN	4.3	4.5	1.0	-0.5	-3.0	0.157	0.013
B-426A	PS7	--	---	PS7/$HPO_4^=$	5.2	6.8	1.2	0	-2.7	0.137	0.016
B-426B	PS7	16	427	PS7/$HPO_4^=$	4.8	4.0	0	0	-2.5	0.153	0.007
B-428A	PS7	--	---	PS7/Fe-CN	3.5	4.0	0	0	-3.0	0.131	0.004
B-428B	PS7	16	427	PS7/Fe-CN	4.6	4.5	0	0	-2.5	0.136	0.009
B-430A	PS7	--	---	$HPO_4^=$/Fe-CN	8.5	7.5	0.5	-0.5	-3.7	0.140	0.017
B-430B	PS7	16	427	$HPO_4^=$/Fe-CN	7.0	6.0	0	-0.5	-2.0	0.155	0.013

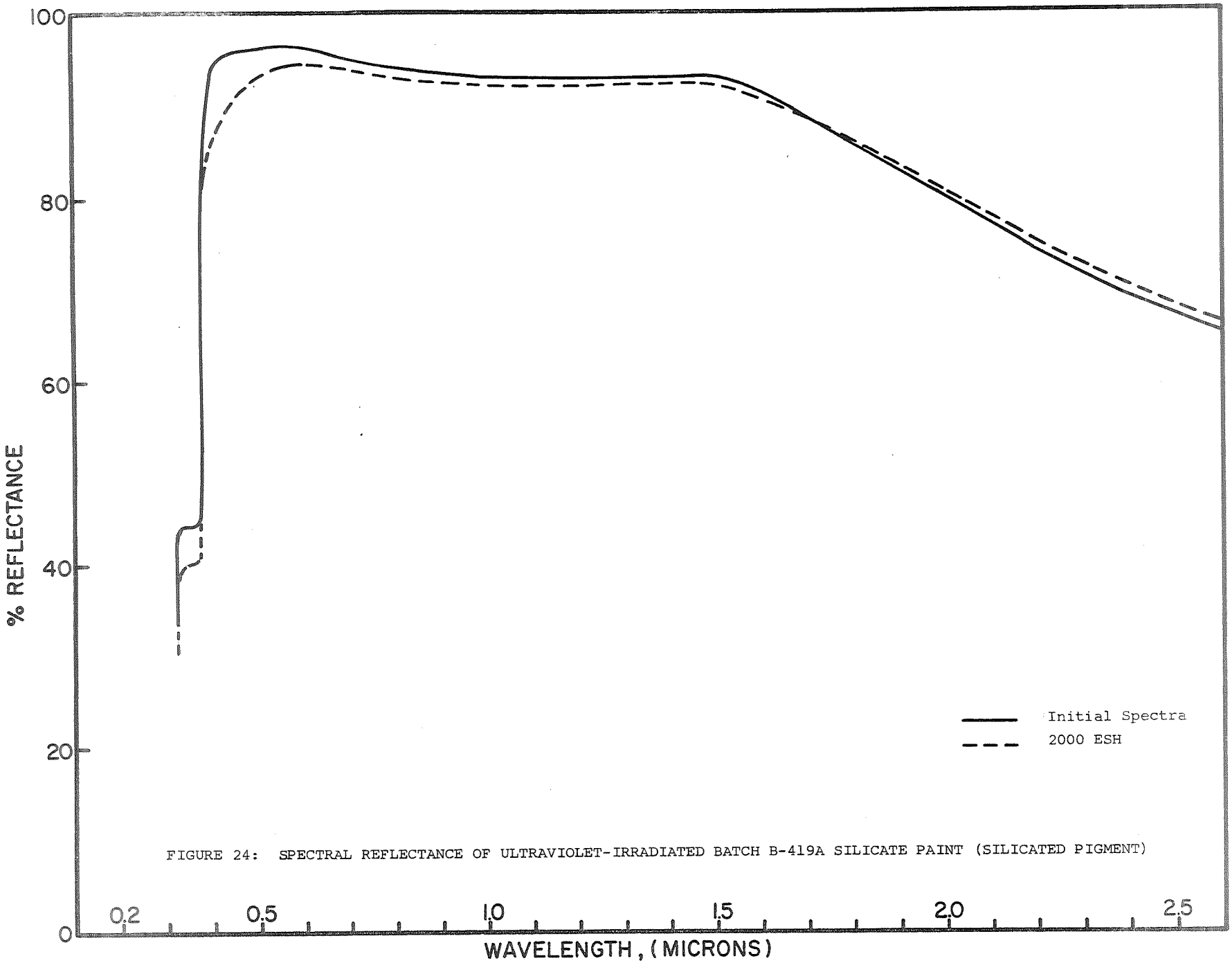


FIGURE 24: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-419A SILICATE PAINT (SILICATED PIGMENT)

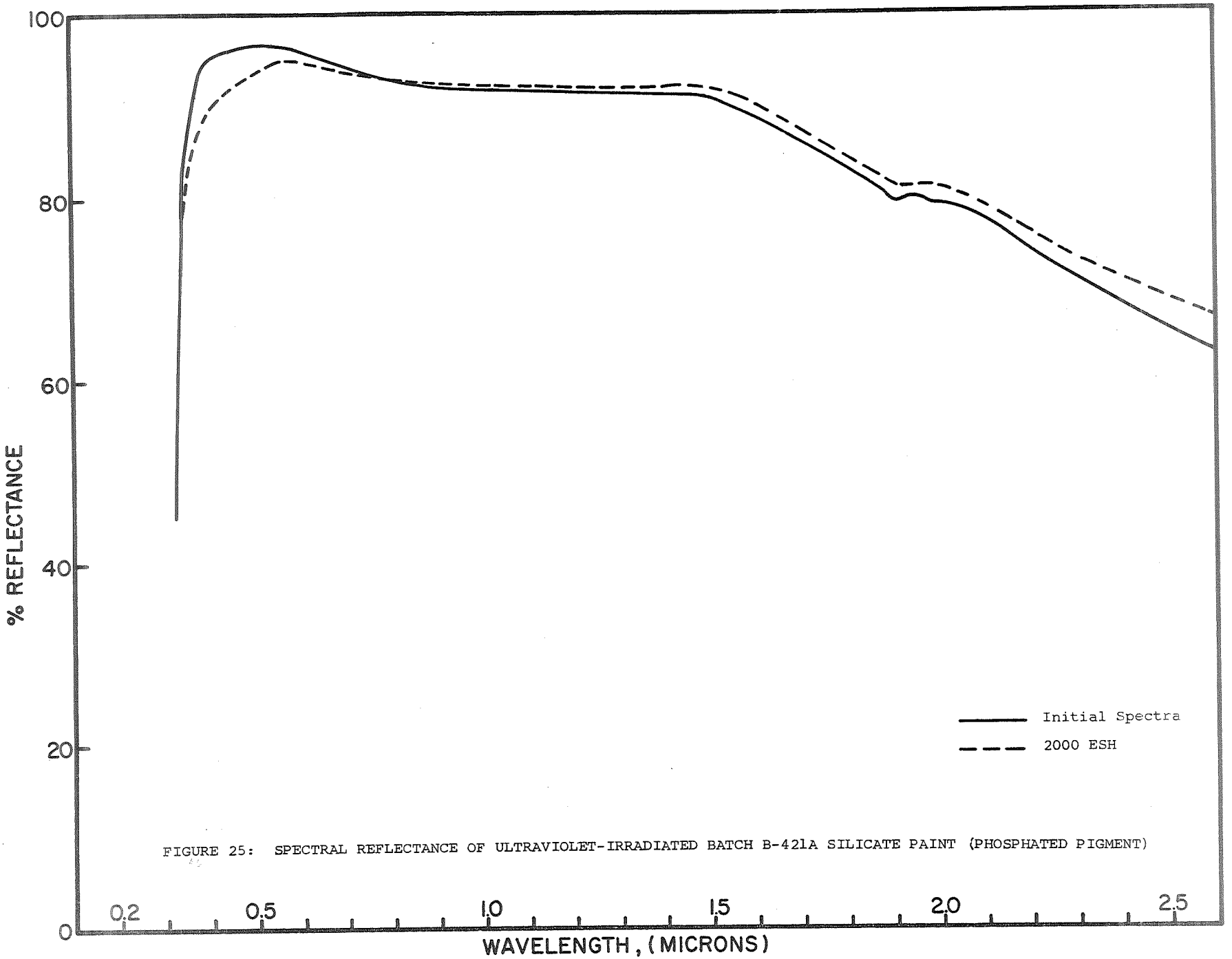


FIGURE 25: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-421A SILICATE PAINT (PHOSPHATED PIGMENT)

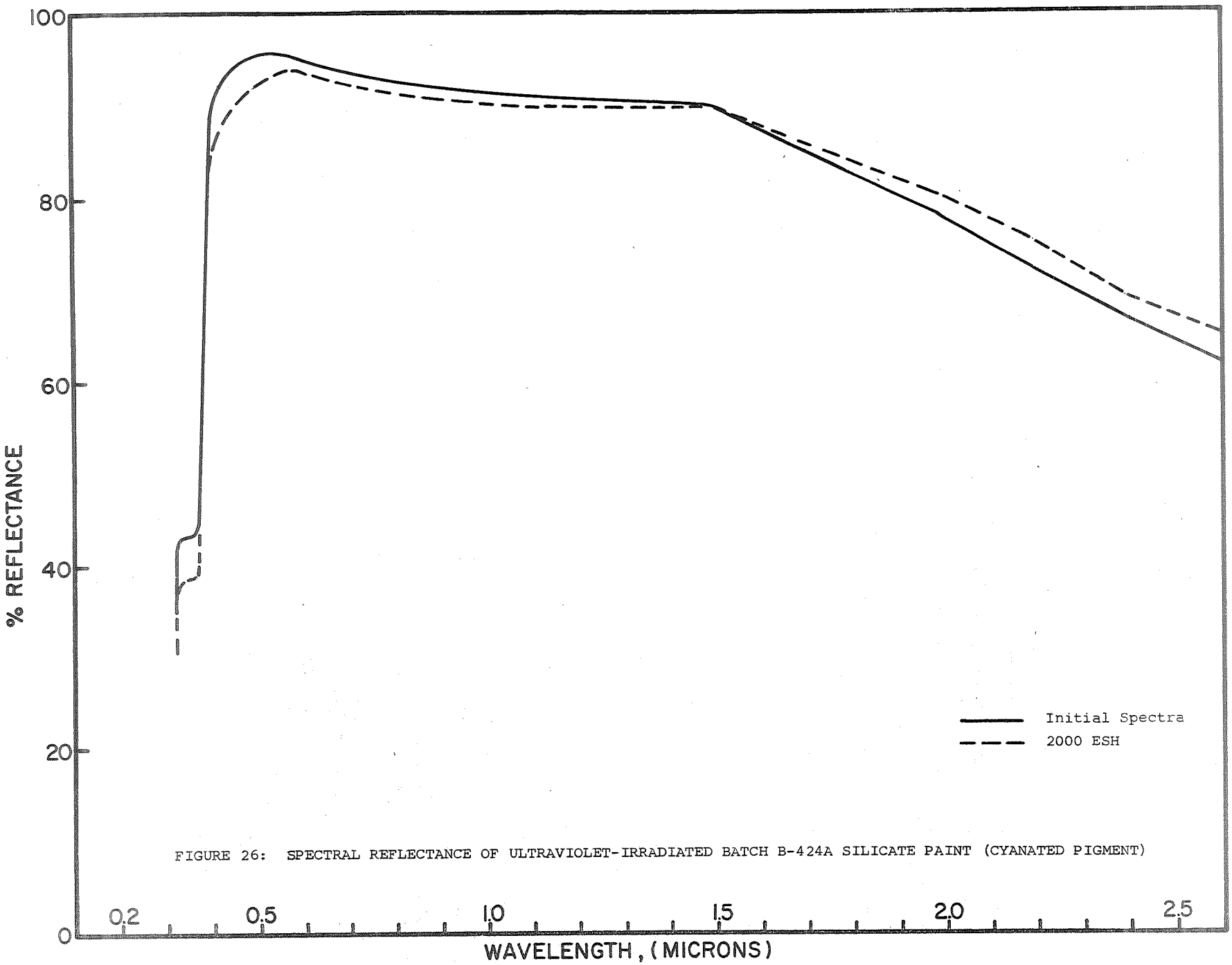


FIGURE 26: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-424A SILICATE PAINT (CYANATED PIGMENT)

