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CASE FILE
COPYTHE BEHAVIOR OF SEVERAL WHITE PIGMENTS AS DETERMINED BY IN SITU
REFLECTANCE MEASUREMENTS OF IRRADIATED SPECIMENS*

by

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This paper is a review of materials research relating primarily to two white pigment materials -- zinc oxide and zinc orthotitanate. The zinc oxide studies include 1) investigation of the photodesorption problem associated with the irradiation of zinc oxide in vacuum, 2) elucidation of the resultant and concomittant generation of an infrared-centered absorption band, and 3) prevention of the development of photodesorption-related infrared absorption by treating the zinc oxide surface with alkali silicates. The zinc orthotitanate studies relate to 1) the synthesis of zinc titanates having various controlled

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stoichiometry and optical properties, 3) the relation between heat-treatment and stability to ultraviolet irradiation in vacuum, and 4) the photodesorption phenomena associated with zinc titanates.

INTRODUCTION

Until 1965, zinc oxide was thought to be the most stable white pigment available in terms of stability of its hemispherical spectral reflectance to ultraviolet irradiation in vacuum.¹⁻³ However, serious discrepancies in zinc oxide's behavior were reported between laboratory-simulation data and flight-experiment data obtained from OSO-II⁴ and the Pegasus⁵ materials' experiments.

These data indicated that zinc oxide-based silicone coatings were considerably less stable than predicted by the extensive space-simulation testing to which they had been subjected. The discrepancy has since been attributed to the formation of an easily (oxygen) bleached infrared absorption band that cannot be observed by classical postexposure reflectance measurements in air. It was first observed in the laboratory by MacMillan et al⁶ while making in situ measurements of the bidirectional reflectance of zinc oxide irradiated in vacuum. Confirmation of the bleachable infrared degradation of zinc oxide first noted by MacMillan et al was reported by Miller⁷ and subsequently by Zerlaut et al.^{8,9}

The observations that zinc oxide exhibits bleachable degradation in the infrared resulted in: 1) the design and

construction of a multiple-sample irradiation facility employing in situ postexposure reflectance measurements (the IRIF),¹⁰ and 2) the initiation of research aimed at securing a satisfactorily stable white pigment.

The IRIF utilizes an evacuated Edwards-type¹¹ integrating sphere with which absolute hemispherical spectral reflectance measurements were obtained. The IRIF, which was used in the studies reported herein, is adequately discussed in Ref. 10 and will not be described in this communication.*

The pigment studies that were begun as a result of zinc oxide's behavior involved 1) investigations relating to the stabilization of zinc oxide against the photodesorption-related infrared degradation observed by the early in situ postexposure measurements, and 2) the search for a stable white pigment that does not exhibit significant photodesorption-related damage.

SURFACE TREATMENT OF ZINC OXIDE

The Ultraviolet Degradation of Zinc Oxide

The effect of irradiation of IITRI's S-13 thermal-control coating, the zinc oxide-pigmented polydimethylsiloxane** paint that had degraded severely in flight tests,^{5,6} is presented in Fig. 1. The spectral data are plotted as a function of equal-energy increments. The damage sustained by surfaces in the

*The General Electric AH-6 lamp was employed as the UV source.

**General Electric's RTV-602 methyl silicone elastomer.

4000- to 7000-Å region (visible), where nearly 50% of the solar energy lies, is more significantly and more accurately represented by graphical presentation of data in this manner.

S-13 exhibits a reflectance decrease of about 35% at 2- μ wavelength after approximately 800 equivalent sun hours (ESH) of ultraviolet irradiation in vacuum (Fig. 1). However, an almost instantaneous increase in infrared reflectance occurs when the irradiated specimen is admitted to the atmosphere; the recovery is almost total after only 2 min. exposure to air. The effect of 1000 ESH of ultraviolet radiation on "water sprayed" SP500 zinc oxide is presented in Fig. 2. Examination of these data show that the bulk of the solar absorptance increase exhibited by zinc oxide and the S-13 coating is due to the bleachable damage sustained in the infrared.

The rapidity with which the ultraviolet-induced infrared-absorption band develops in zinc oxide and the abruptness with which air (oxygen) annihilates the absorption are conclusive evidence that the infrared phenomenon is associated with the photodesorption of absorbed gases. The solid-state and surface chemistry associated with the mechanism of damage are not completely understood. One theory is that the infrared behavior of zinc oxide can be explained on the basis of a free-carrier absorption mechanism. Gilligan¹², in studies at IIT Research Institute for the Jet Propulsion Laboratory, concluded that the valence band holes are attracted to the surface, where they dis-

charge absorbed oxygen (and other absorbate gases) by capturing their electrons -- accounting for the accumulation of electrons in the conduction band. However, Greenberg et al.,¹³ in studies for the NASA-Marshall Space Flight Center, attribute the infrared band to bound donor states associated with oxygen vacancies at the surface.

The solid state chemistry associated with zinc oxide's behavior is too broad and too complex for inclusion here, however germane. The reader is referred to Refs. 12 and 13 and to the references cited in these communications for a comprehensive review of current thinking on the subject.

Protection of Zinc Oxide Against Degradation

Of particular significance to the ensuing studies was the fact that IITRI's Z93 thermal-control coating, an SP500 zinc oxide-pigmented potassium silicate paint, does not undergo the bleachable infrared damage exhibited by S-13 and pure zinc oxide. Figure 3 is a typical example of the spectra of irradiated and unirradiated Z93.

The absence of damage to zinc oxide-pigmented alkali silicate coatings suggested that the reactivity of zinc oxide with, for example, potassium silicate may have precluded the bleachable infrared degradation exhibited by zinc oxide powder and zinc oxide-pigmented silicone paints. The polydimethylsiloxanes do not "wet" the pigment particles and as a consequence offer no effective barrier to photodesorption reactions on the surface of zinc oxide. We therefore performed a series of experiments

in which zinc oxide was first reacted with potassium silicate and showed that a treated-zinc oxide powder that does not exhibit infrared degradation can be prepared. The treated zinc oxide can be formulated into methyl silicone paints that also do not exhibit infrared damage on irradiation in vacuum^{8,9}. The reflectance spectra of an irradiated silicate-treated zinc oxide specimen are presented in Fig. 4.

Silicone Paints Pigmented with Stabilized Zinc Oxide

It was quickly realized that the development of stabilized-zinc oxide-pigmented RTV-602 silicone paints is largely a process-related problem. IIT Research Institute was subsequently awarded a research contract¹⁴ from the Jet Propulsion Laboratory to engineer these silicone paints, generically termed S-13G.

Factors that had to be considered in engineering S-13G were: 1) initial zinc oxide-silicate reaction parameters such as the materials' balance, reaction temperature, reaction time and mixing during reaction, 2) pigment filtration and silicate extraction (washing) procedures, 3) pigment drying and grinding procedures, 4) silicone paint manufacturing procedures, and 5) optimization of paint formula relative to pigment volume concentration (PVC), solvents employed, catalyst concentration etc.

The initial materials' ratio, a materials' balance still employed, was 1.7 parts PS-7 potassium silicate (Sylvania Electric) to 1.0 parts of SP500 zinc oxide (New Jersey Zinc). The reaction was carried out by ball-milling for one-half hour and

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allowing to stand sealed for 16 hr. The pigment was let-down with distilled water, filtered through Büchner funnels, washed with distilled water, oven dried at 100°C, dry-ground in a ball mill and finally, prepared as an S-13-type coating at 30% PVC.

The paint prepared as described above possessed the following characteristics: 1) the pigment treatment did not offer complete protection against photodesorption-related infrared damage, 2) the cured, virgin (unirradiated) films exhibited significant yellowing, 3) the paint films exhibited more than twice the visible damage sustained by S-13 pigmented with untreated zinc oxide, and 4) the paints often gelled within 72 hrs.

The initial reaction temperature was increased from room temperature to approximately 77°C. employing a double boiler; the slurry was rapidly stirred at temperature for 30 min. The slurry was let-down with distilled water, filtered and re-dispersed twice more. This process resulted in a softer, whiter pigment that offered almost complete protection to degradation in the infrared. In addition, an accompanying change to a "slower" solvent system greatly extended the shelf life of the coatings.

The paints prepared from hot-process pigment still exhibited some degradation in both the visible and infrared. The concept of "sweating", a process utilized in the organic-pigment industry was employed with considerable success. This involved sealing

the wet filter cake from the first filtration in aluminum foil and allowing it to stand for 6 to 72 hr. The resultant pigment was exceptionally soft and white, it easily was dry ground and milled into paints and did not yellow on curing. Paints prepared from 24-hr. sweated pigment have extended shelf lives; a formulation prepared without retarder solvents exhibited a shelf life of 10 weeks. A minimum of 6 hr. sweating time is required to provide satisfactory softness, whiteness and protection against ultraviolet irradiation. Although longer periods provide improved protection, sweating times greater than 24 hr. result in unusable pigment. Paint milled from pigment that is sweated 48 hr. is extraordinarily thixotropic and cannot be easily applied or cured. The pigment is thought to absorb the solvated silicone to the extent that both flow and curing are prevented.

Figure 5 presents the spectra of S-13G prepared from 16-hr. sweated pigment that has been irradiated with 600 ESH of ultraviolet irradiation. These data indicate that the infrared problem largely has been solved; the visible damage sustained by this specimen of S-13G ($\Delta\alpha_s = 0.01$) is little greater than that exhibited by S-13 (see Fig. 1).

The enhancement of optical properties by increasing the temperature and initiating a sweating period -- which effectively increases the reaction time -- is believed to be due simply to the increase in zinc silicate "fixed" on the surface.

Analysis of the treated pigment and the wash water for K_2O and SiO_2 confirmed this hypothesis since the SiO_2 content of the pigment and the K_2O content of the wash water was found to increase with increasing reaction temperature and reaction time (sweat). Typical pigment analyses are presented in Table 1.

Table 1
COMPARISON OF SWEATED WITH HOT-
AND COLD-PROCESS-POWDER CAKES

<u>Process</u>	<u>K_2O %</u>	<u>Silica, %</u>
Cold Mix	0.4	1.0
Hot Mix	0.8	5.0
Sweated: 6 hr.	1.0	6.5
18 hr.	1.0	7.0
42 hr.	1.0	8.0

Experiments to determine the effect of calcining the sweated pigment were undertaken in the belief that heat treatment would increase the silicate "fixed" on the surface of the zinc oxide and thereby further improve stability to ultraviolet radiation as well as the shelf life. This was based on consideration of the data presented in Table 1 as well as the fact that precalcination of the SP500 zinc oxide enhances the stability of the zinc oxide in the Z93 formulation.

The spectra of S-13G prepared from sweated pigment pre-heat treated for 16 hr. at $650^\circ C$. is presented in Fig. 6. The

stability in the infrared was decreased by calcination, resulting in an increase in $\Delta\alpha_s$ from 0.01 (Fig. 5) to 0.03 (Fig. 6). These results are due presumably to the greater grinding required to reduce the calcined pigment -- thereby generating new, unprotected surfaces which are subsequently photodesorbed in the paint. Analogously, the greater infrared damage exhibited by paint prepared from unsweated, cold-process pigment is believed due to physical removal of the non-fixed silicate during the paint-milling operation.

Because even the new, sweated pigment is still too alkaline -- and cannot be used in the Owens-Illinois 650 polymethylsiloxane and resin system (such paints gell in the mill) -- we made two attempts to neutralize the triple-redispersed, sweated pigment prior to manufacture of S-13G. Figures 7 and 8 depict the stability of S-13G prepared from sweated pigment neutralized with formic acid and sodium acid phosphate, respectively; the pigments were then calcined for 16 hr. at 650°C. prior to formulation into paints. Examination of these data show that the stability at most wavelengths was destroyed by neutralization with formic acid. On the other hand, the specimen prepared from the acid phosphate-neutralized pigment exhibited the greatest ultraviolet stability that has been observed for an S-13G prepared from calcined pigment. Space simulation tests on Owens-Illinois 650 resin-based paints prepared from the phosphate-treated pigment have yet to be performed, however.

As mentioned earlier, the use of multiple solvents in

addition to toluene greatly extended the shelf life of S-13G even before the use of sweated pigment. Retarder solvents and diluents employed in addition to toluene are isopropanol, xylene, n-butanol, isopropyl acetate and petroleum ether. Of these, only films applied from solutions containing petroleum ether have shown inferior stability. A specimen prepared from paint retarded with petroleum ether was irradiated in the IRIF; its reflectance spectra are shown in Fig. 9. The increase in solar absorptance was 0.03 after 800 ESH compared to a $\Delta\alpha_s$ of 0.01 for the identical paint employing toluene only (Fig. 5).

Summary

The S-13G formulation currently providing the most satisfactory optical and physical characteristics is prepared from SP500 zinc oxide that is slurried with PS-7 potassium silicate at 77°C. for 20 min. The slurry is diluted with distilled water, vacuum filtered, wrapped in aluminum foil and allowed to sweat for 16 hr. The sweated pigment is then redispersed in distilled water and again filtered; the redispersion and filtration are performed for the third time. The cake is then spread to dry in an oven for 16 hr. at 100°C. It is then hand milled, sieved (80 mesh) and packaged ready for manufacture into paint.

The RTV-602 silicone-based S-13G coating is prepared at 30% PVC by milling for 3½ hr. in a porcelain ball mill employing a minimum of grinding media. The solvent system currently

employed is given in Table 2. Paints catalyzed with General Electric's SRC-05 catalyst at 0.4% by weight based on RTV-602 solids cure to the touch in 4 to 6 hr. and can be handled in 16 hr. The uncured paint possesses a shelf life in excess of 3 months.

Table 2
S-13G SOLVENT SYSTEM

<u>Solvent</u>	<u>%</u>
Toluene	50
Xylene	25
Isopropanol	15
n-Butanol	10

The engineering values of solar absorptance and hemispherical emittance currently quoted for 8-mil films of S-13G are 0.19 ± 0.02 and 0.88 ± 0.05 , respectively. The engineering value currently quoted for $\Delta\alpha_s$ is 0.03 for 1000 ESH of simulated space ultraviolet radiation employing in situ postexposure reflectance measurements and AH-6-lamp irradiation.

GENERAL PIGMENT SCREENING STUDIES

Although we have continued the pigment screening efforts that were begun in 1962 for the Jet Propulsion Laboratories,¹ these efforts have until the past year proceeded at a rather modest rate. However, the observations that zinc oxide exhibits a photodesorption-related degradation in the infrared region⁴⁻⁹

prompted an intensification of our screening efforts to secure an ultraviolet-stable white pigment.

The certainty that "pigments which had previously been rejected by tests that employed postexposure reflectance measurements in air would be even more decisively rejected by performing the postexposure measurements in vacuum (in situ)" has made the search for a stable pigment to replace zinc oxide a formidable task. Because of the comprehensiveness of the screening studies previously performed at IIT Research Institute and elsewhere, we were essentially forced to re-examine the potentially most promising candidates suggested in the earlier studies. Pigments that were subsequently re-examined by providing greater emphasis on purity, stoichiometry, etc., and employing the new in situ reflectance techniques now available, included: Yttrium oxide; lanthanum oxide; tantalum oxide; chloride-process rutile; the double-metal zirconium silicates of calcium, zinc and magnesium; the zinc titanates; and zirconium oxide.

Our interest in zirconium oxide historically has involved the fact that it is relatively insensitive to dose rate and, being moderately unstable, is ideal for use as a dosimeter-type control in space-simulation tests. The reflectance spectra of a zirconia-pigmented potassium silicate paint are presented in Fig. 10; the $\Delta\alpha_s$ of 0.08 after 800 ESH of ultraviolet radiation is typical for such an exposure and represents the degree of damage that was previously observed by reflectance measurements in air after about 1000 ESH.

The greater stability of the chloride-process compared to the sulfate-process rutile titanium dioxides that were studied earlier prompted the emphasis that was subsequently placed on the very white, easily dispersed RF-1 "Flame Process" rutile manufactured by Cabot. Postexposure reflectance measurements in air showed RF-1 to be the most stable of the chloride-process rutiles available at that time.¹⁵ The apparent stability plus the high brightness of the RF-1 encouraged further evaluation with the construction of the IRIF.¹⁰ The effect of 600 ESH of ultraviolet irradiation on a wet-sprayed*, powder specimen of RF-1 is presented in Fig. 11; the $\Delta\alpha_s$ of 0.06 was disappointing insofar as its brightness was manifested in an initial solar absorptance of only 0.13, an exceptionally low value for a pigment with an absorption edge at 4000-Å wavelength.

Although the use of RF-1 in potassium silicate may enhance its stability, the fact that rutile can be pigmented safely to only about 40% PVC in alkali silicates, which consequently precludes the attainment of solar absorptances below about 0.2 for reasonably thick films, prompted us to discontinue further investigations with rutile coatings. We are, however, currently examining encapsulated rutiles from du Pont (R-960) and from Lexington Laboratories (NASA Contract NAS8-20162).

The stabilities exhibited by yttria, lanthana and tantala were generally very poor. The reflectance spectra of a tantala-

*Wet-sprayed specimens are prepared by spraying a water mull of the powder onto an aluminum substrate that is heated to 100°C.

pigmented potassium silicate paint is presented in Fig. 12; its $\Delta\alpha_s$ of 0.13 represented an increase in solar absorptance of greater than 50% in 800 ESH. Tantalum oxide appears to be the most stable of the three oxides.

Like zirconia, lithium fluoride has been considered for use as a dosimeter-type control specimen. Also, since its propensity for developing classical color centers has received much attention, it was suggested as one of the flight coupons for the Pegasus materials' experiment. Lithium fluoride was furnished in a potassium silicate binder for this experiment. The principal objective of a program underway at IITRI¹⁷ is the laboratory evaluation of selected Pegasus specimens with the view that the flight coupons might eventually be retrieved by a rendezvousing astronaut.

The effect of 800 ESH of ultraviolet irradiation in vacuum on a lithium fluoride-pigmented specimen prepared at the same time as the Pegasus flight coupon is presented in Fig. 13. The $\Delta\alpha_s$ of 0.18 represents an 140-% increase in the initial solar absorptance and indicates that, while lithium fluoride may be an excellent dosimeter for short exposure times, the extent of damage which it developed may preclude its use for moderate to long exposure times.

The double zirconium silicates appeared to have considerable merit in space-simulation tests employing postexposure measurements in air. However, their behavior in the early in situ tests, combined with the potential shown by the zinc orthotita-

nates in these same tests, prompted the discontinuance of their evaluation in favor of zinc orthotitanate.

THE EVALUATION OF ZINC TITANATE

Introduction

The only commercial zinc titanate to have both high reflectance and good stability to ultraviolet irradiation in vacuum was found to be New Jersey Zinc Company's A-54-2, which was chemically designated as Zn_2TiO_4 , the orthotitanate. The results of 2000-ESH space-simulation tests on several methyl silicone paints pigmented with A-54-2 were encouraging and further research was indicated.¹⁵

An attempt to obtain larger working samples of A-54-2 was unsuccessful and it became necessary to prepare zinc titanate in our own laboratories.

A search of the literature on "zinc titanate" revealed at the onset some very interesting conflicts between various research papers on the subject. Careful work has been performed by some laboratories but at the time we commenced work in our own laboratory, complete agreement existed among all sources only on one zinc titanate, the orthotitanate (Zn_2TiO_4). The orthotitanate is a spinel which is formed from 2 moles of ZnO and 1 mol of TiO_2 . The reader is referred to the discussion of the pertinent literature contained in IIT Research Institute's Triannual Report No. IITRI-U6002-47¹⁵ prepared for the George C. Marshall Space Flight Center.

A pertinent publication in 1961 by Bartram and Slepetys¹⁸ to some extent cleared up the discrepancies in the literature. They listed the orthotitanate as most easily prepared from sulfate-process anatase; they stated that a reaction time of 3 hr. at from 800 to 1000°C. is required. The metatitanate, $ZnTiO_3$, they found, required chloride-process rutile and an optimum temperature of 850°C. The solid solution phenomenon claimed by earlier writers appeared to be explained by the claim of Bartram and Slepetys to a third zinc titanate ($Zn_2Ti_3O_8$), the sesquititanate. This is a defect spinel structure made from anatase and zinc oxide in ratios of 2 moles ZnO to 3 moles of TiO_2 reacted at a temperature of 700°C. for at least 100 hr.

In 1962, Loshkarev in three Soviet papers¹⁹⁻²¹ found only orthotitanate as a compound using only rutile and zinc oxide and temperatures up to 1400°C. The reaction between rutile and zinc oxide did not begin below 740°C.

The existence of unreacted zinc oxide in the final product, regardless of composition, temperature or time, was found by Loshkarev and later confirmed by ourselves.¹⁵ Loshkarev reported "very intense shrinkage" (from 15 to 18%) in forming the orthotitanate at temperatures above 1000°C. They therefore recommended slow heating when reaching this range. (We followed this advice in our studies; the shrinkage was quite apparent). The Russian papers do not concede the existence of the metatitanate, $ZnO \cdot TiO_2$, nor the sesquititanate listed by Bartram and Slepetys.

The most recent publication on the subject is a Japanese

paper by Kubo et al.²² in which they acknowledge the existence of the three titanates and report success in making the metatitanate of exceptional purity.

Summarizing the literature, all workers agree on the orthotitanate as to composition, crystal structure and characteristics. A few agree upon the existence and structure of the metatitanate, and one only claimed the existence and structure of the defect spinel, $Zn_2Ti_3O_8$, which we will refer to in the future as the sesquititanate. Although it was considered necessary to first synthesize the orthotitanate, the ensuing discussion first treats the synthesis of the meta- and sesquititanates in order to provide a comprehensive review of the reaction between zinc oxide and titanium dioxide.

Experimental Procedures

The general synthetic procedure, regardless of the specific titanate to be prepared, involved the following general recipe: A distilled-water slurry of the appropriate titanium dioxide was adjusted to a pH of 8.5 with NH_4OH and, along with a distilled-water slurry of zinc oxide, was agitated for 5 min. The two slurries were combined and agitated together for 15 min. The combined slurry was then vacuum filtered using a Buchner funnel. The filter cake was then spread on an aluminum sheet and dried at $100^\circ C$. for 3 hr. in a forced-air oven. The material was next dry ground with a glass muller, packed into a porcelain crucible and fired at the appropriate temperature for the necessary length of time.

The spectra of all three precursor oxides employed are presented in Fig. 14. They are: SP500 zinc oxide (New Jersey Zinc); RF-1 rutile titanium dioxide (Cabot); and, TiPure FF anatase titanium dioxide (du Pont). These spectra, as well as those presented in Figs. 15 and 16, were obtained using our Edwards-type integrating-sphere attachment for the Beckman DK-2A spectrophotometer. These specimens (and all other zinc titanate specimens whose properties are discussed in this paper) were prepared by the "wet-spray" technique discussed earlier. The spectra in Fig. 14 are presented to provide the necessary background against which the spectra of the synthetic zinc titanates may be evaluated.

The synthesis schedule for the three zinc titanates that were prepared is presented in Table 3. The metatitanate was the

Table 3

SYNTHESIS SCHEDULE OF ZINC TITANATES OF DIFFERENT STOICHIOMETRY

<u>Mol ratio of React.</u>			<u>Time</u>	<u>Temp.</u>	<u>Structure</u>	<u>Spectra (Fig.)</u>
<u>ZnO</u>	<u>a-TiO₂</u>	<u>r-TiO₂</u>	<u>Hr.</u>	<u>°C</u>		
1	-	1	17	850	meta	15
1	1	-	64	700	sesqui	15
2	1	-	3	800	ortho	16 (A)
2	1	-	16	800	ortho	16 (C)
2	1	-	18	1050	ortho	16 (D)

yellowist of the three stoichiometries prepared and possessed an absorption edge (Fig. 15) similar but considerably more gentle in slope than the rutile from which it was prepared. Like the orthotitanates discussed in a later paragraph, the metatitanate possessed unreacted zinc oxide which can be extracted easily with acetic acid.¹⁵ Although the metatitanate possessed only 0.8 % excess ZnO, it had a profound influence on the absorption spectra as shown by the broken line in Fig. 15.

The sesquitanate was whiter than the unextracted metatitanate but did not, unlike either the meta- or the many orthotitanates examined, exhibit a reflectance increase on extraction of zinc oxide (Fig. 15); the sesquitanate possessed ~ 1 % excess ZnO. Its absorption edge was not only at a shorter wavelength than either precursor oxide, but it was more gentle in slope than either anatase or zinc oxide. This structure, which we have termed the sesquitanate, is of a definite stoichiometry since its absorption edge is always observed to fall at approximately 3665-A wavelength intermediate between those of the meta- and the orthotitanates. (The absorption edge of the metatitanate is about 4000 A whereas that of the orthotitanate is at 3310 A.)

For reasons which will become apparent, it is the orthotitanate which exhibits the most promise as a thermal-control pigment and to which we have therefore addressed our principal efforts. The product from the 2:1 mol ratio of ZnO: α -TiO₂ is a very white pigment, brighter to the eye and more reflective than any of the commercial zinc titanates examined. The products

from this reaction also appear whiter than either of the pigments from which they are prepared.

The reflectance spectra of the orthotitanates are presented in Fig. 16 and show unmistakably the formation of a compound with a reflectance in the near ultraviolet and short end of the visible spectrum totally unlike any other white pigment previously tested except for early batches of New Jersey Zinc's A-54-2, which also showed the "step" in the reflectance spectra at about 3500-A wavelength.

The "step" in the reflectance spectra at 3500-A wavelength of all four heats is interpreted as being due to unreacted zinc oxide since, in all cases, extraction with acetic acid resulted in a powder that exhibited the spectra presented in Curve E of Fig. 16. (These spectra required about 2% normalization to 95% reflectance at 6000 A for the purpose of comparison.)

Batch A (Fig. 16) possessed the lowest "Step" (20% reflectance) and the highest unreacted zinc oxide (6%). Recalcination of Batch A at 900°C. for 2 hr. increased the step reflectance to about 38% (5% excess ZnO). Calcination of Batch C for 16 hr. at 800°C. resulted in a significant increase in the reflectance at 3500 A; the increase in reflectance of 55% corresponded to 3% excess ZnO).