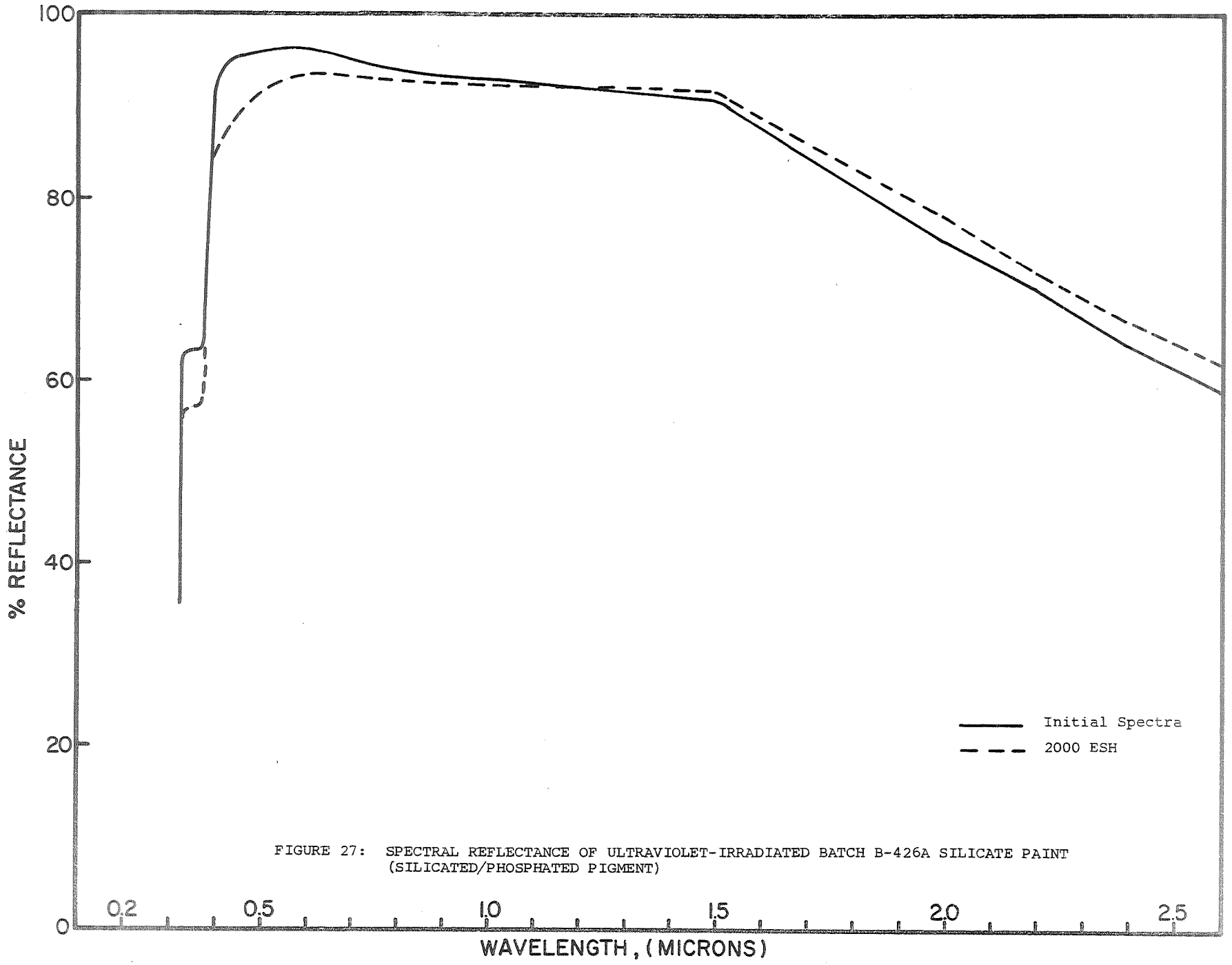


FIGURE 27: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-426A SILICATE PAINT (SILICATED/PHOSPHATED PIGMENT)

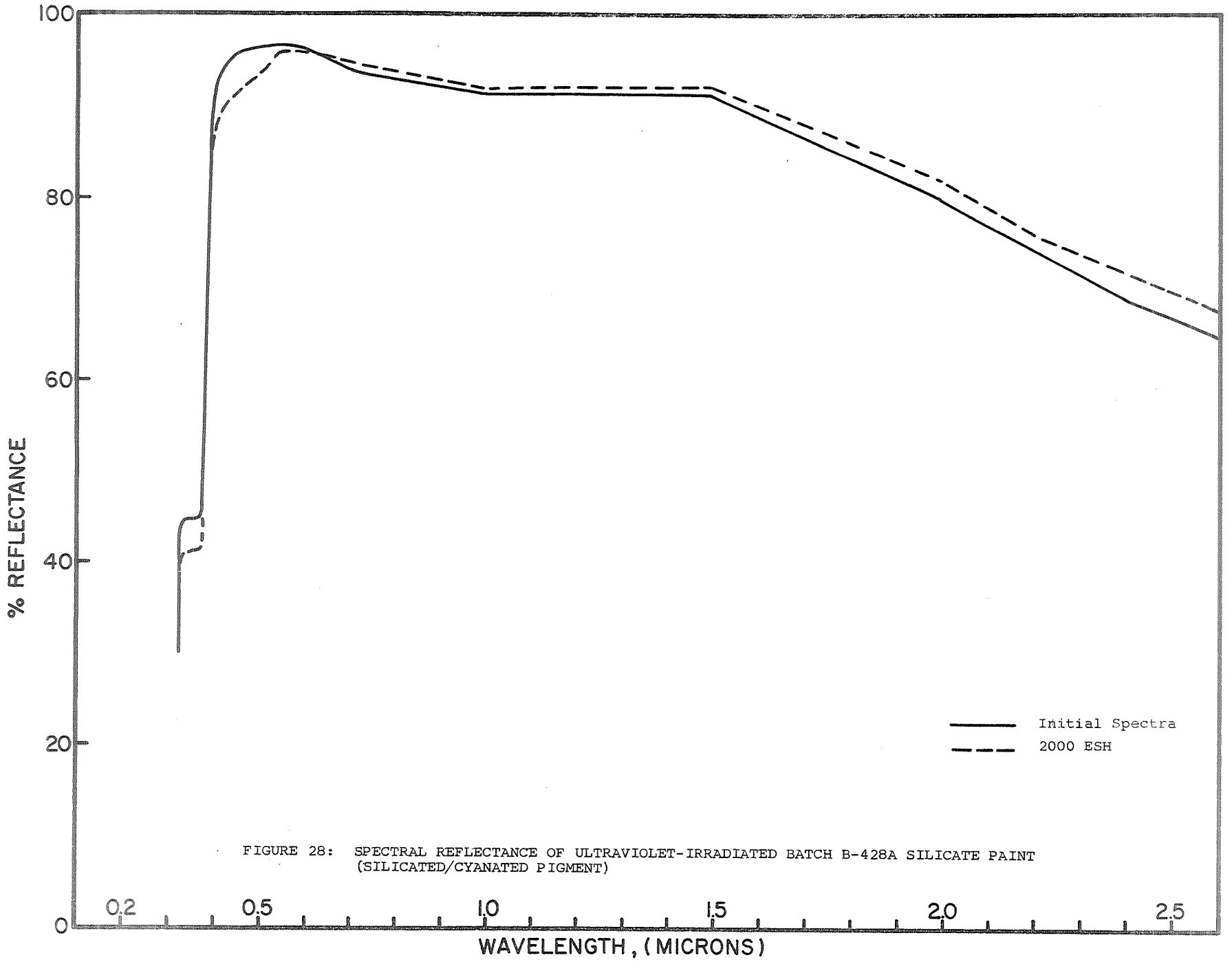


FIGURE 28: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-428A SILICATE PAINT (SILICATED/CYANATED PIGMENT)

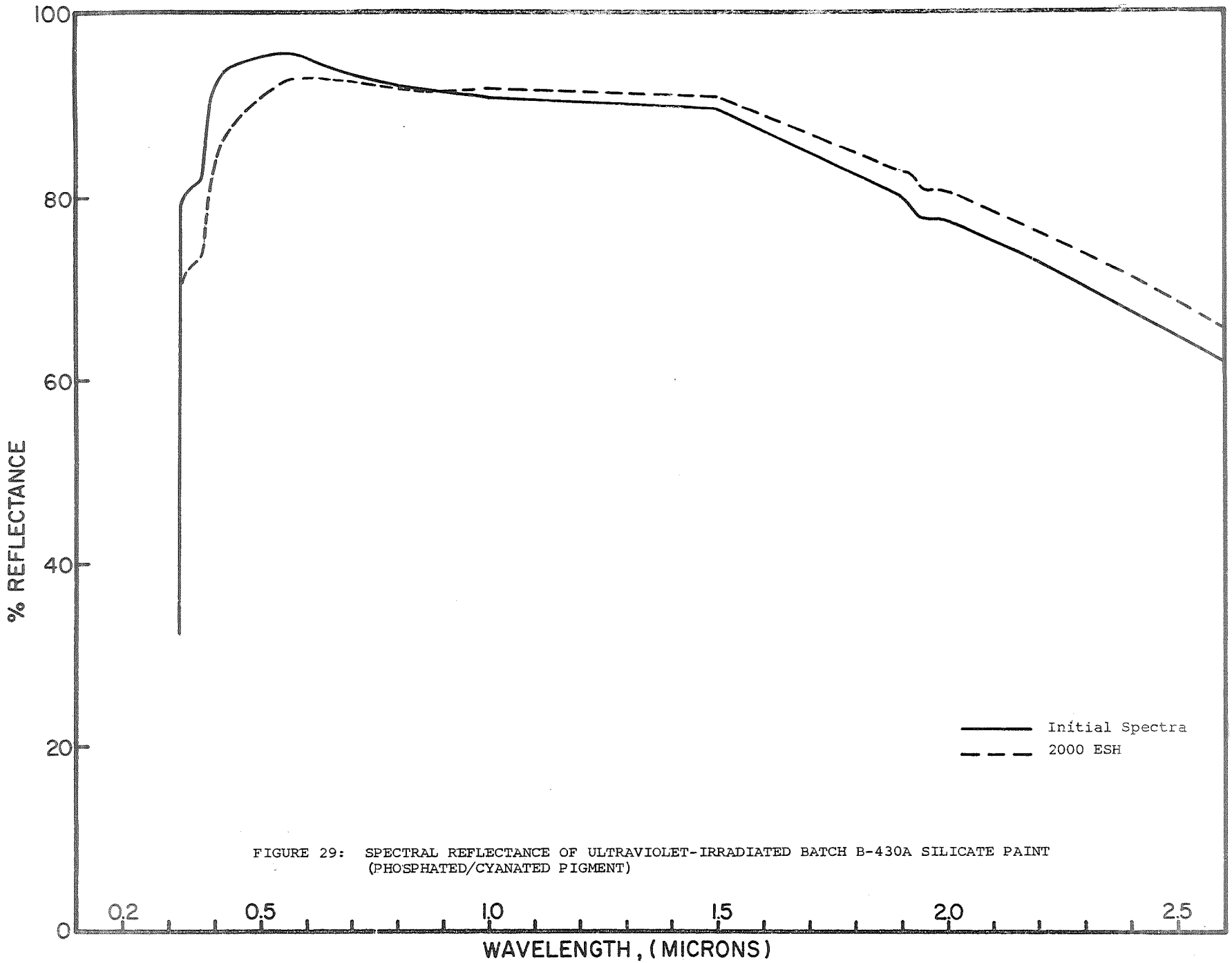


FIGURE 29: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-430A SILICATE PAINT (PHOSPHATED/CYANATED PIGMENT)

present studies (see the digital reflectance data in Table 7). These results are more consistant with our experience with Z93's behavior as a function of heat treating (Ref. 2).

The data for the heat-treated silicate paints prepared from pigment that was phosphated and treated with potassium ferro/ferricyanide (Batches B-421B and B-424B, respectively) compared favorably with the data reported previously (see Batches B-246A and B-231A, Test II-19, Table 2, Reference 1). The spectra of the air-dried paints are presented in Figures 25 and 26.

Paints B-426, B-428 and B-430 were pigmented with treated zinc orthotitanate that had not been prepared previously. The spectra of air-dried paints are presented in Figures 27 through 29.

5. Paints Prepared from New Encapsulated Pigment

Although paints were prepared from reactively encapsulated zinc orthotitanate that had and had not been heat treated, only those silicone and silicate paints prepared from pigment that was heat treated for 7 hr at 500°C were irradiated. These data are presented in Table 8 and Figures 30 through 37.

6. Plasma Calcined Zn_2TiO_4 Powders and Silicone Paints

Although the significance of the specific plasma calcination parameters will be discussed in the Final Triannual Report, these data are presented here in an attempt to determine if plasma treatment in the SRI facility (Ref. 3) would prevent the anomalous degradation observed when zinc orthotitanate is pigmented in Owens-Illinois 650 silicone resin, which is otherwise stable. These data are presented in Table 9 and Figures 38 through 43.

C. Discussion

1. Reactively Encapsulated Powders

The silicating of zinc orthotitanate clearly stabilizes the surface against formation of the broad damage spectra in the region 1000- to 2600-nm wavelength. However, as with the silicated

Table 8

EFFECT OF 1200 ESH OF UV IRRADIATION ON AIR DRIED Zn_2TiO_4 PAINTS

Batch No.	Paint	Pigment Treatment: Batch No.	Pigment Treatment: Chemical	Heat: Hr	Heat: °C	Solar Absorptance: α_s	Solar Absorptance: $\Delta\alpha_s$	Reflectance at 362 nm	Reflectance Decrease, ΔR_λ (λ = nm), %: 362	425	700	950	2400
B-561	PS7	B-454	Li_2SiF_6	7	500	0.132	0.015	66.0	2.0	3.0	1.0	1.0	1.8
B-563	PS7	B-458	K_2SiF_6	7	500	0.122	0.002	80.0	2.2	2.8	0	0	1.0
B-565	PS7	B-462	K_2SnF_6	7	500	0.139	0.012	76.0	2.7	3.5	0.4	0	0
B-567	PS7	B-547	$K_4Si_4W_{12}O_{40}$	7	500	0.139	0.013	43.0	1.2	2.2	1.0	0.5	-1.0
B-553	OI	B-454	Li_2SiF_6	7	500	0.211	0.041	62.0	0	5.0	4.5	5.6	4.0
B-555	OI	B-458	K_2SiF_6	7	500	0.212	0.041	72.0	2.0	4.5	4.5	5.7	3.2
B-557	OI	B-462	K_2SiF_6	7	500	0.215	0.105	72.0	20.0	15.5	6.5	9.5	11.0
B-559	OI	B-547	$K_4Si_4W_{12}O_{40}$	7	500	0.254	0.051	35.0	1.5	11.0	5.5	4.0	1.3

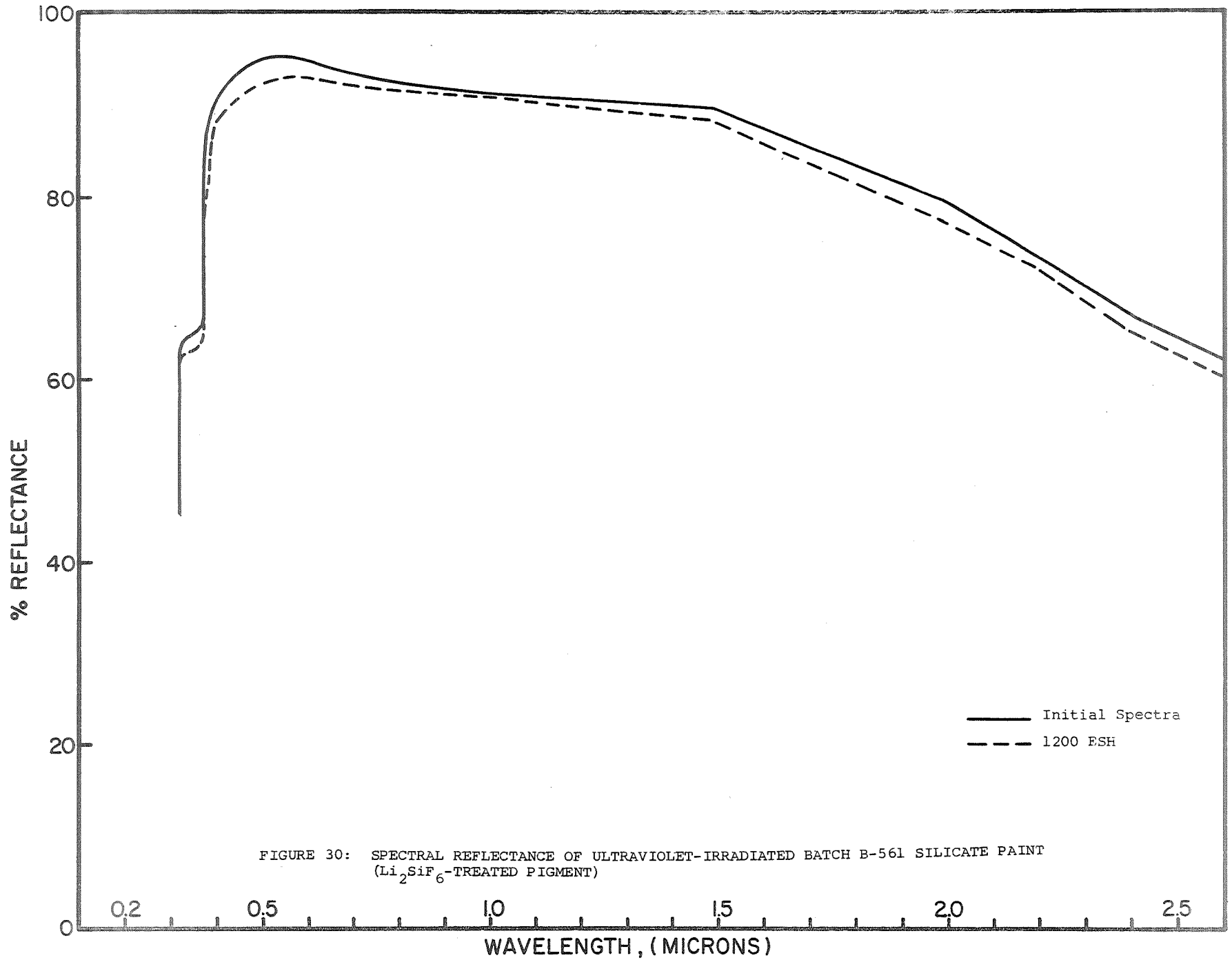


FIGURE 30: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-561 SILICATE PAINT (Li_2SiF_6-TREATED PIGMENT)

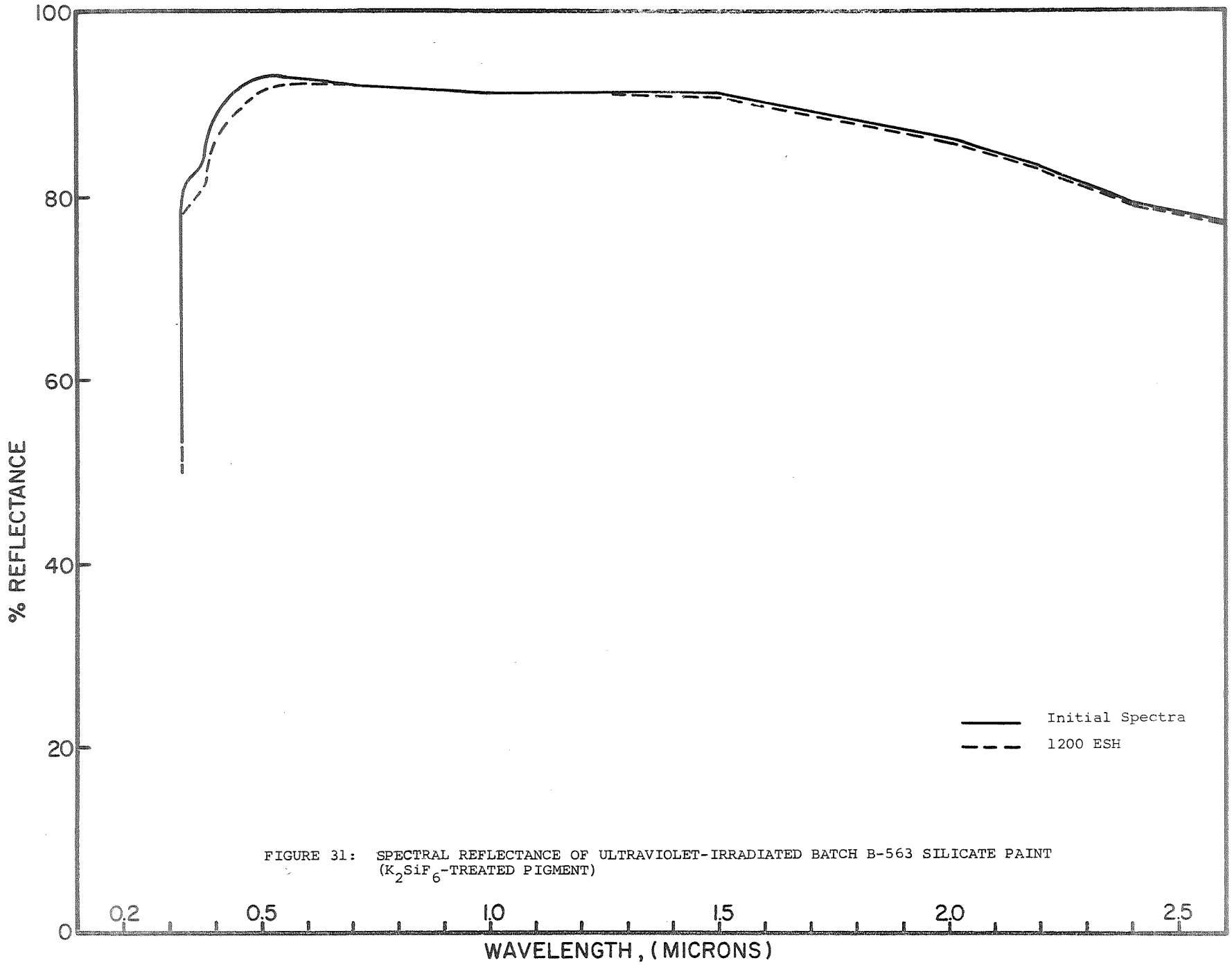


FIGURE 31: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-563 SILICATE PAINT (K_2SiF_6-TREATED PIGMENT)