Batch D (Fig. 16), calcined for 18 hr. at 1050°C., exhibited very slight, extractable, yellowing and extreme hardness. The fact that residual zinc oxide still existed (2%), even after additional heating, confirms the work of Loshkarev.¹⁹⁻²¹ How-

ever, the Russian papers list the hardness as 5 mho; our own impression is that the high-temperature product possesses a hardness of 6 mho.

In summary, the metatitanate $ZnTiO_3$ must be prepared from rutile titanium dioxide, preferably of the chloride-type. The reaction temperature should be between 800 and 950°C.; the reaction is preferably carried out at 850°C. The metatitanate possesses an ilmenite crystal structure and requires a rutile: zinc oxide mol ratio of 1:1 for preparation.

The sesquitanate $Zn_2Ti_3O_8$ also requires a mol ratio of 1:1 but is prepared from anatase at temperatures in the 700 to 800°C. range. It is a defect spinel crystal that, like the metatitanate, transforms to the orthotitanate at temperatures in excess of 950°C.

The orthotitanate Zn_2TiO_4 , by far the hardest and most reflective of the zinc titanates, must be prepared at a 2:1 mol ratio of $ZnO:TiO_2$ at temperatures above 950°C. for maximum conversion of zinc oxide. The orthotitanate is a spinel-type crystal that will scratch glass.

X-ray diffraction patterns have shown no evidence of intermediate solid solutions of zinc titanates.

Stability to Ultraviolet Radiation in Vacuum

The stability of zinc orthotitanate was at first reported by the author²³ to be excellent after 200 ESH of ultraviolet irradiation; the material examined was prepared at 800°C. for 3 hr. However, subsequent space-simulation tests on a zinc

orthotitanate calcined for 16 hr. at 800°C. resulted in severe degradation. Figure 17 presents the spectra of an unextracted specimen irradiated for 1000 ESH of ultraviolet radiation in the IRIF. The initial solar absorptance was 0.12 and the $\Delta\alpha_s$ was found to be 0.05.

The unusual aspect of the degradation sustained by the zinc orthotitanates is that their reflectance decreases severely from the absorption edge to about 1.5- μ wavelength, with the severest degradation occurring at about 0.8 μ -- degradation that, like zinc oxide at still longer wavelengths, is instantaneously bleached on admission of air to the space chamber.

A specimen of zinc orthotitanate that was extracted with acetic acid exhibited even greater degradation in the same test (see Fig. 18). The $\Delta\alpha_s$ of 0.08 was 85% bleached back on admission of air to the IRIF. The rate at which the reflectance increased at 0.65- μ wavelength on admission of air is presented in Fig. 19 and is comparable to the rate of bleaching exhibited by zinc oxide at 2.0- μ wavelength.

The importance of calcination temperature on the bleachable degradation of zinc orthotitanate is presented in Figs. 20 and 21. Calcination at 1050°C. for 18 hr. produced a material that exhibited a $\Delta\alpha_s$ of only 0.01 after 1000 ESH of ultraviolet irradiation in the same test. The acetic acid-extracted specimen whose spectra is presented in Fig. 21 exhibited a slight loss in reflectance in the 0.6- to 1.2- μ region only -- degradation that was countered in calculating $\Delta\alpha_s$ by a reflectance increase (pre-

sumably due to a loss of adsorbed water) at wavelengths beyond 1.2μ .

Summary

Although we cannot explain the stability exhibited by the first zinc orthotitanate that was irradiated in the IRIF, we are of the opinion that the considerably greater damage exhibited by zinc orthotitanates prepared at 800°C . (Figs. 17 and 18) compared to those prepared at 1050°C . (Figs. 20 and 21) may largely be due to unreacted titanium dioxide present in the 800°C . specimens. Also, excess titanium dioxide, which is inert to acetic acid, may therefore be responsible for the severe damage exhibited by the orthotitanate calcined at 800°C . that was extracted. (However, the extent to which the acetic acid was incompletely removed is unknown and could conceivably account for the increased degradation exhibited by the extracted specimen.) Nevertheless, the higher temperatures at which the "stable" specimen was prepared most likely serves to more completely react the excess zirconium titanium dioxide employed in the reaction.

We have not irradiated specimens of the meta- and sesquitanates in the IRIF, although we plan to do so. However, like rutile, due to their strong absorption of ultraviolet light, they are not expected to offer any advantages over zinc oxide unless they prove exceptionally stable; this is particularly true of the metatitanate which has an absorption edge at 4000 \AA .

In conclusion, a complete reaction between zinc oxide

and anatase titanium dioxide is suggested by these data as being necessary to the preparation of stable zinc orthotitanates. Studies are currently proceeding which involve emphasis on the stoichiometry of the resultant product, on the purity and stoichiometry of the reagents, on longer calcination times, and on the efficiency of the zinc oxide-extraction procedure.

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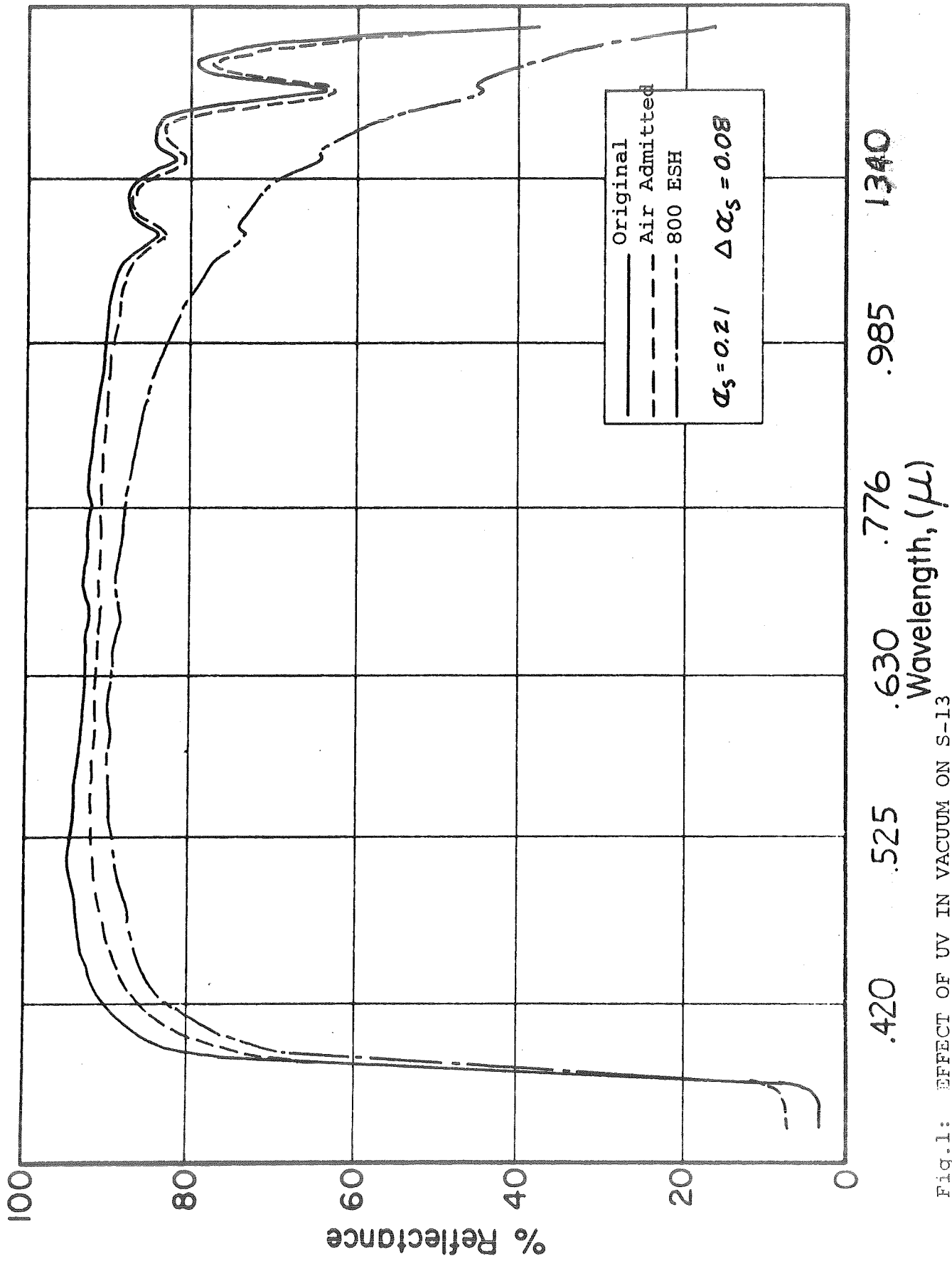