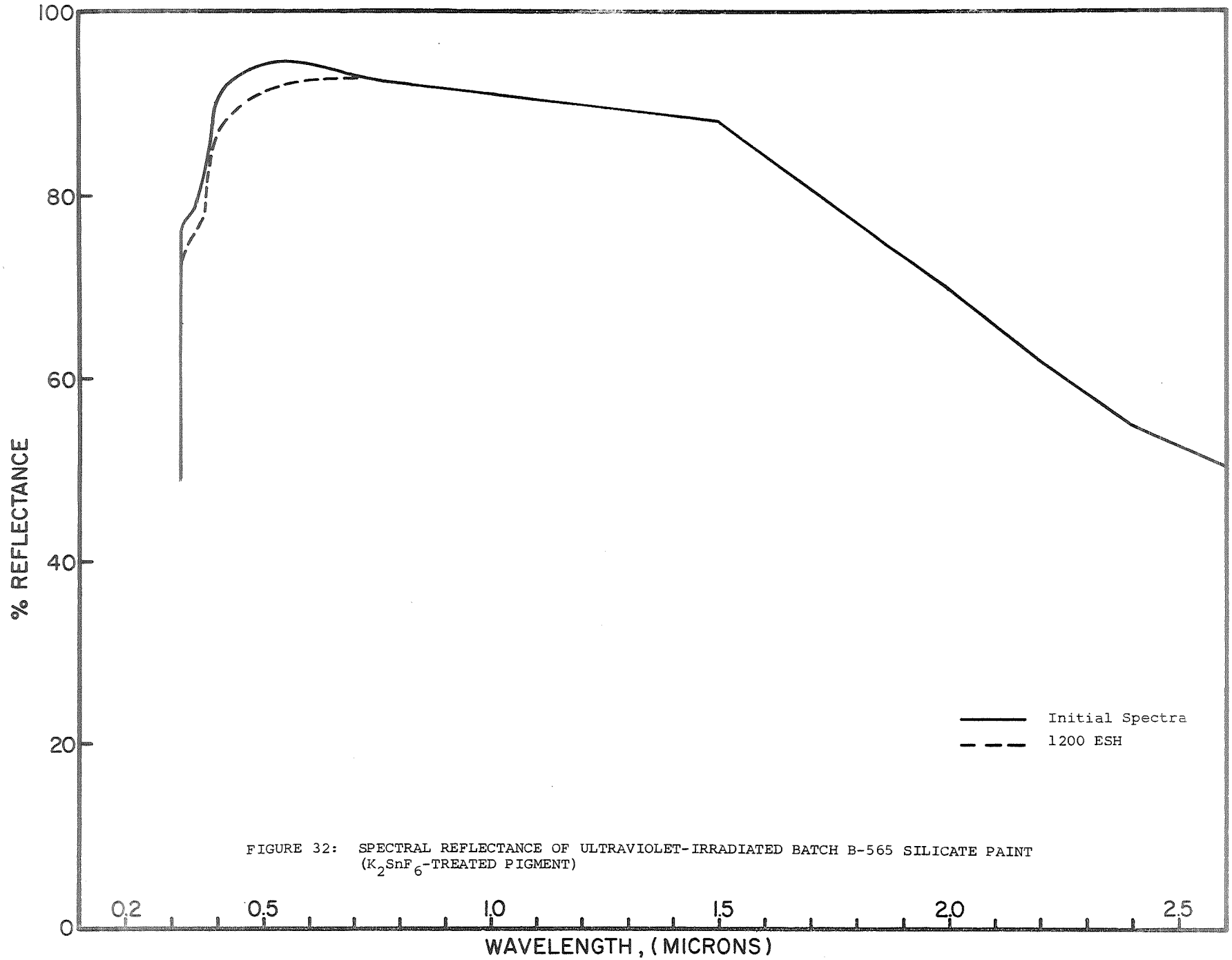


FIGURE 32: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-565 SILICATE PAINT (K_2SnF_6-TREATED PIGMENT)

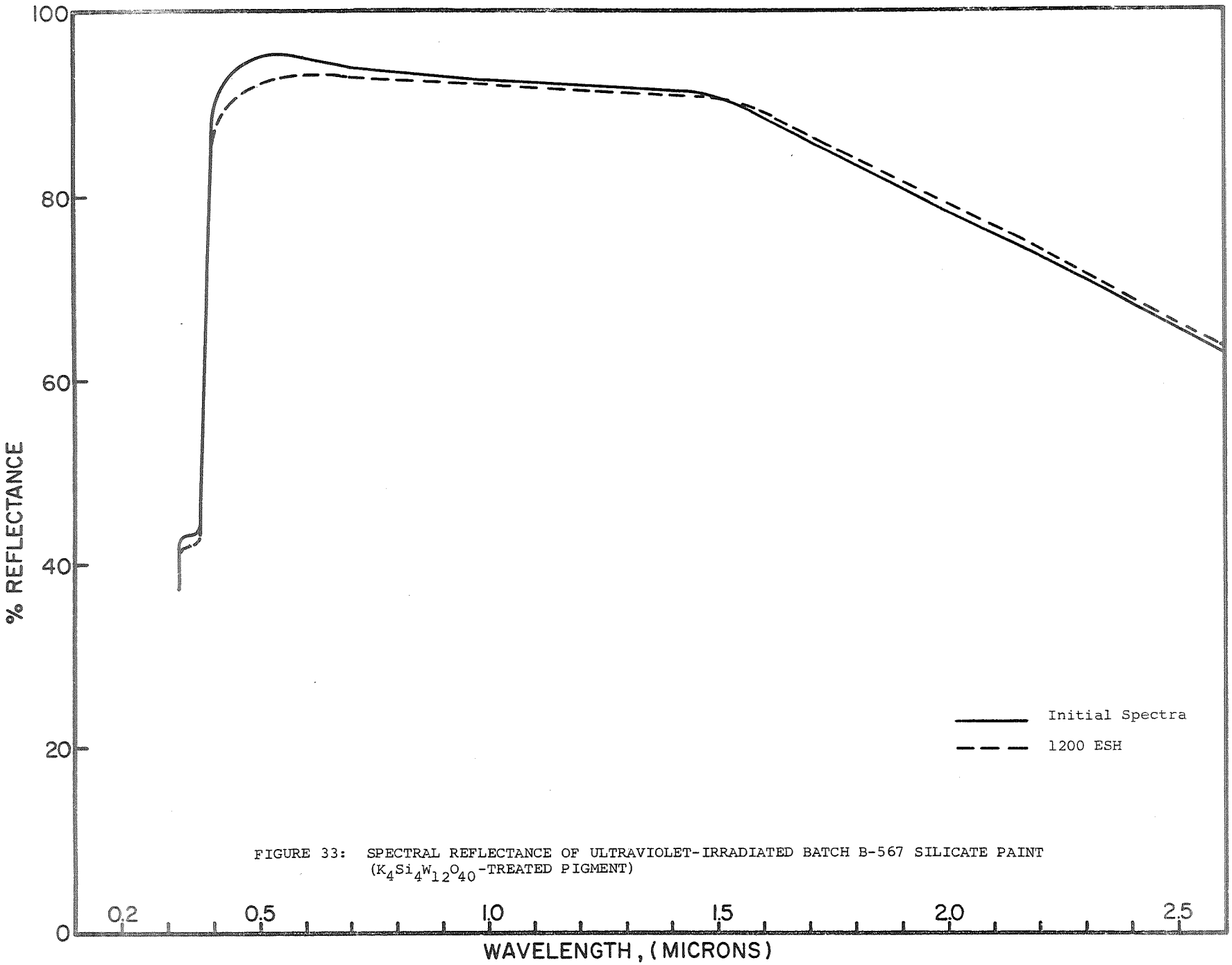


FIGURE 33: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-567 SILICATE PAINT ($K_4Si_4W_{12}O_{40}$-TREATED PIGMENT)

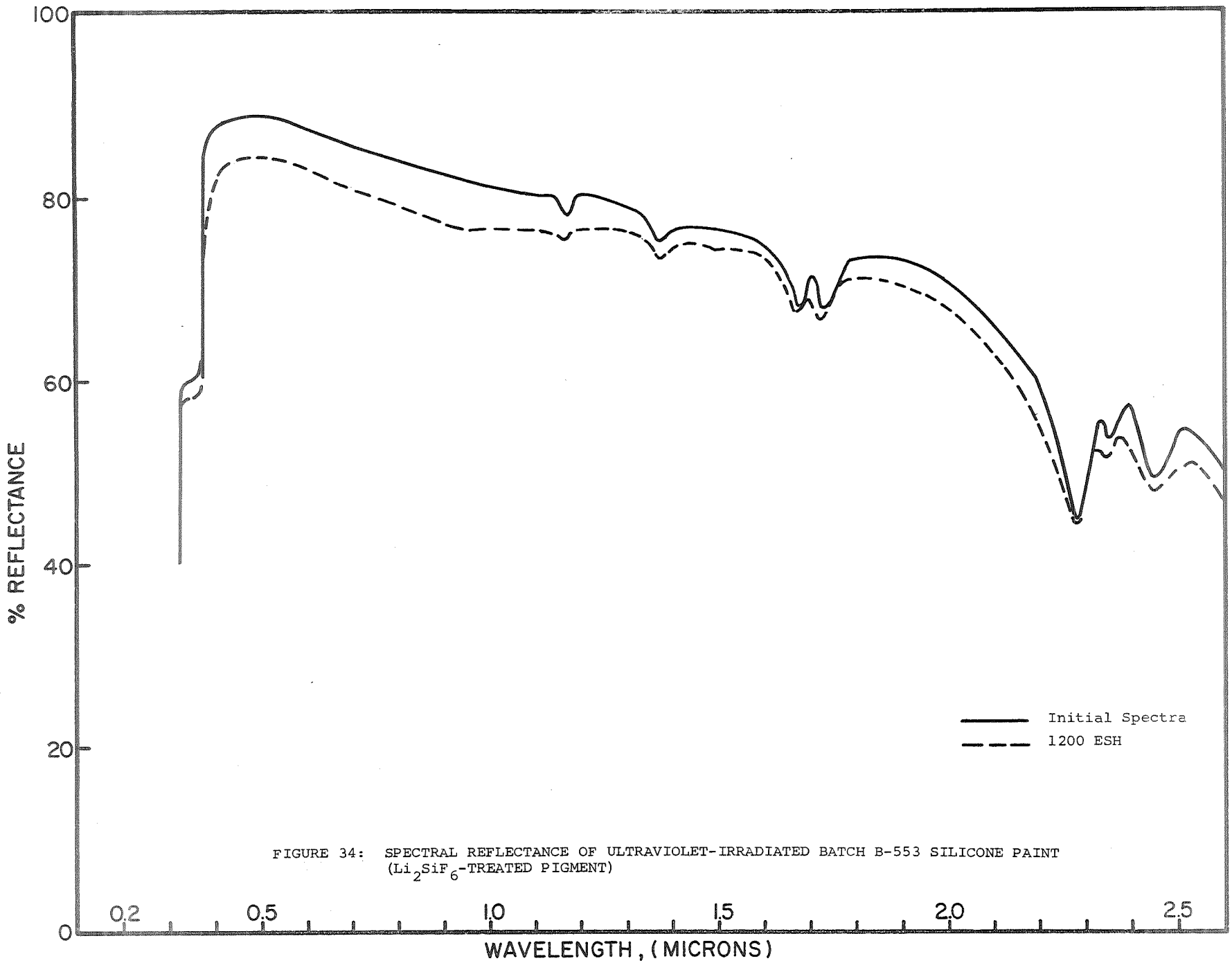


FIGURE 34: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-553 SILICONE PAINT (Li_2SiF_6-TREATED PIGMENT)

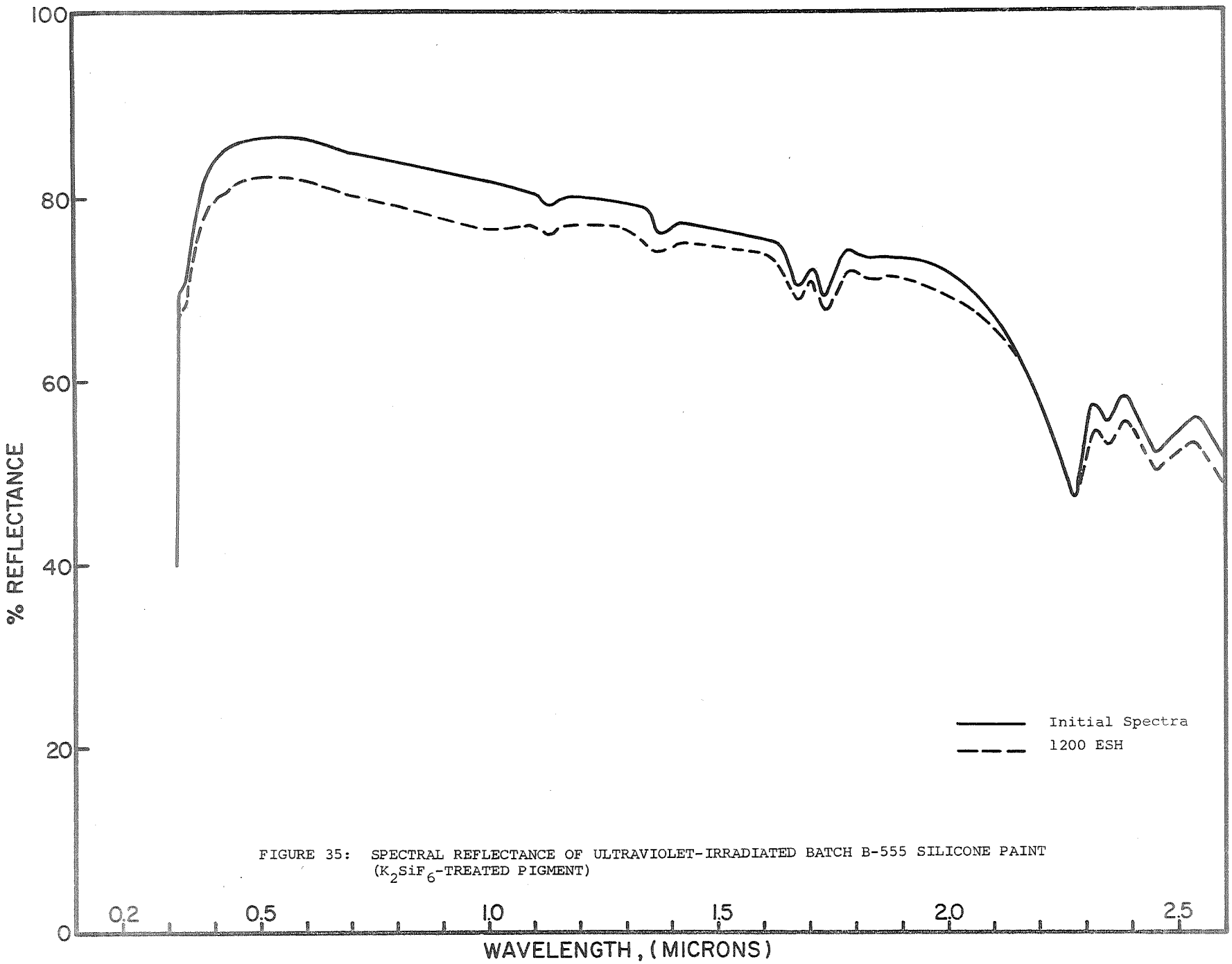


FIGURE 35: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-555 SILICONE PAINT (K_2SiF_6-TREATED PIGMENT)

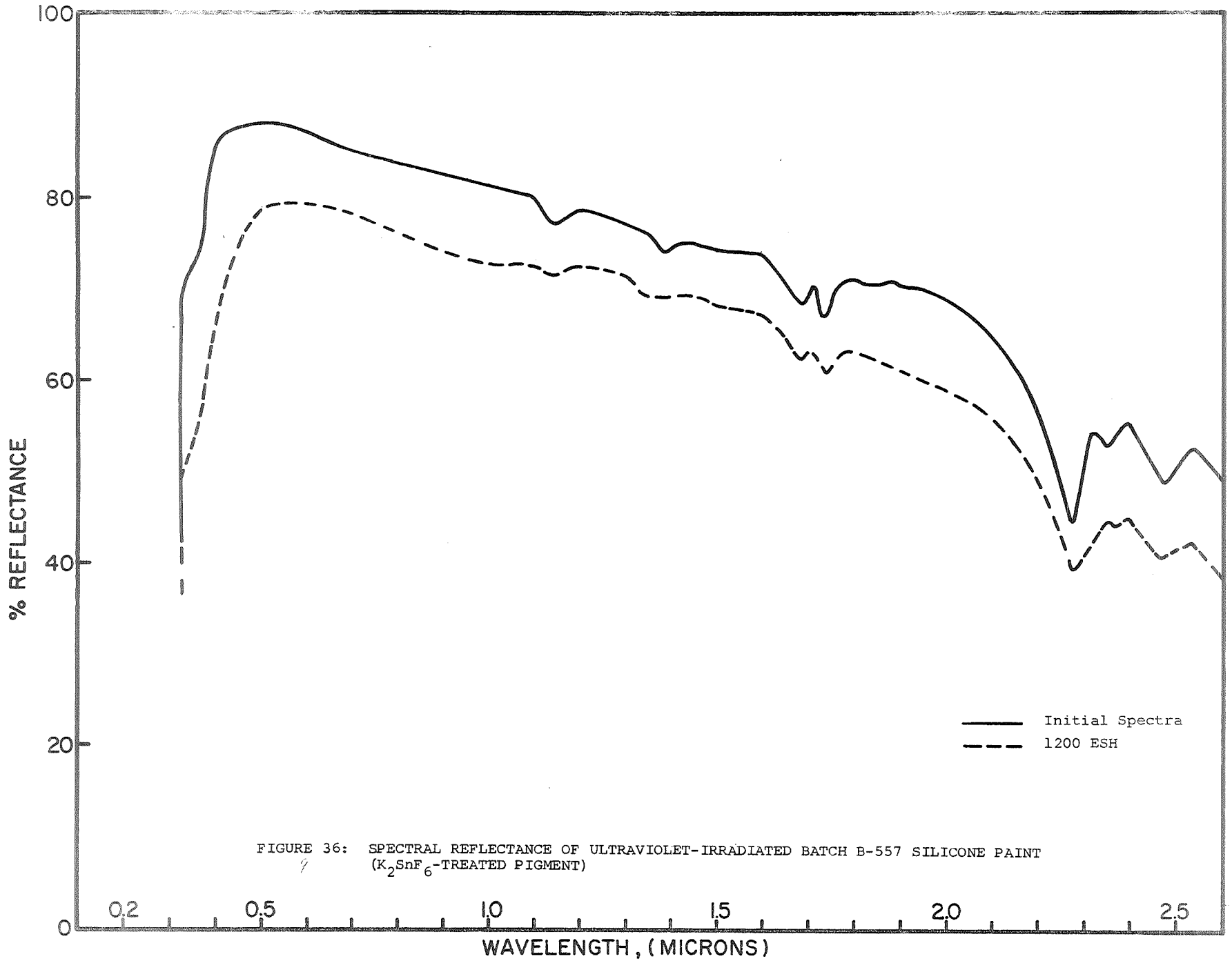


FIGURE 36: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-557 SILICONE PAINT (K_2SnF_6-TREATED PIGMENT)

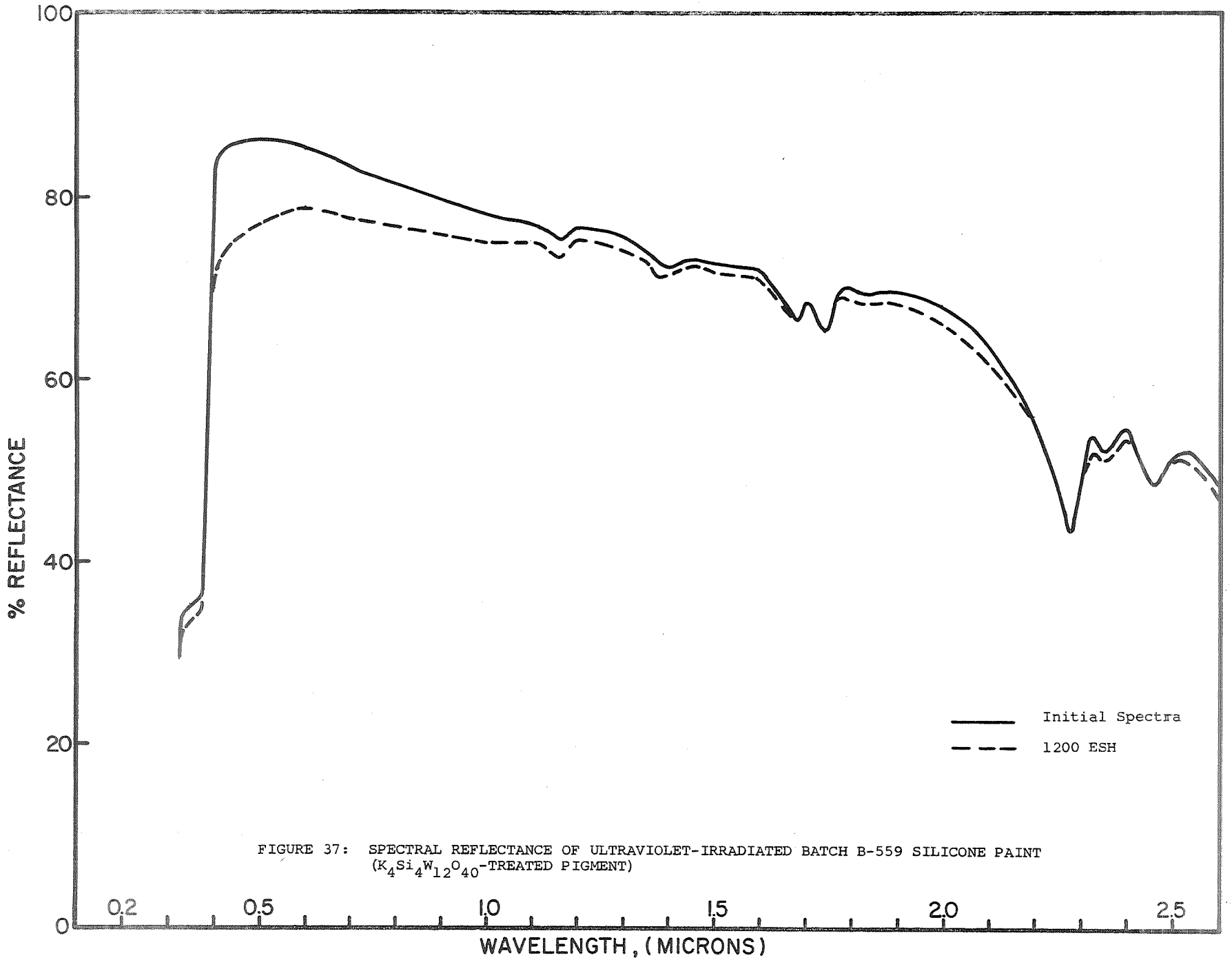


FIGURE 37: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH B-559 SILICONE PAINT ($K_4Si_4W_{12}O_{40}$-TREATED PIGMENT)