Fig.1: EFFECT OF UV IN VACUUM ON S-13

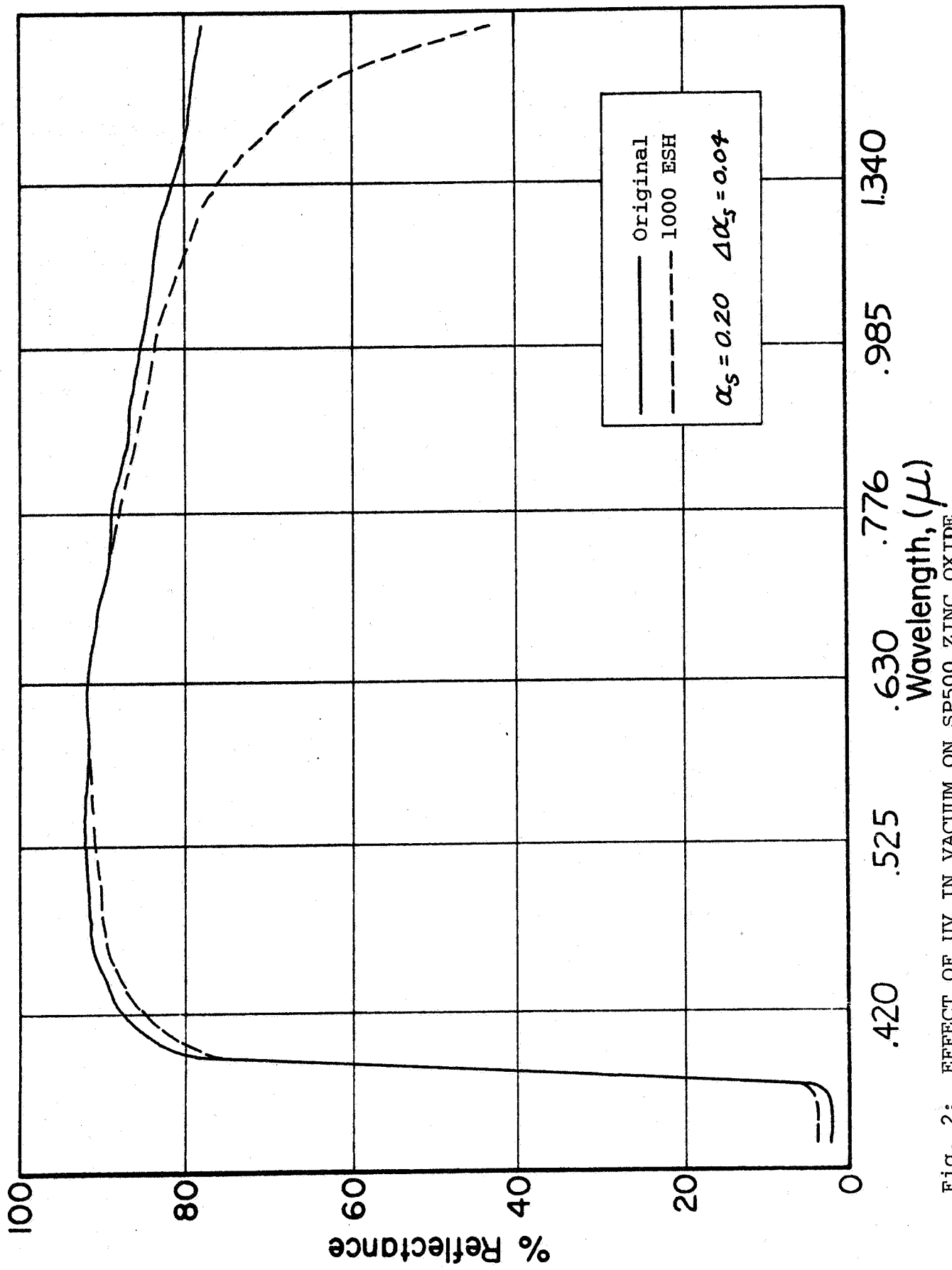


Fig. 2: EFFECT OF UV IN VACUUM ON SP500 ZINC OXIDE

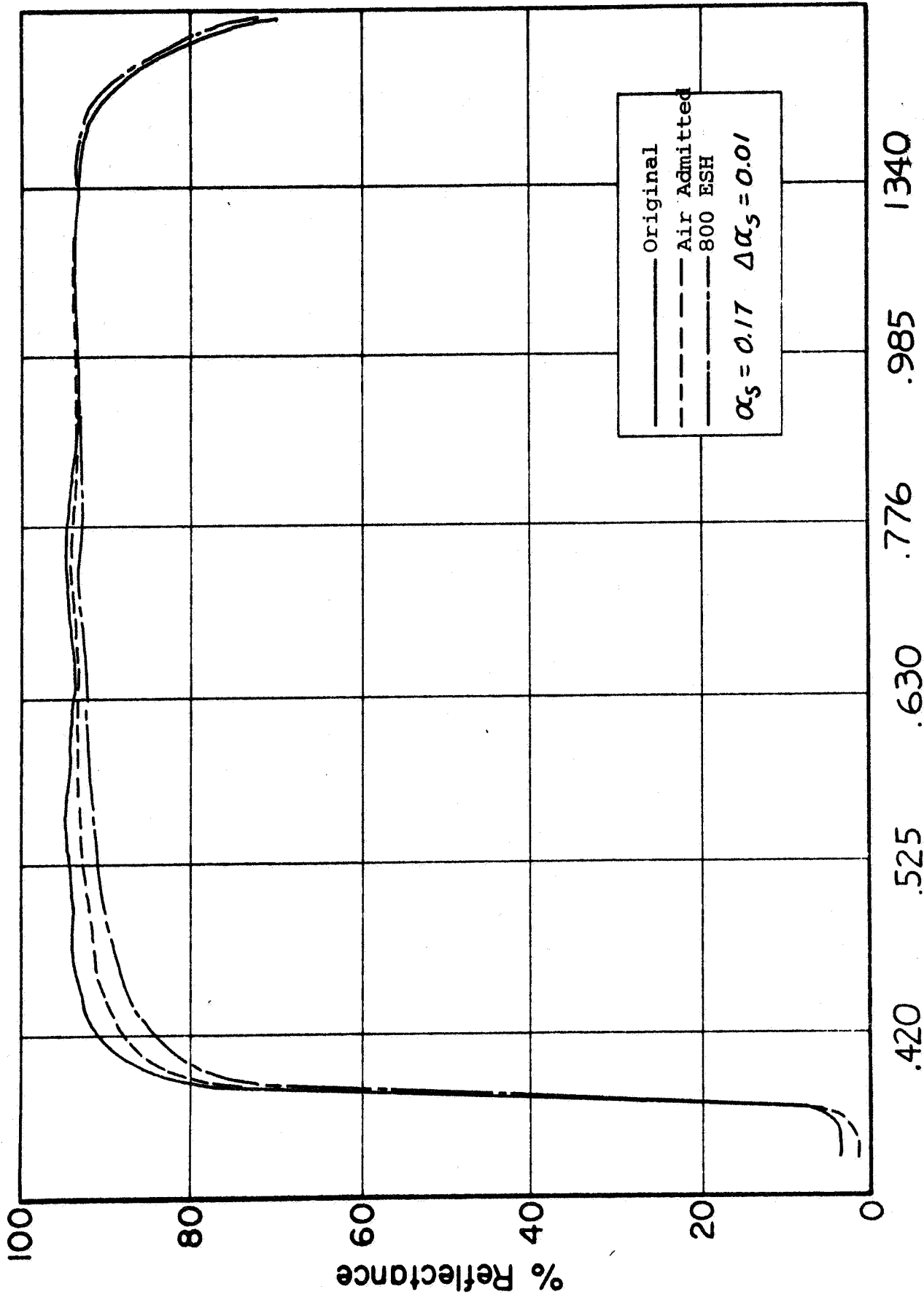


Fig. 3: EFFECT OF UV IN VACUUM ON Z93 Wavelength, (μ)

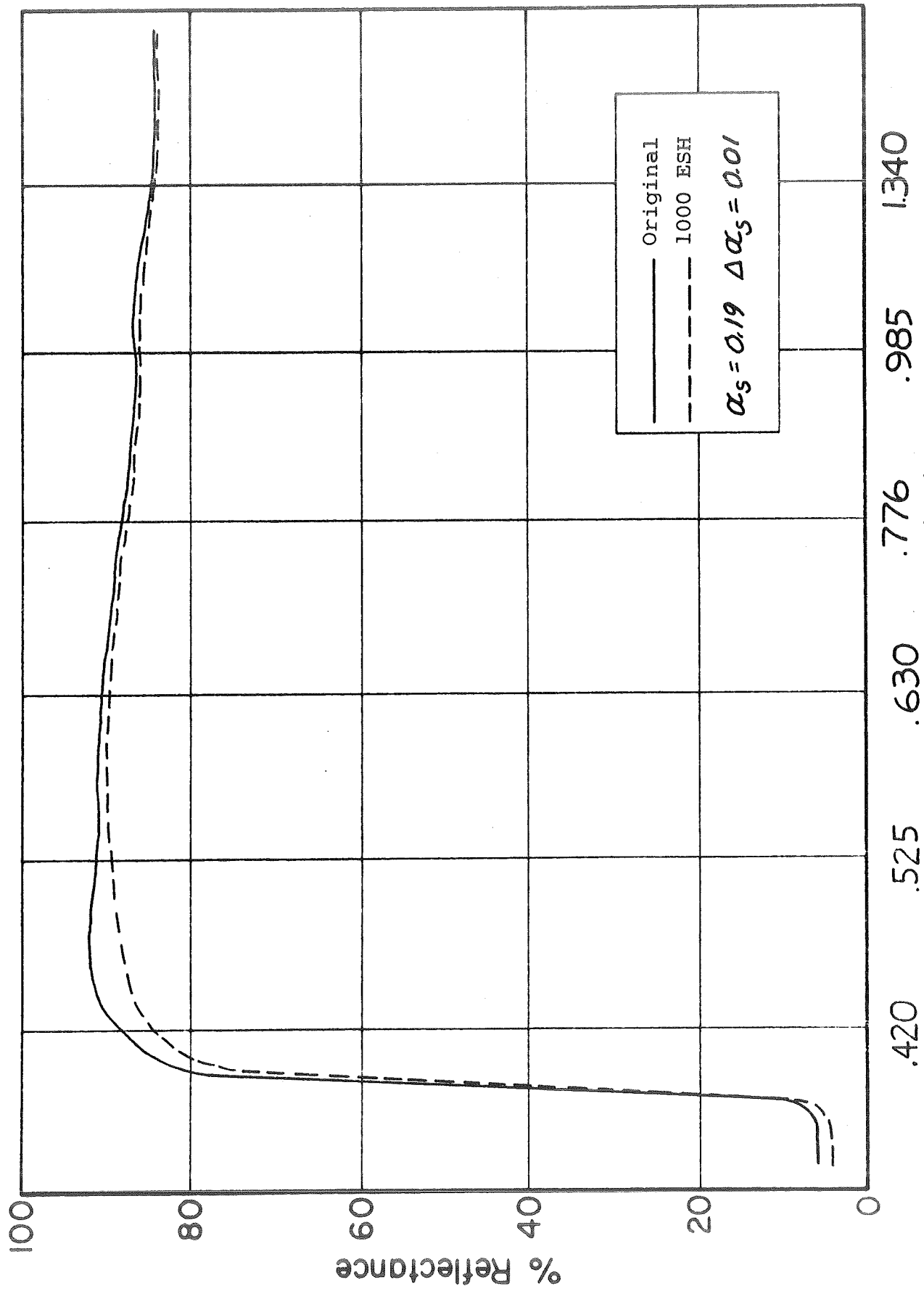


Fig. 4: EFFECT OF UV IN VACUUM ON SILICATE-TREATED SP500 ZINC OXIDE

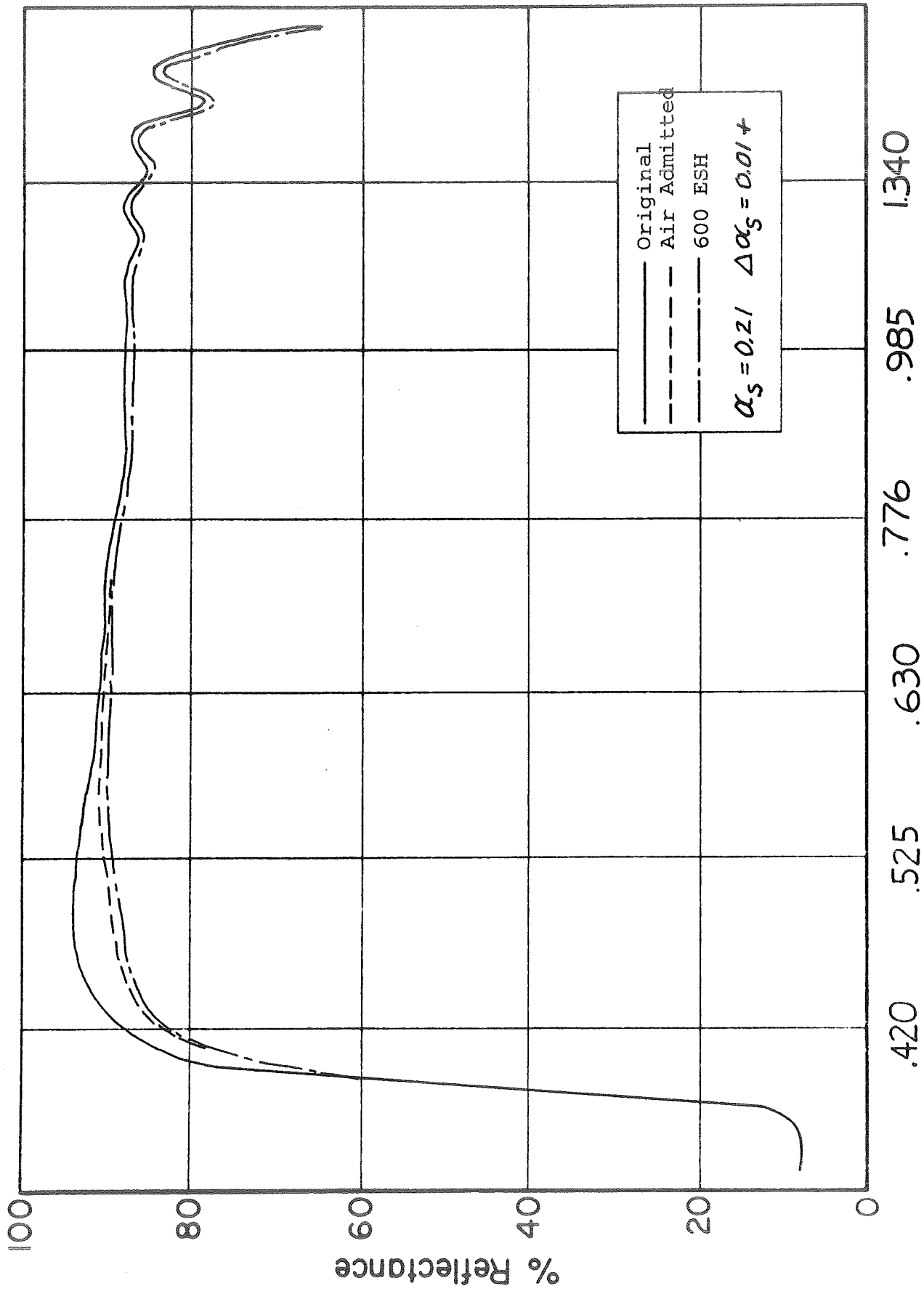


Fig. 5: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; TOLUENE ONLY)

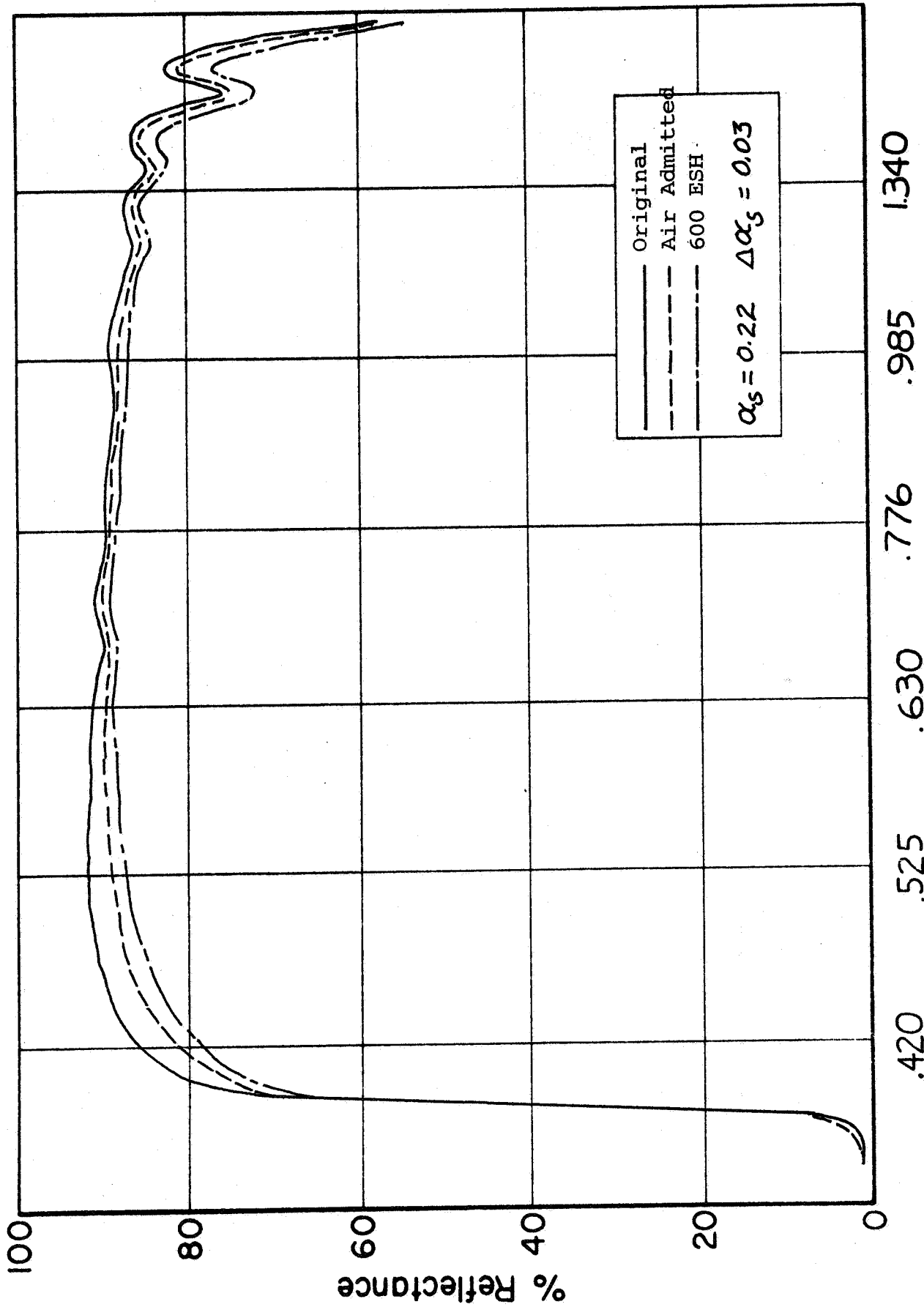


Fig. 6: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; CALCINED)