Table 9

EFFECT OF 1010 ESH OF UV IRRADIATION ON PLASMA-TREATED Zn_2TiO_4
(AS POWDERS AND PAINTS)

Specimen	SRI Pigment Batch No.	Plasma t (sec)	Plasma ΔT (°C)	% R at 362-nm	Reflectance Decrease, ΔR_λ (λ = nm), % 362	425	700	950	2400	α_s	$\Delta\alpha_s$
Powder	9-20	1.1	2000	34.0	0.4	2.4	2.0	2.6	8.2	0.160	0.028
Powder	3-5	1.1	1400	78.0	1.0	1.8	3.5	5.8	-1.2	0.130	0.029
Powder	3-3	1.1	2450	71.0	-2.6	0	2.5	6.0	3.5	0.143	0.026
OI650 Paint	9-20	1.1	2000	20.0	-1.5	0.5	2.3	4.8	9.0	0.278	0.039
OI650 Paint	3-5	1.1	1400	64.3	1.0	2.0	3.6	4.6	-1.8	0.348	0.031
OI650 Paint	3-3	1.1	2450	55.0	-2.0	1.5	3.0	4.4	0	0.331	0.017

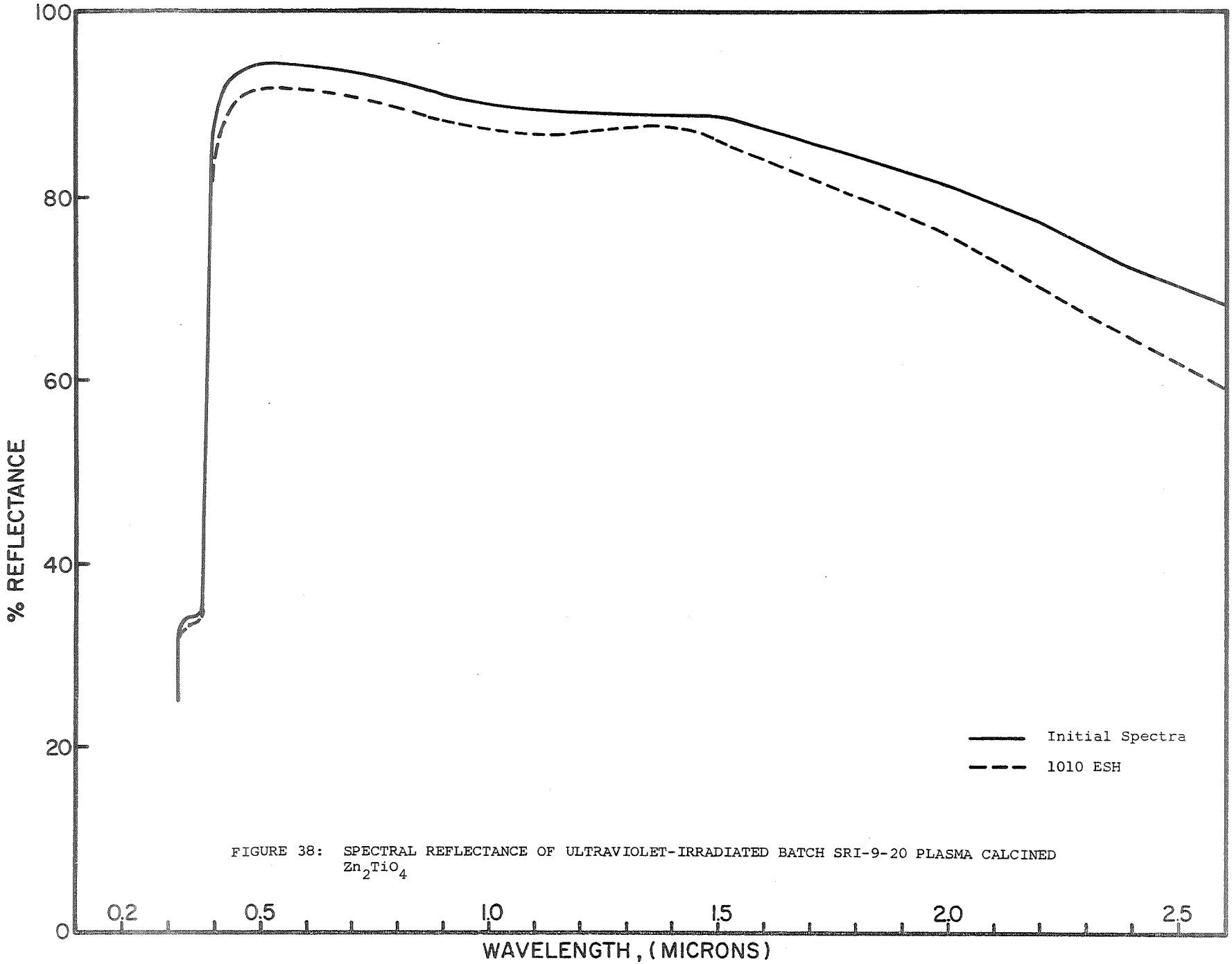


FIGURE 38: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH SRI-9-20 PLASMA CALCINED Zn_2TiO_4

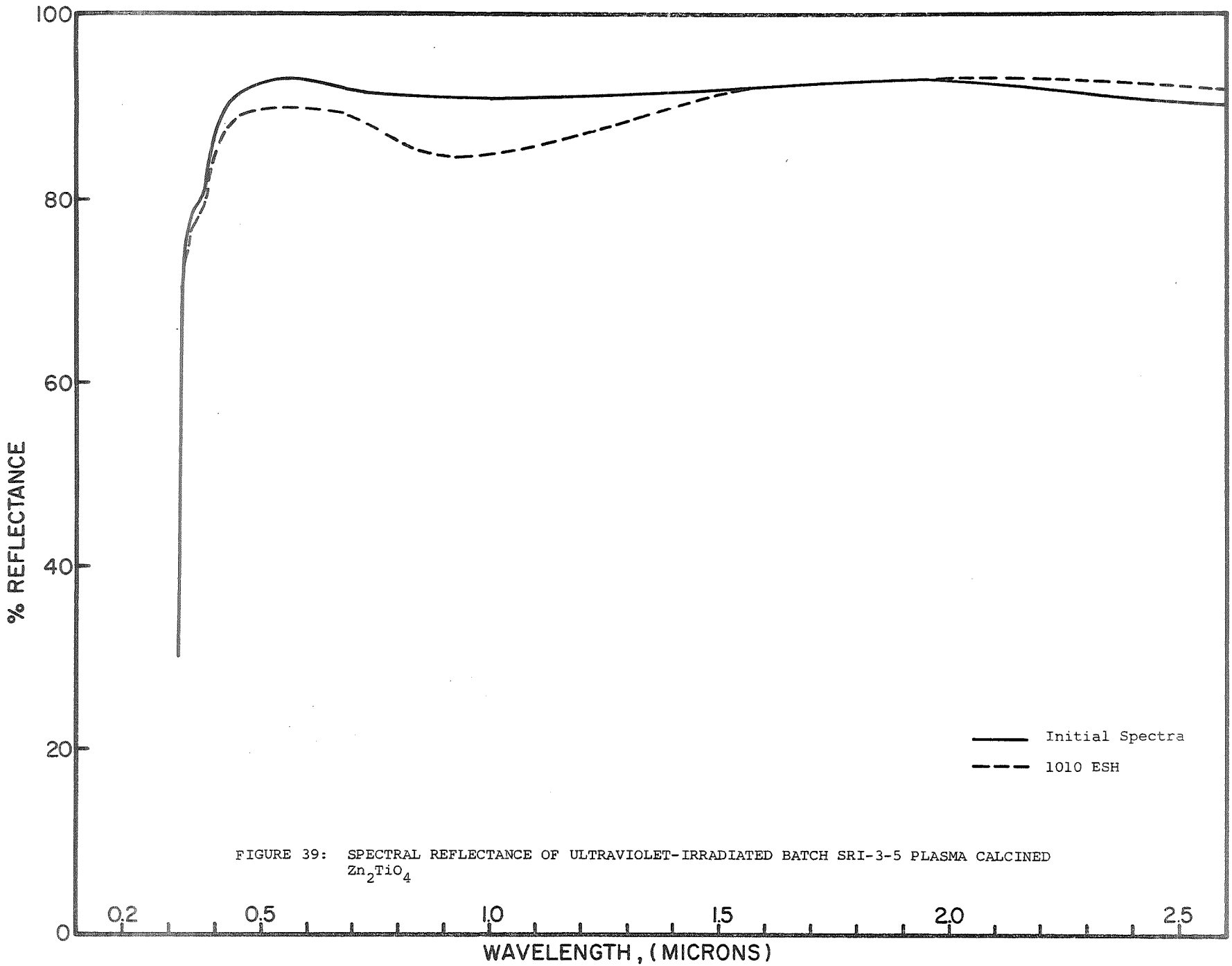


FIGURE 39: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH SRI-3-5 PLASMA CALCINED Zn_2TiO_4

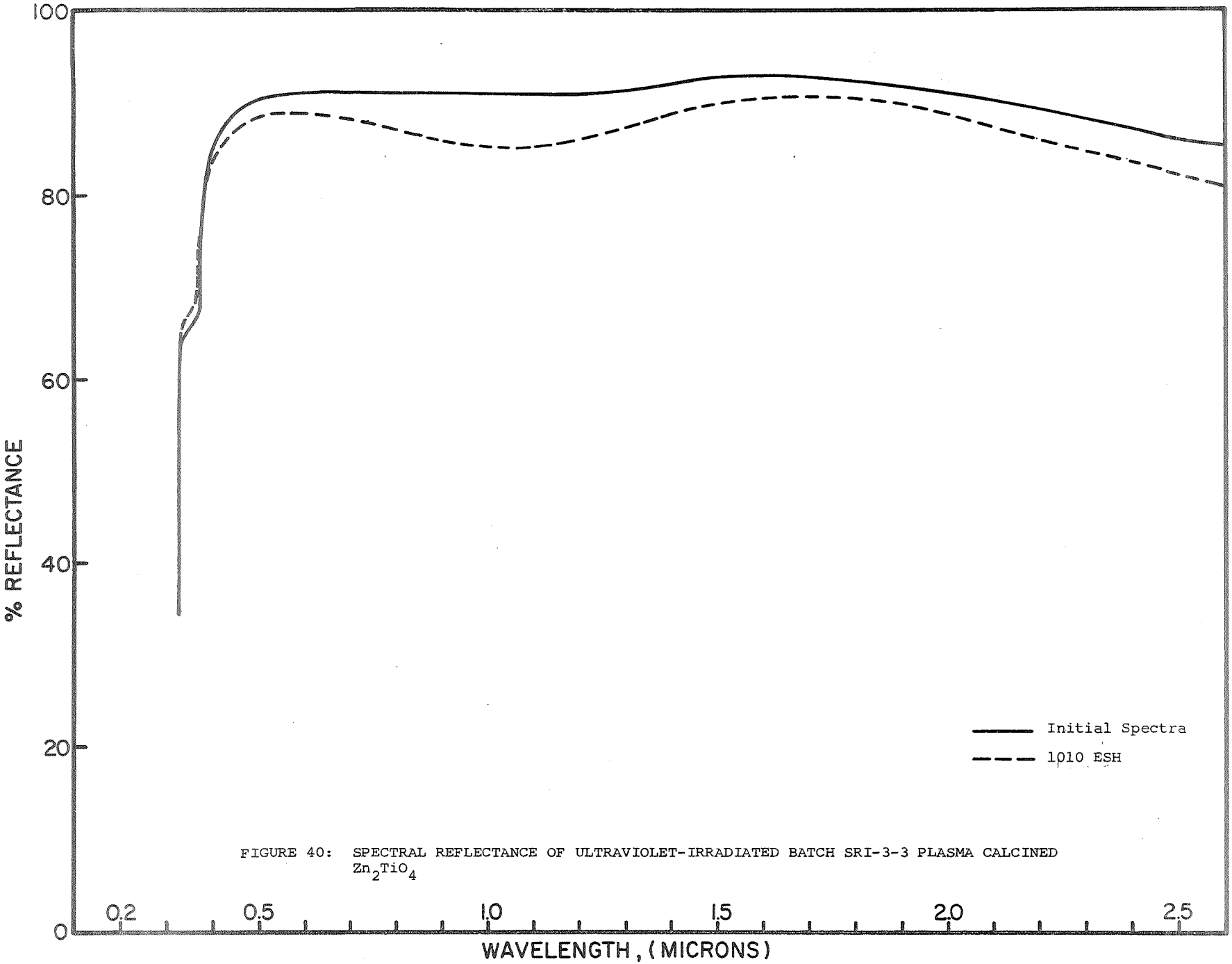


FIGURE 40: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED BATCH SRI-3-3 PLASMA CALCINED Zn_2TiO_4