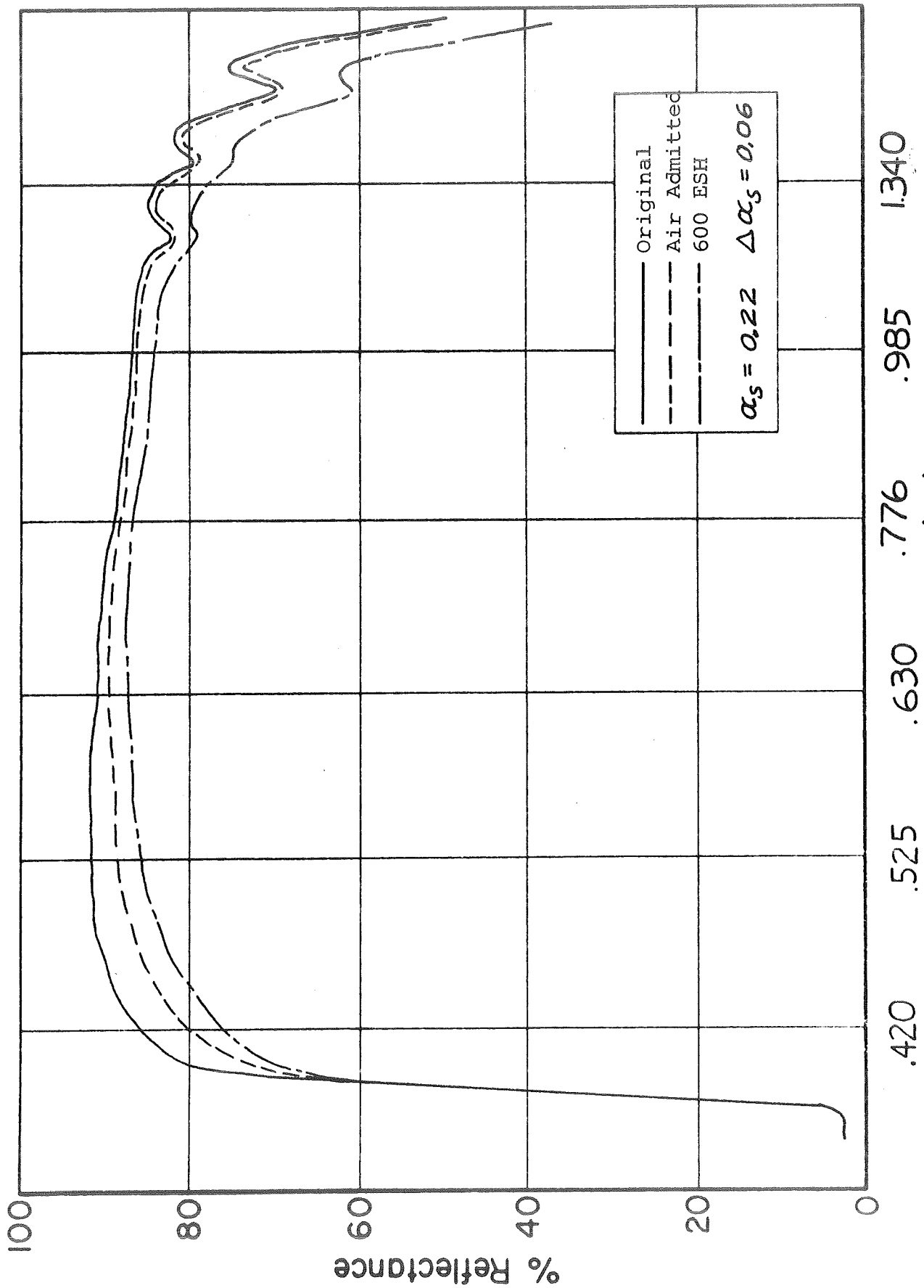


Fig. 7: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENTS; FORMIC ACID; CALCINED)

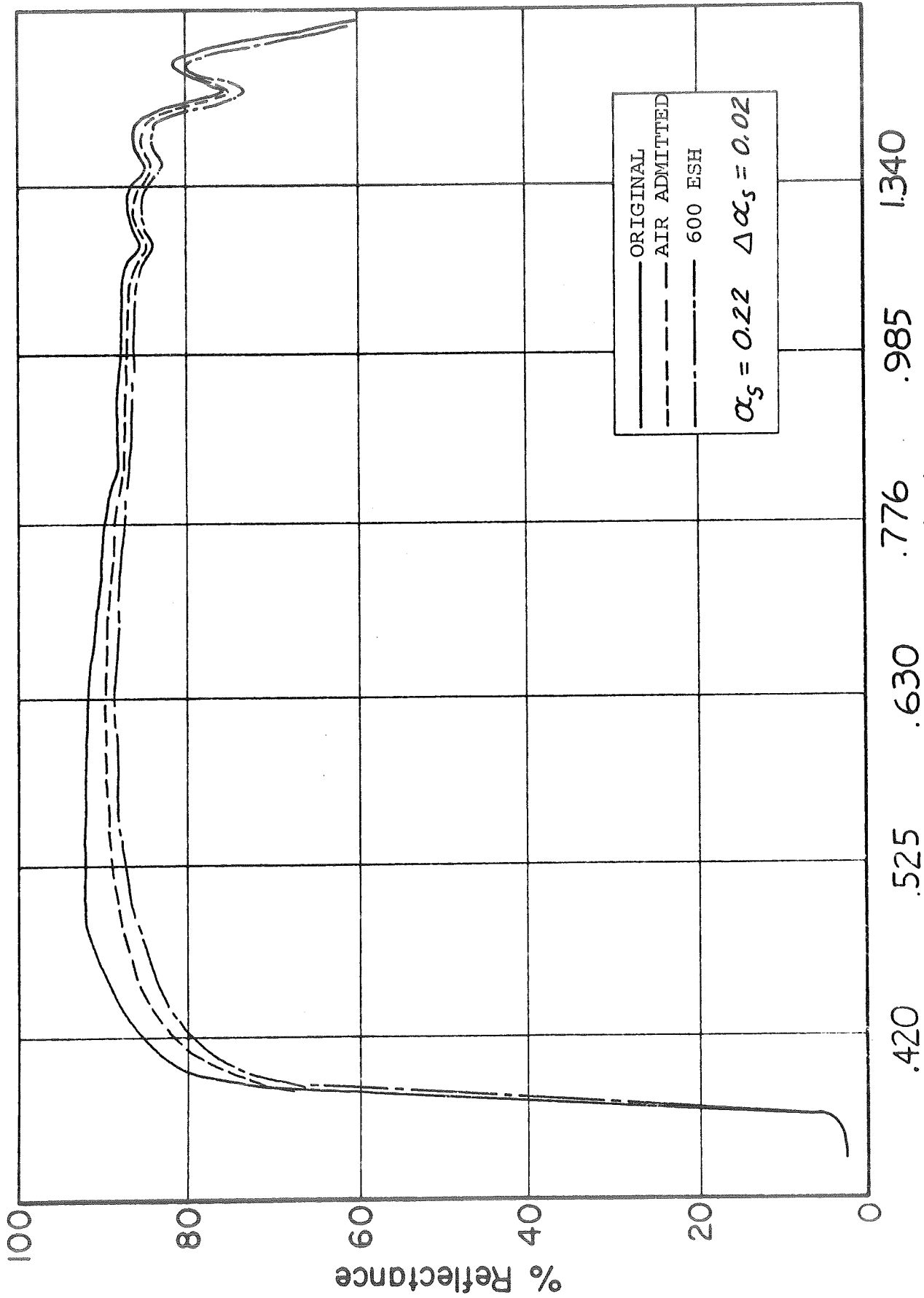


Fig. 8: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; ACID PHOSPHATE; CALCINED)

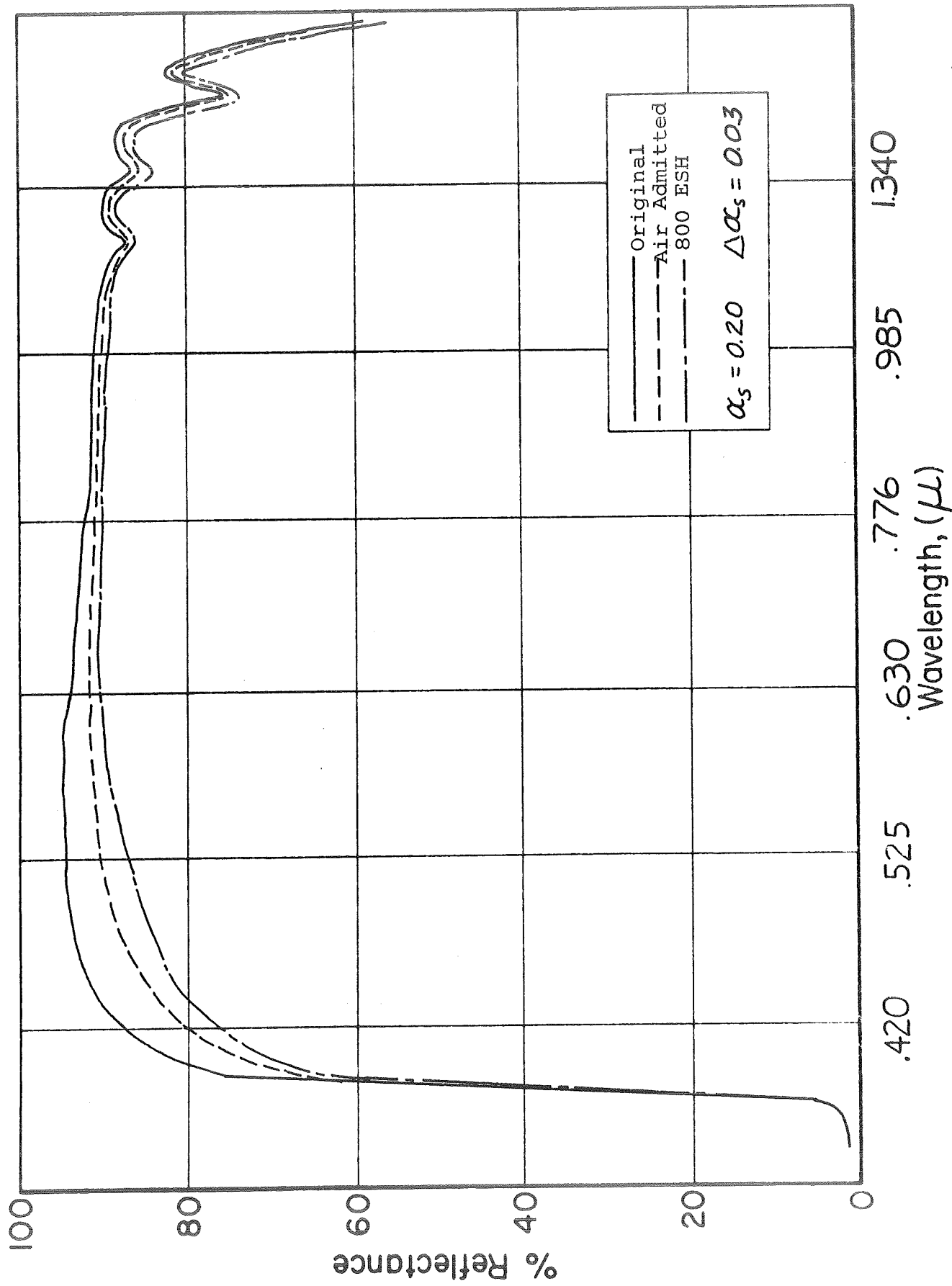


Fig. 9: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT); TOLUENE & PETROLEUM ETHER)

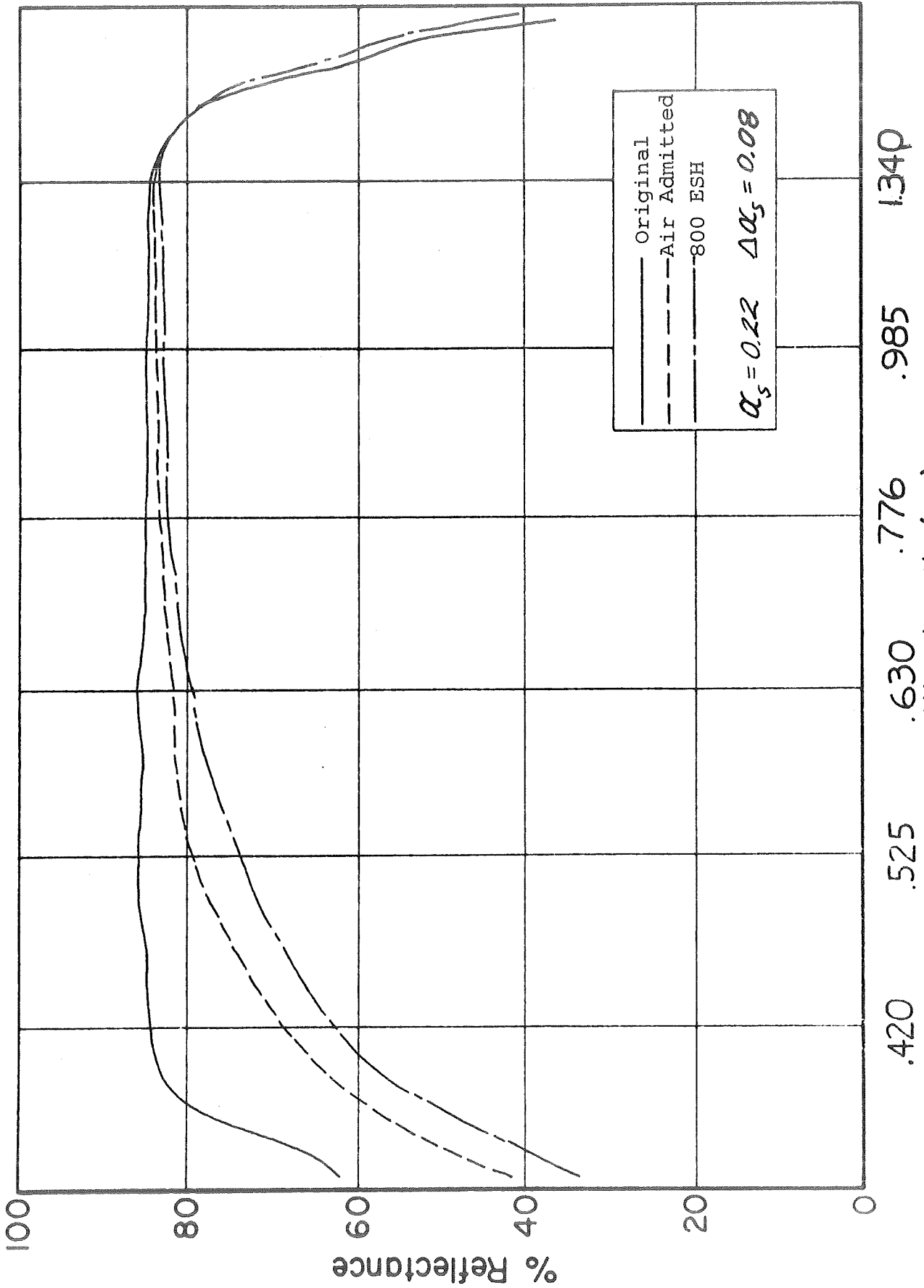


Fig. 10: EFFECT OF UV IN VACUUM ON TAM OF ZIRCONIUM PIGMENTED POTASSIUM SILICATE PAINT

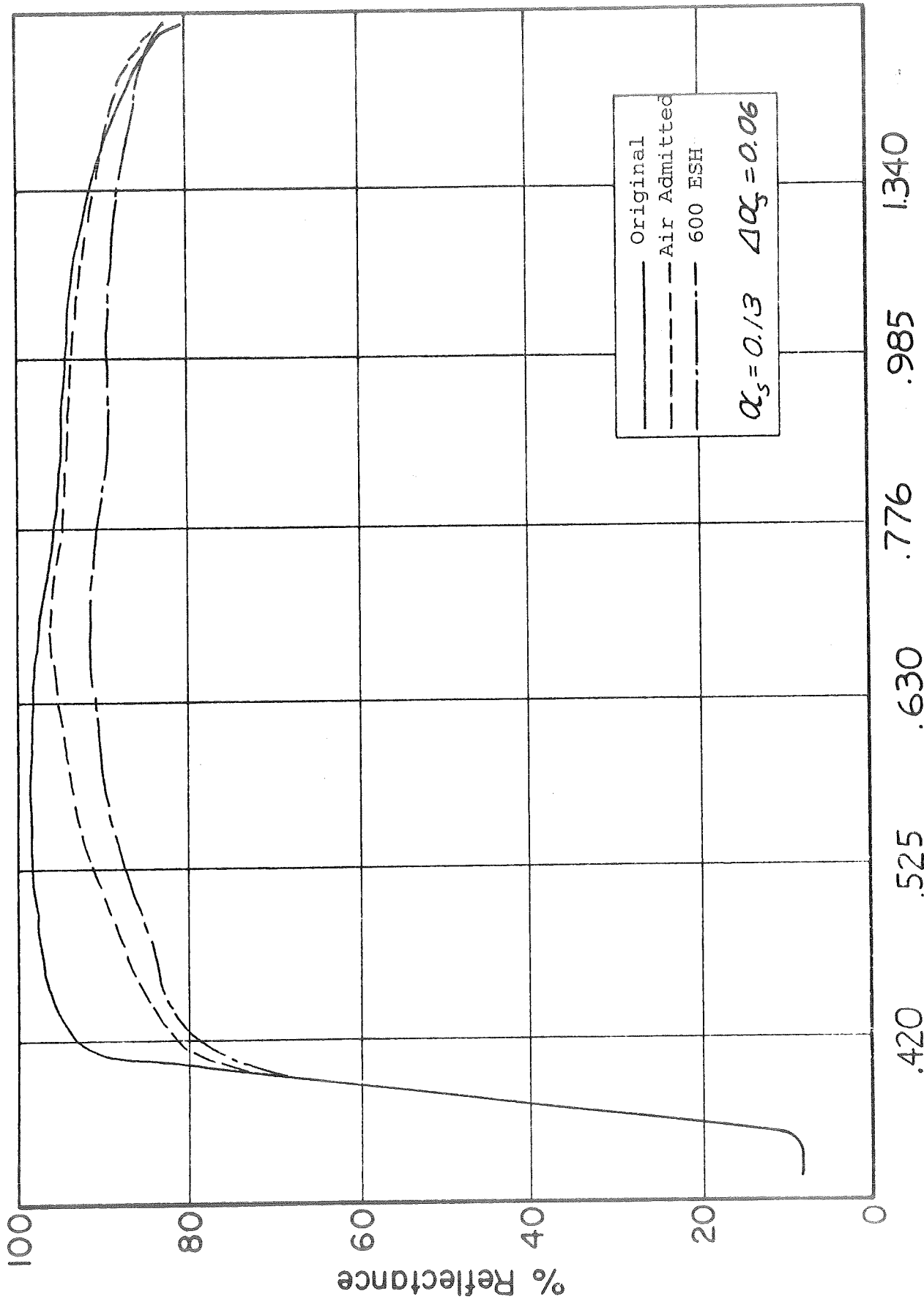


Fig. 11: EFFECT OF UV IN VACUUM ON CABOT "RF-1" RUTILE POWDER.