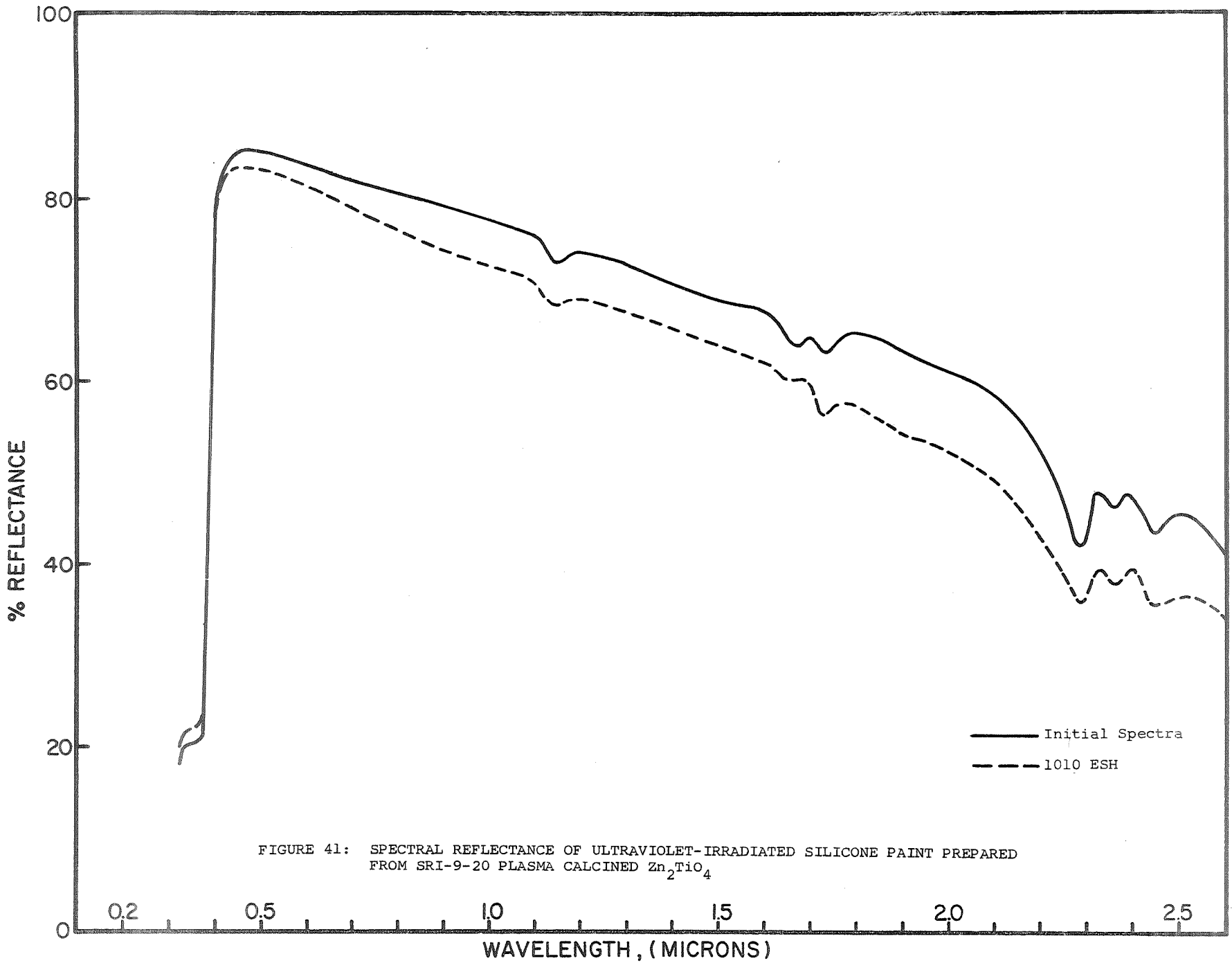


FIGURE 41: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED SILICONE PAINT PREPARED FROM SRI-9-20 PLASMA CALCINED Zn_2TiO_4

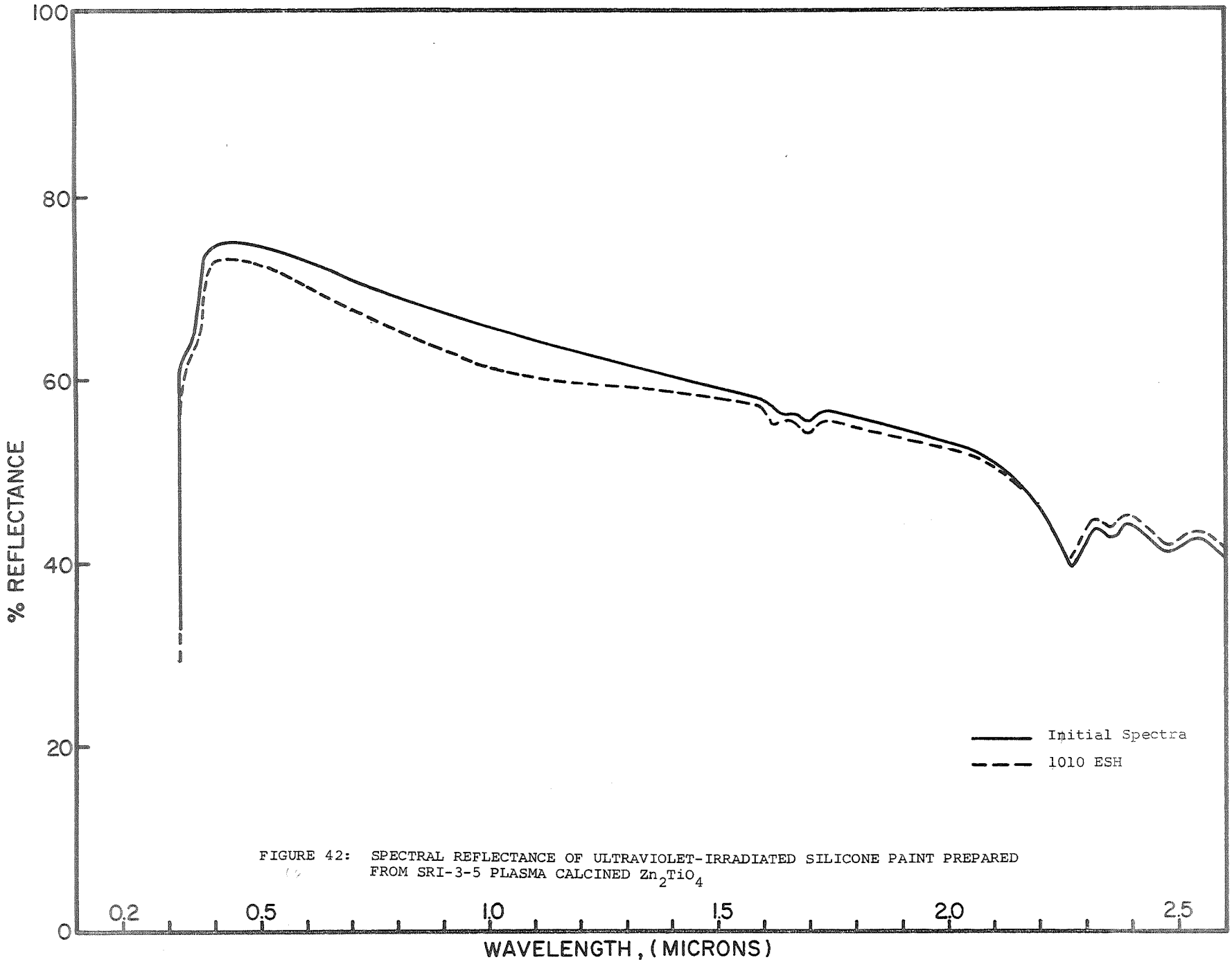


FIGURE 42: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED SILICONE PAINT PREPARED FROM SRI-3-5 PLASMA CALCINED Zn_2TiO_4

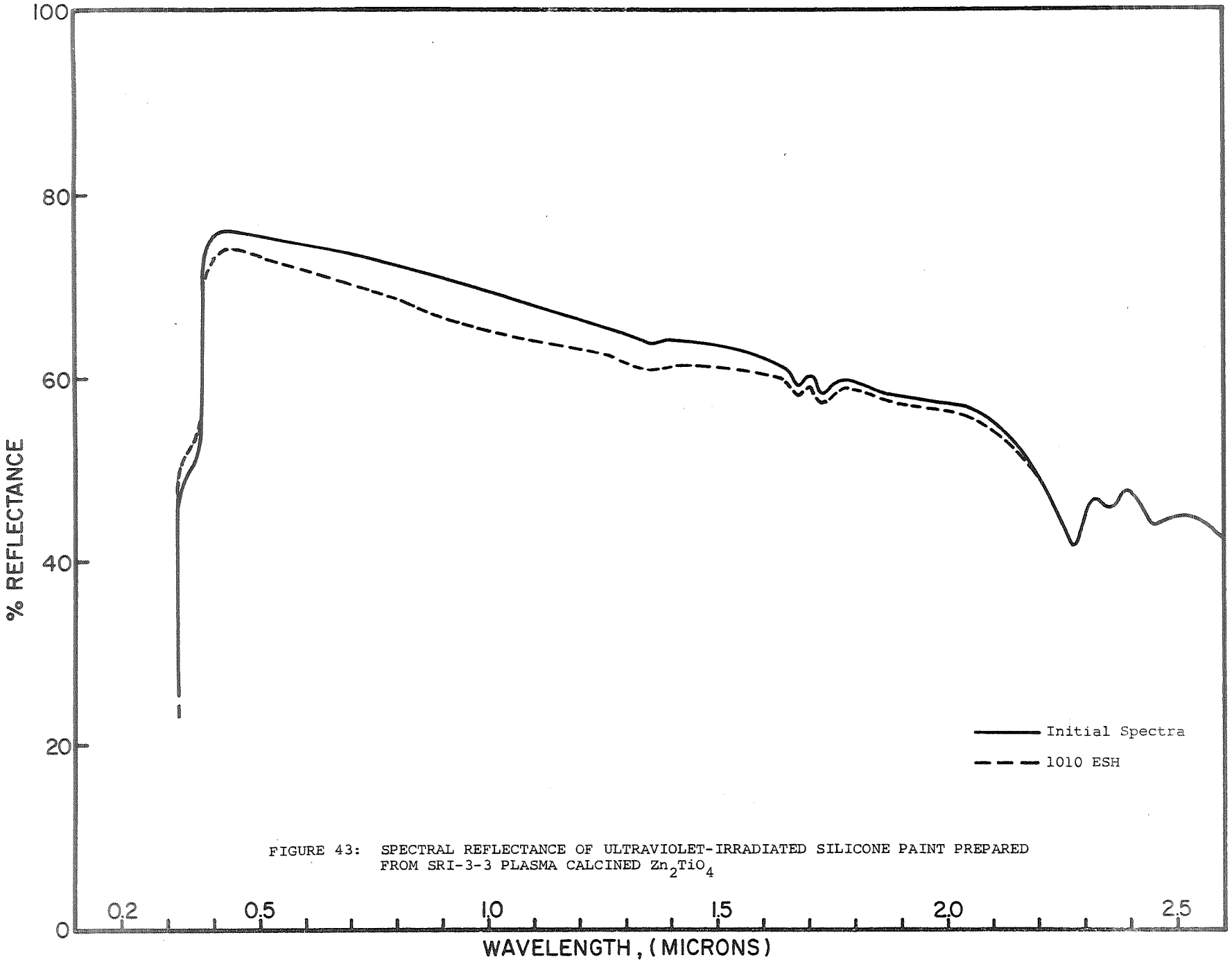


FIGURE 43: SPECTRAL REFLECTANCE OF ULTRAVIOLET-IRRADIATED SILICONE PAINT PREPARED FROM SRI-3-3 PLASMA CALCINED Zn_2TiO_4

zinc oxide employed in IITRI's S-13G (Ref. 4), the stability of the the powder (as opposed to a silicate, or silicone, paint) is decreased in the 400-nm wavelength region by silicating. No explanation is available for this phenomenon except to note that, in the case of zinc oxide, the stability of the pigment in this region of the spectrum is greater than that of the potassium silicate.