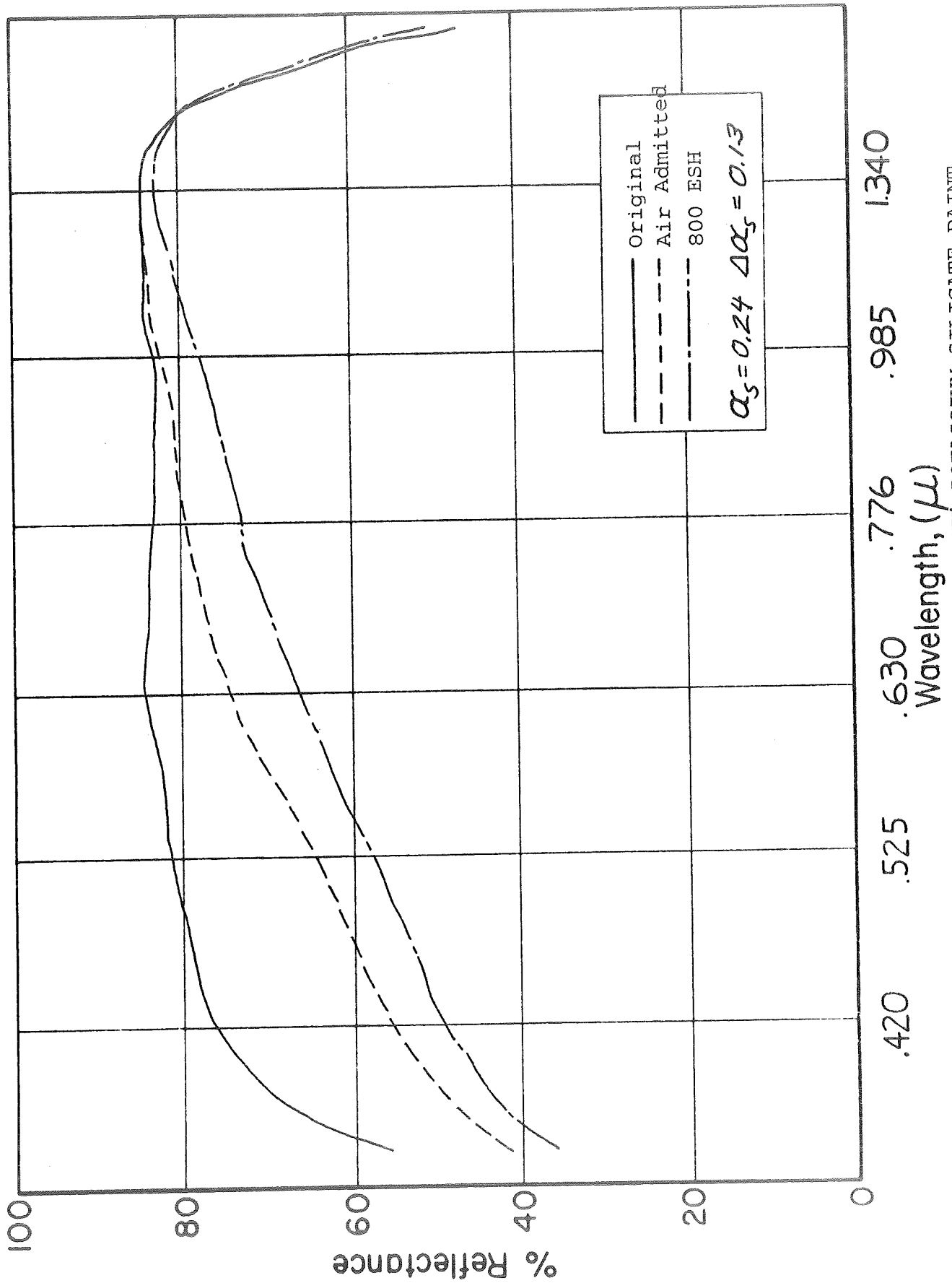


FIG. 12: EFFECT OF UV IN VACUUM ON TANTALA-PIGMENTED POTASSIUM SILICATE PAINT

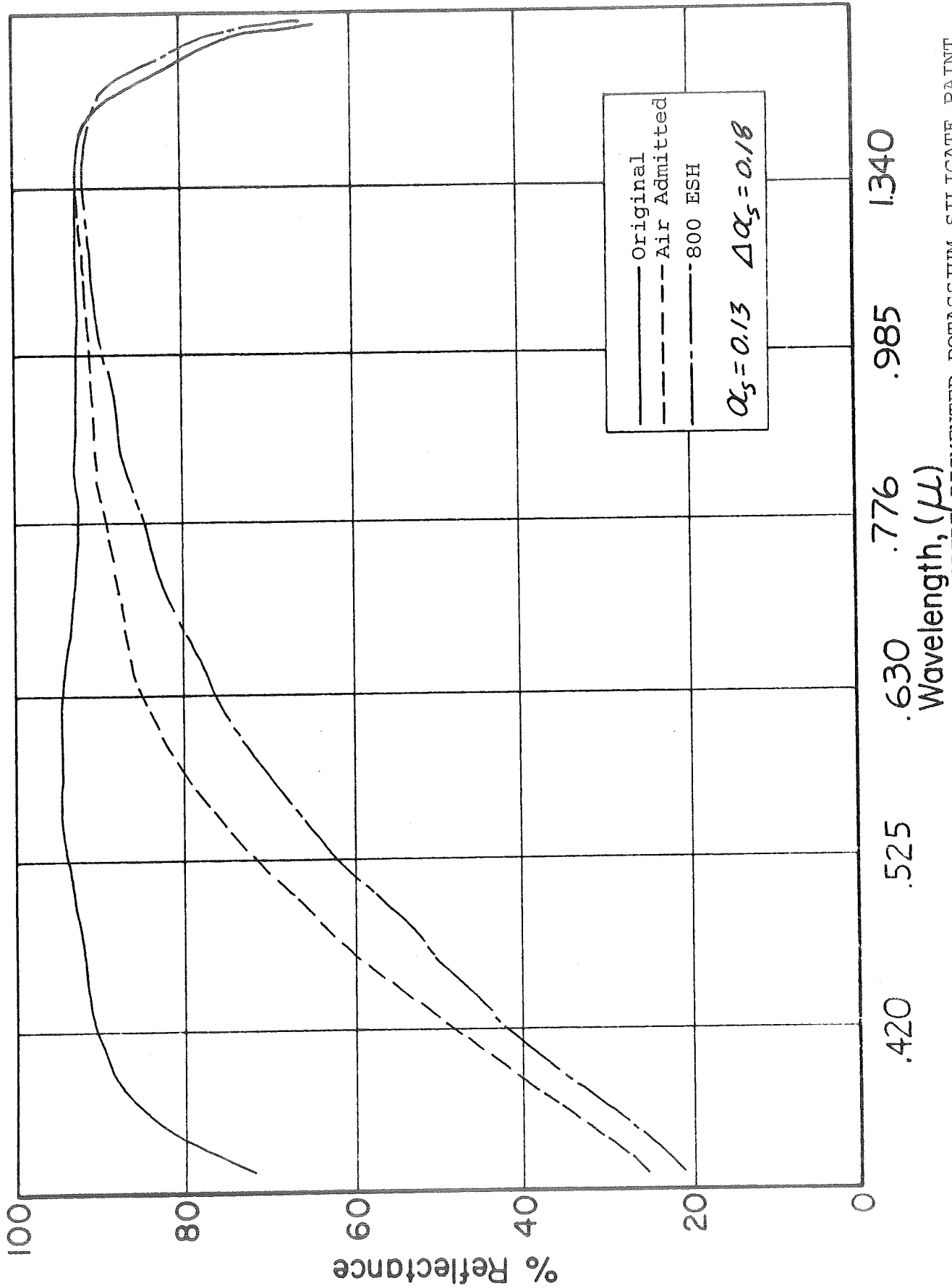


Fig. 13: EFFECT OF UV IN VACUUM ON LITHIUM FLUORIDE-PIGMENTED POTASSIUM SILICATE PAINT

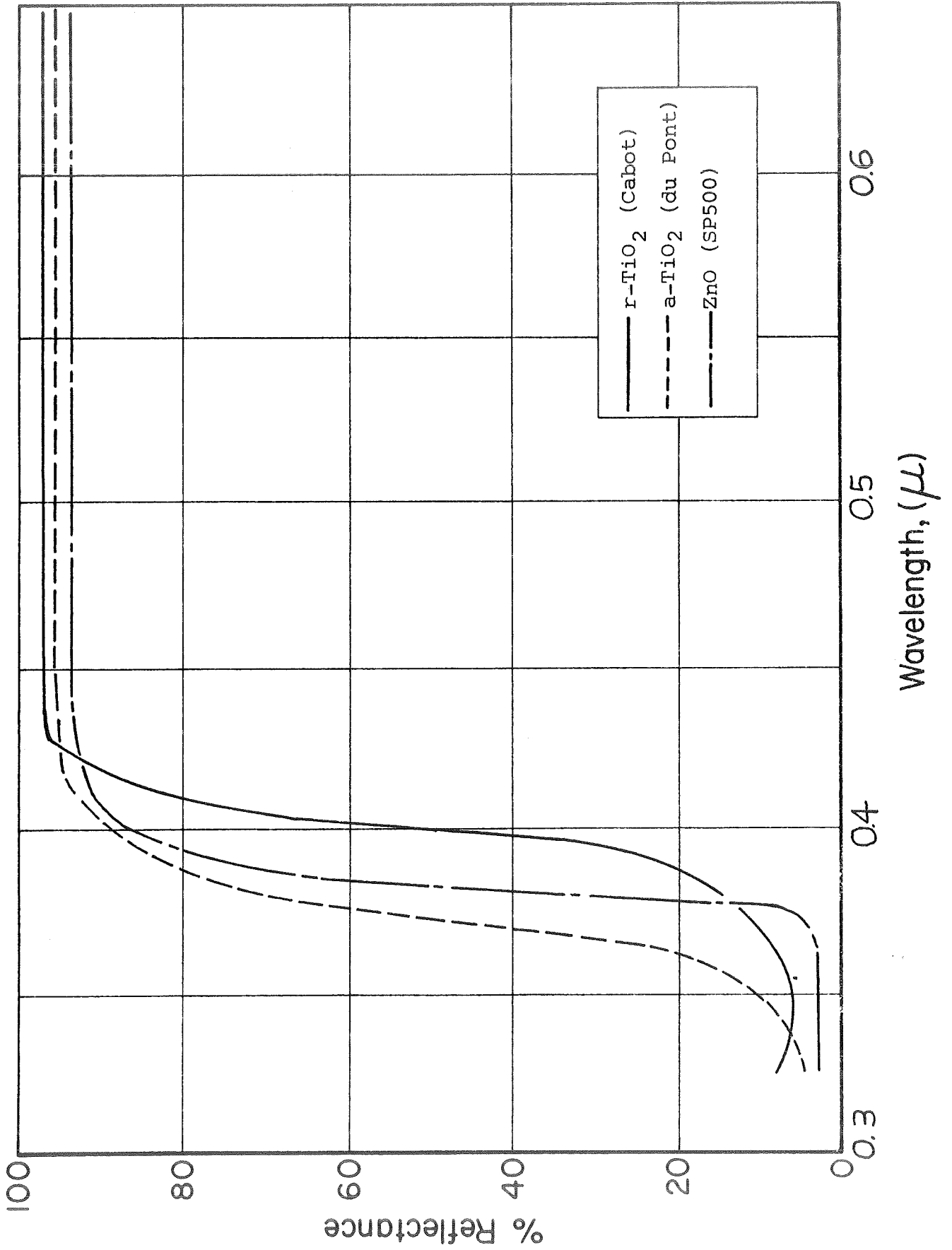


Fig. 14: REFLECTANCE SPECTRA OF ZINC TITANATES' PRECURSORS: ZINC OXIDE, ANATASE & RUTILE

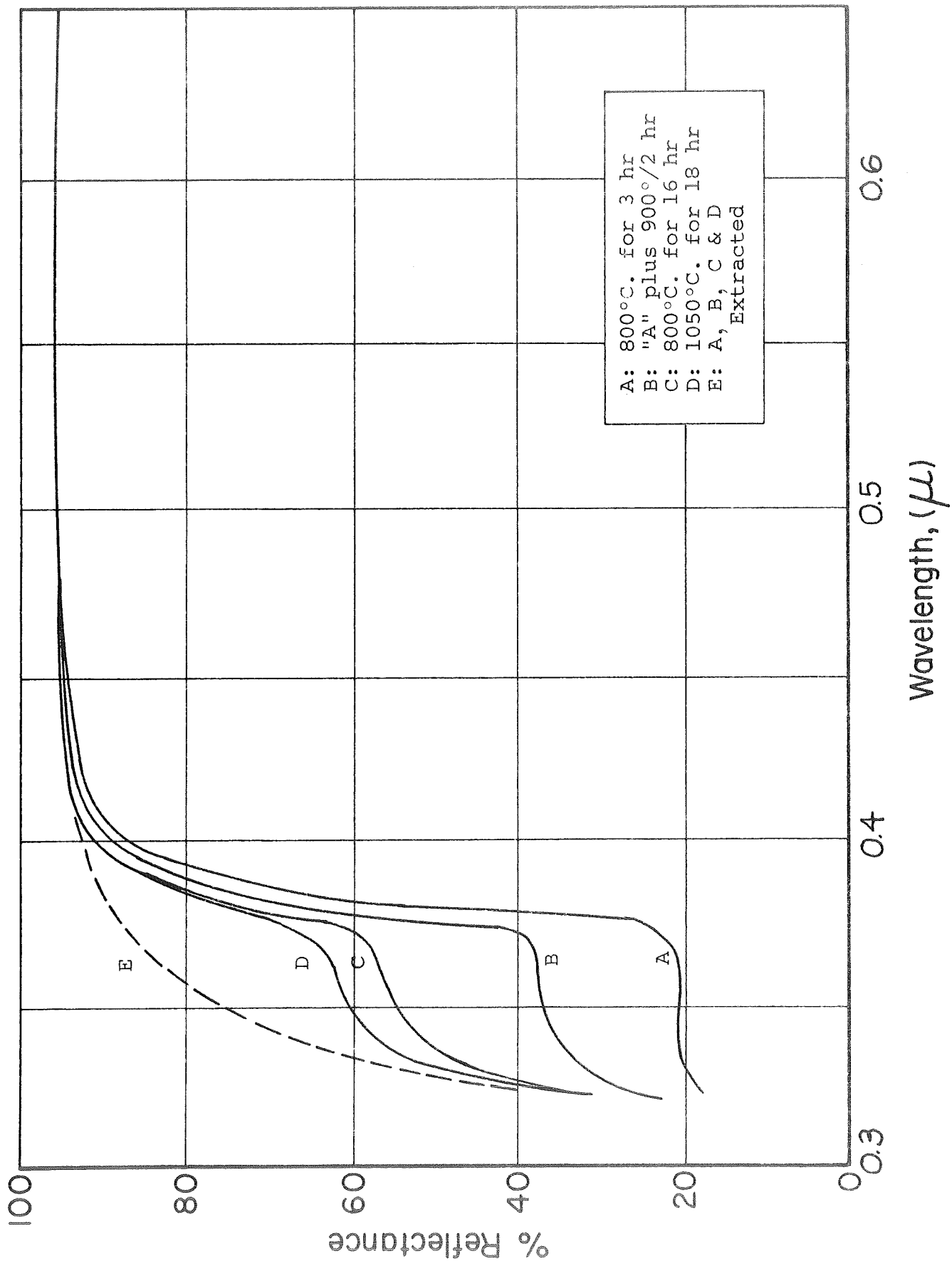


Fig. 15: REFLECTANCE SPECTRA OF ZINC ORTHOTITANATE POWDERS