The phosphate treatment improved the reflectance in the ultraviolet by essentially removing the shoulder at ~362-nm that has been attributed to unreacted zinc oxide (Ref. 5). The much greater damage exhibited by the phosphated powder compared to the previously studied powder cannot be explained except that it is conceivable that, in the present case, not all unreacted NaH_2PO_4 was removed from the surface by washing after phsophating.

Treatment with ferro(ferri) cyanide also had a deleterious effect on the spectral stability of zinc orthotitanate powders.

Careful examination of the data contained in Table 5 and Figures 6 through 15 indicate the following:

a. Of the new reactive encapsulants (Li_2SiF_6, K_2SiF_6, K_2SnF_6, $H_4Si_4W_{12}O_{40}$ and $K_4Si_4W_{12}O_{40}$), all three fluorinated materials substantially reduced the infrared damage in the 700- to 2400-nm wavelength region that is characteristic of untreated zinc orthotitanate (without subsequent heat treatment of the reacted powder). Of these, the fluorostannate treatment was the most effective in precluding infrared damage; however, the fluorostannate treatment had a highly deleterious effect on the stability of zinc orthotitanate in the 350- to 600-nm wavelength region and, in this respect, was far more deleterious than either the potassium or acid silicotungstate treatments.

b. Treatment with potassium silicotungstate had little effect on the optical properties of zinc orthotitanate. However, the silicotungstic acid treatment caused severe infrared damage to Zn_2TiO_4 under ultraviolet irradiation.

c. Heat treatment of all five chemically-treated zinc orthotitanate powders resulted in pigment having greater stability than the untreated control (B-229) in the infrared region 700- to 2400-nm wavelength. The lithium and potassium silicofluoride- (hexafluorosilicate) treated pigment that was heat treated for 7 hr at 500°C exhibited improved stability in the near-ultraviolet and visible wavelength regions, as well.

d. Although the heat-treated product prepared from the potassium silicotungstate-treated powder (B-547) was nearly as stable, this chemical treatment was not effective in removing the 362-nm shoulder absorption that is present in the Zn_2TiO_4 control--an absorption band that contributes significantly to the solar absorptance of coatings prepared from this pigment. Treatment with the three fluorinated salts resulted in considerably decreased, if not completely eliminated, absorption at 362-nm wavelength (B-458, Figure 9); this change is presumably due to the extraction of unreacted zinc oxide during the reflux operation.

e. The poorer reflectance of the heat-treated powders (Figures 7 and 9) is attributed primarily to the lesser thickness of the treated oxide when "wet sprayed." The heat treated, encapsulated powder, perhaps by virtue of the decreased surface free energy, is more difficult to build-up by the "wet spray" method than the non-heat-treated, encapsulated powders.

2. Paints Prepared from Reactively-Encapsulated Pigment

Examination of Table 6 and Figures 16 through 19 confirm the results obtained previously--namely that potassium silicate paints pigmented with zinc orthotitanate are, even in the absence of reactive encapsulation, quite stable to ultraviolet irradiation in vacuum. Also, as discussed in a previous section of this report, heat treatment of silicate paints improves their stability.

The silicone paints prepared from untreated zinc orthotitanate were less stable in the near infrared (700-2600-nm) than the pigment itself, thus confirming the earlier studies. Indeed, the silicone paint prepared from RTV-602 silicone elastomer was very badly damaged in the near ultraviolet and visible spectrum (Figure 19), although this coating did not exhibit a noticeable "belly damage" at 950-nm wavelength as did the Owens-Illinois 650-resin analog (Figure 18). The severe visible damage is attributed to two synergistic factors--the employment of a near ultraviolet-scattering pigment (compared to ZnO) in a less stable binder (compared to Owens-Illinois 650 resin)--RTV-602 is less stable only by virtue of the requirement for amine curing.

Owens-Illinois 650 resin paints prepared from phosphated, silicated, and "cyanated" pigments (Figures 20 through 23) were either less stable, or no more stable, than the corresponding control pigment (B-415B, Figure 18). Indeed, both formulations B422 (Figure 20) and B-431 (Figure 23), each prepared from a phosphated pigment, were seriously damaged in the 700- to 2000-nm region by ultraviolet irradiation. Batch B-427 did not exhibit such serious damage, presumably due to neutralization of the NaH_2PO_4 by the silicate already present on the B-233 powder (see Figure 1A).

It was these data that prompted the examination of new reactive encapsulants in order to attempt the stabilization of zinc orthotitanate in silicone paints.

* * * *

The excellent stability exhibited by zinc orthotitanate-pigmented potassium silicate paints is nowhere better illustrated than by the data of Table 7 and Figures 24 through 29. The reflectance spectra are presented for the air-dried paints only, since the specimens that were heat treated for 16 hr at 427°C were generally only a little more stable. Additionally, they do not possess the ultimate practicality of the air-dry formulations.

The best stability and lowest solar absorptance (0.12) was exhibited by the silicate paint prepared from phosphated pigment (Batch B-421, Figure 25). In this case, unlike the phosphated-pigment irradiated as a powder, since the phosphate treatment preceeded pigmentation in the silicate vehicle, neutralization of any excess acid phosphate was assured by the highly alkaline silicate solution. It should be noted that removal of water during the irradiation of these paints accounts for the increased reflectance in the infrared region with its attendant contribution to the low $\Delta\alpha_s$'s observed (see Figures 24 through 29).

* * * *

Paints prepared from zinc orthotitanate that was reactively encapsulated with the new fluorinated salts and with potassium silicotungstate were generally the most stable paints examined in these studies (see Table 8 and Figures 30 through 37). Indeed, <u>the potassium silicate paint pigmented with potassium hexafluorosilicate-treated zinc orthotitanate possessed both the lowest solar absorptance (0.122) and the greatest stability ($\Delta\alpha_s$ = 0.002) of any paint ever evaluated at IIT Research Institute.</u>

The Owens-Illinois 650 resin paints prepared from Zn_2TiO_4 pigments reactively encapsulated with lithium hexafluorosilicate and potassium hexafluorosilicate exhibited stabilities that were moderately improved over the control paint (B-415) and the silicone paints prepared from pigment that had been phosphated, or similarly treated (compare Tables 6 and 8).

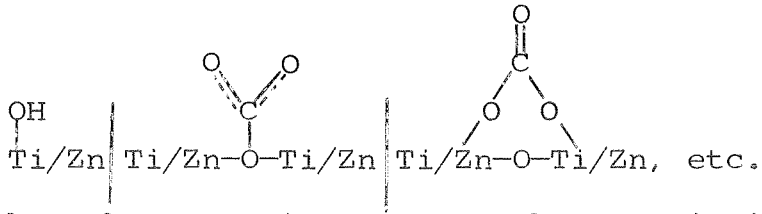
3. Powders and Paints Prepared from Plasma-Treated Pigment

Although the significance of the subtleties in the damage spectra of the plasma-calcined powders (Table 9) will not be drawn until the data are available for the entire series of plasma-calcined zinc orthotitanates, the objective of these particular tests was to determine the degree to which plasma calcination stabilizes the Zn_2TiO_4 surfaces against the anomolous degradation in silicone paints. Examination of these data, including Figures 38 through 43, show that two of the silicone paints exhibit improved stability to ultraviolet (paints prepared from SRI-calcined pigments 3-5 and 3-3). The reflectance data suggests that stabilization is possible; that is, the damage sustained by the paints was essentially no different than that exhibited by the powder analogs. (The poor reflectance, i.e., high solar absorptance, of the Owens-Illinois "650" paints prepared from the plasma-calcined products is attributed to very thin coatings as a result of insufficient pigment starting material.)

4. Summary

It is becoming increasingly obvious that reactive encapsulation and plasma calcination both serve to reduce the surface state of zinc orthotitanate, and thus may make increasingly difficult the injection of electrons into the surface for reduction of Ti^{+4} to Ti^{+3}.

Both water and carbon dioxide, among other species, are highly adsorbed on the surface of zinc orthotitanate.



We believe that these species promote the association of O_2^- (and/or O^-, or $O^=$) on the surface, the photodesorption of which injects an electron into the surface where, in the case of zinc oxide, it is available for conduction absorption (e.g., broad-

based, free-carrier absorption) that has been discussed by Gilligan (Ref. 6), and, in the case of zinc orthotitanate, where it is available for reduction of Ti^{+4} to Ti^{+3}. We have shown that the 950-nm absorption may be explained by photodesorption of $O^{=}$ (Ref. 7), and, on the basis of epr studies (Ref. 5), have suggested that the 950-nm absorption may be due to an electron trap associated with Ti^{+3}.

This concept is wholly consistant with the considerable improvements obtained by plasma calcination and reactive encapsulation of zinc orthotitanate. Plasma calcination would dehydroxalate the surface (and oxidize absorbed carbonate as well), thus reducing the sites for adsorbed O_2^- (or O^-, or $O^{=}$). Similarly, reactive encapsulation is thought to tie up the surface, and again, the availability of sites for adsorption of O_2^- (and/or O^-, or $O^{=}$) is greatly diminished. Thus, photodesorption of oxygen and the injection of an electron into the lattice surface is precluded and ultraviolet-induced damage does not occur.

IV. SUMMARY AND CONCLUSIONS

The excellent optical properties and ultraviolet stability of zinc orthotitanate-pigmented potassium silicate paints have been confirmed. It is apparent that straight-forward optimization of the silicate paint formulations will result in coatings that possess solar absorptances of 0.10 and excellent stability to the near-earth space environment. The efficacy of the surface treatments in stabilizing zinc orthotitanate paints to the combined ultraviolet-plus-proton (and electron) radiation of deep space has yet to be established.

On the basis of the reactive encapsulation studies reported herein, we believe that the anomalous degradation observed in zinc orthotitanate when employed in silicone paints can be prevented. Solution of this problem, coupled with the hoped for improvement of the physical properties of Owens-Illinois 650 resin (that is being attempted at IITRI), will make possible the specification of a second, new, white radiator coating, one that can be spray applied easily, is cleanable, and is dirt resistant.

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