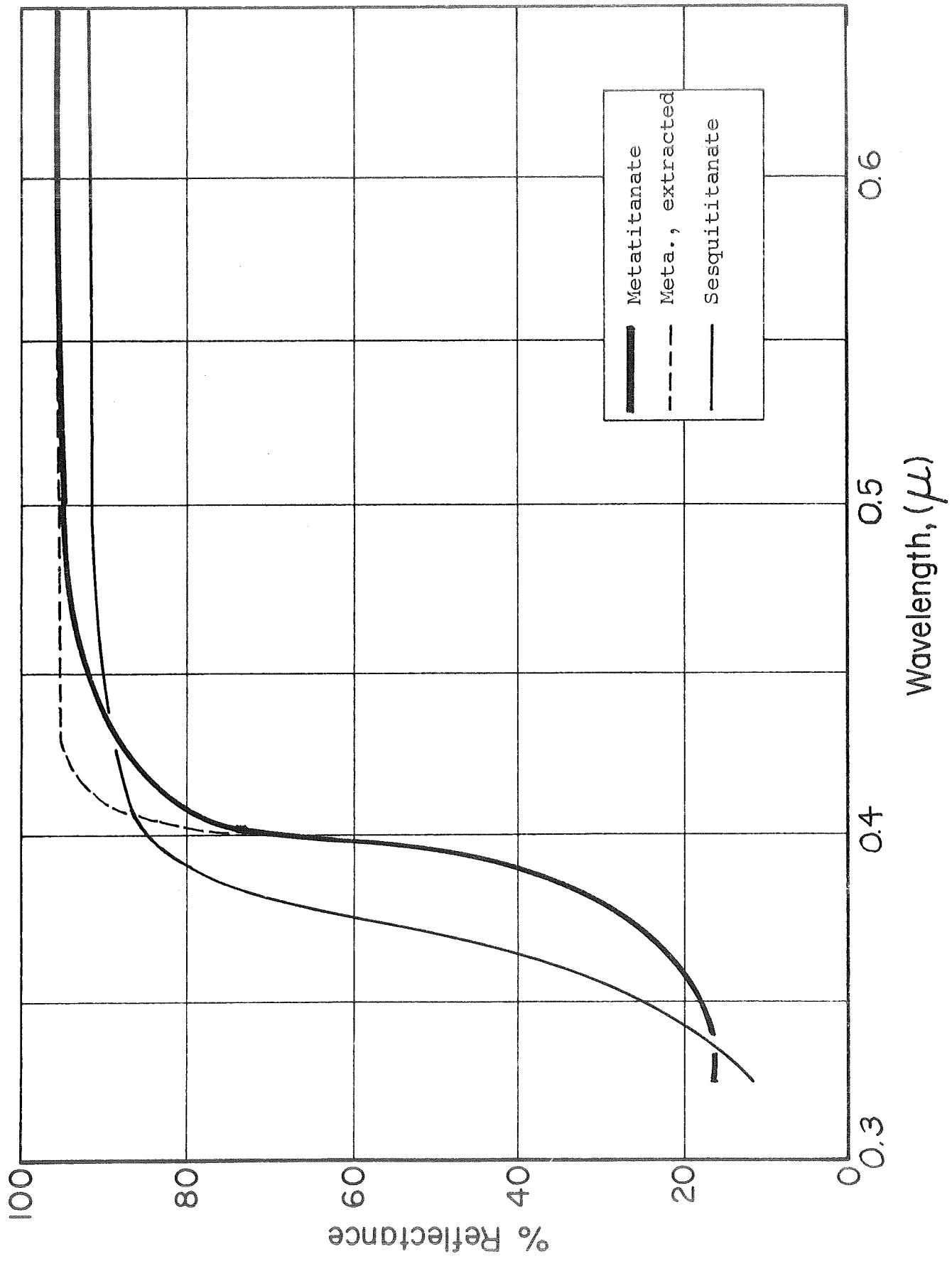


Fig. 16: REFLECTANCE SPECTRA OF ZINC META- AND SESQUITITANATE POWDERS

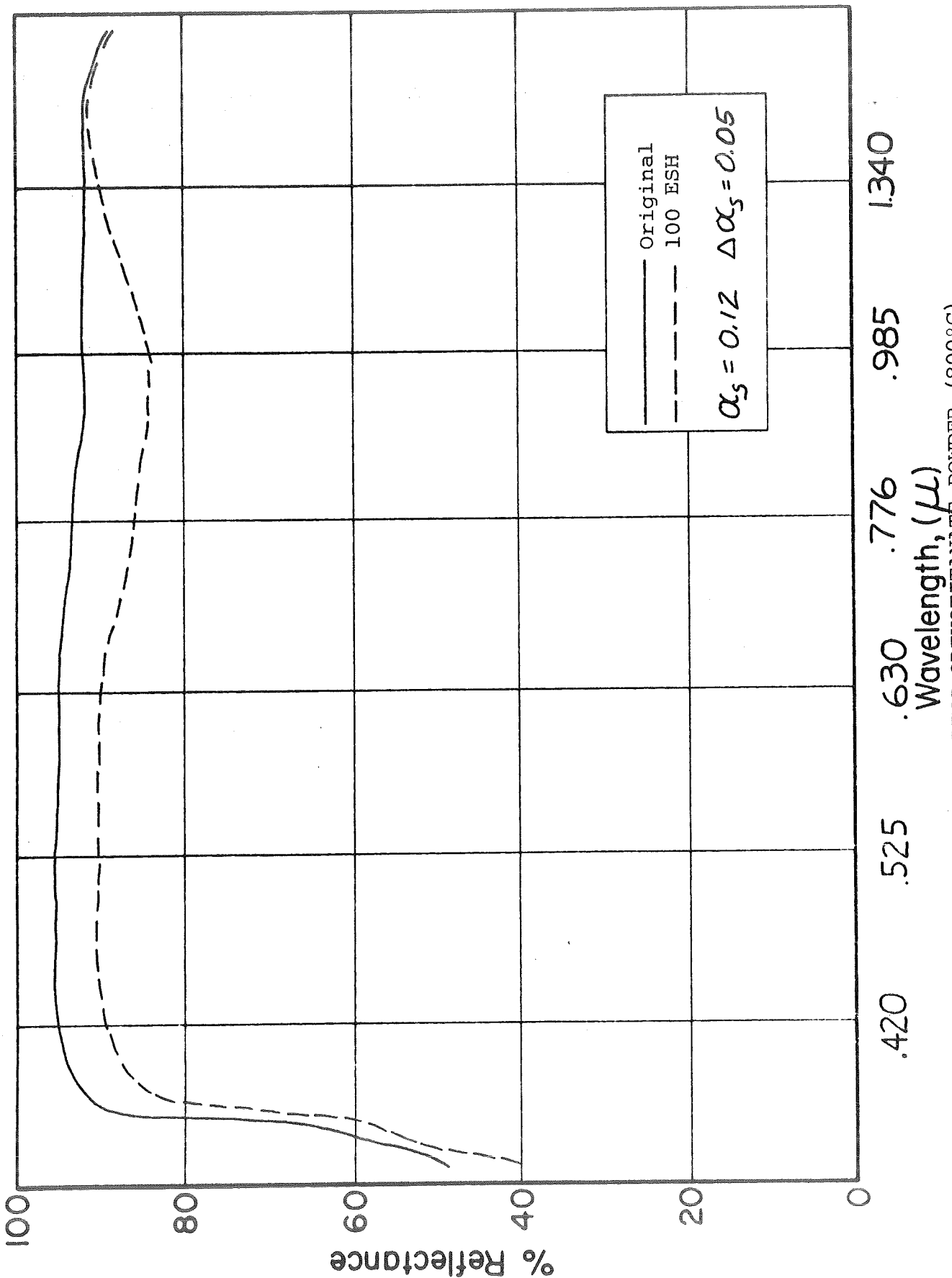


Fig. 17: EFFECT OF UV IN VACUUM ON ZINC ORTHOTITANATE POWDER (800°C)

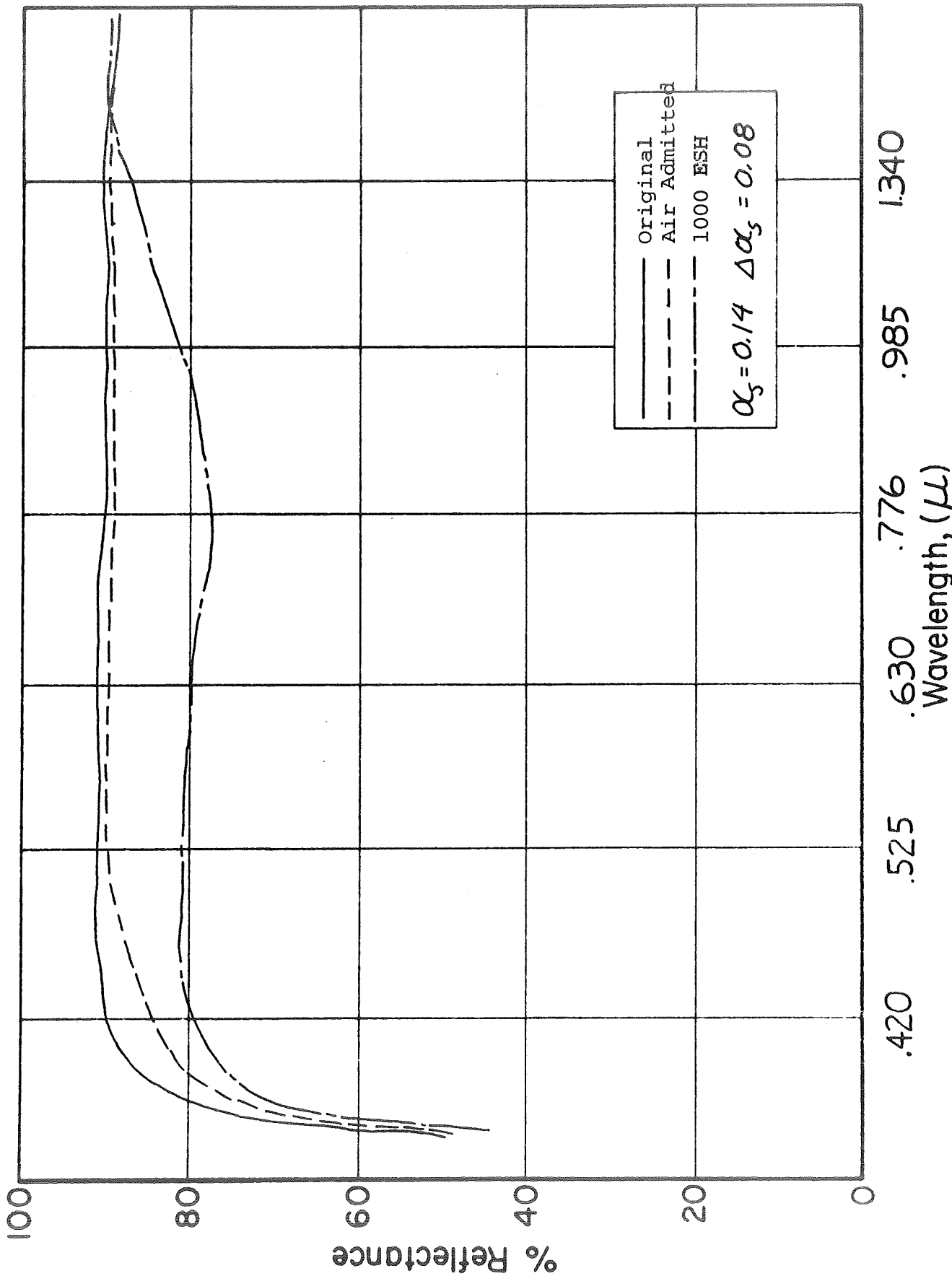


Fig. 18: EFFECT OF UV IN VACUUM ON ZINC ORTHOTITANATE POWDER (800°C; EXTRACTED ACETIC ACID)

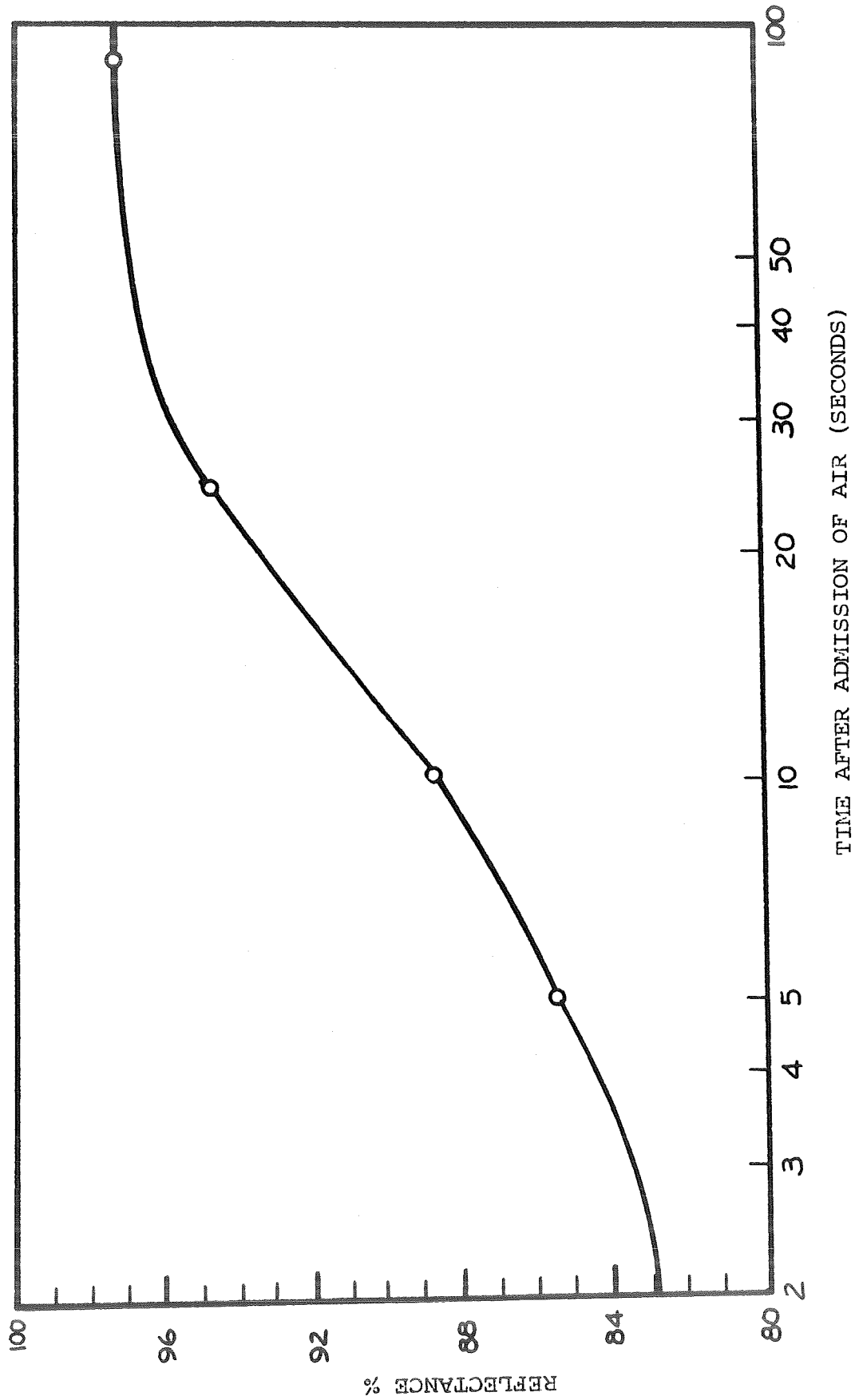


Fig. 19: EFFECT OF ADMISSION OF AIR IN THE REFLECTANCE OF BATCH A-190 ZINC ORTHOTITANATE
(AT 0.65 μ)

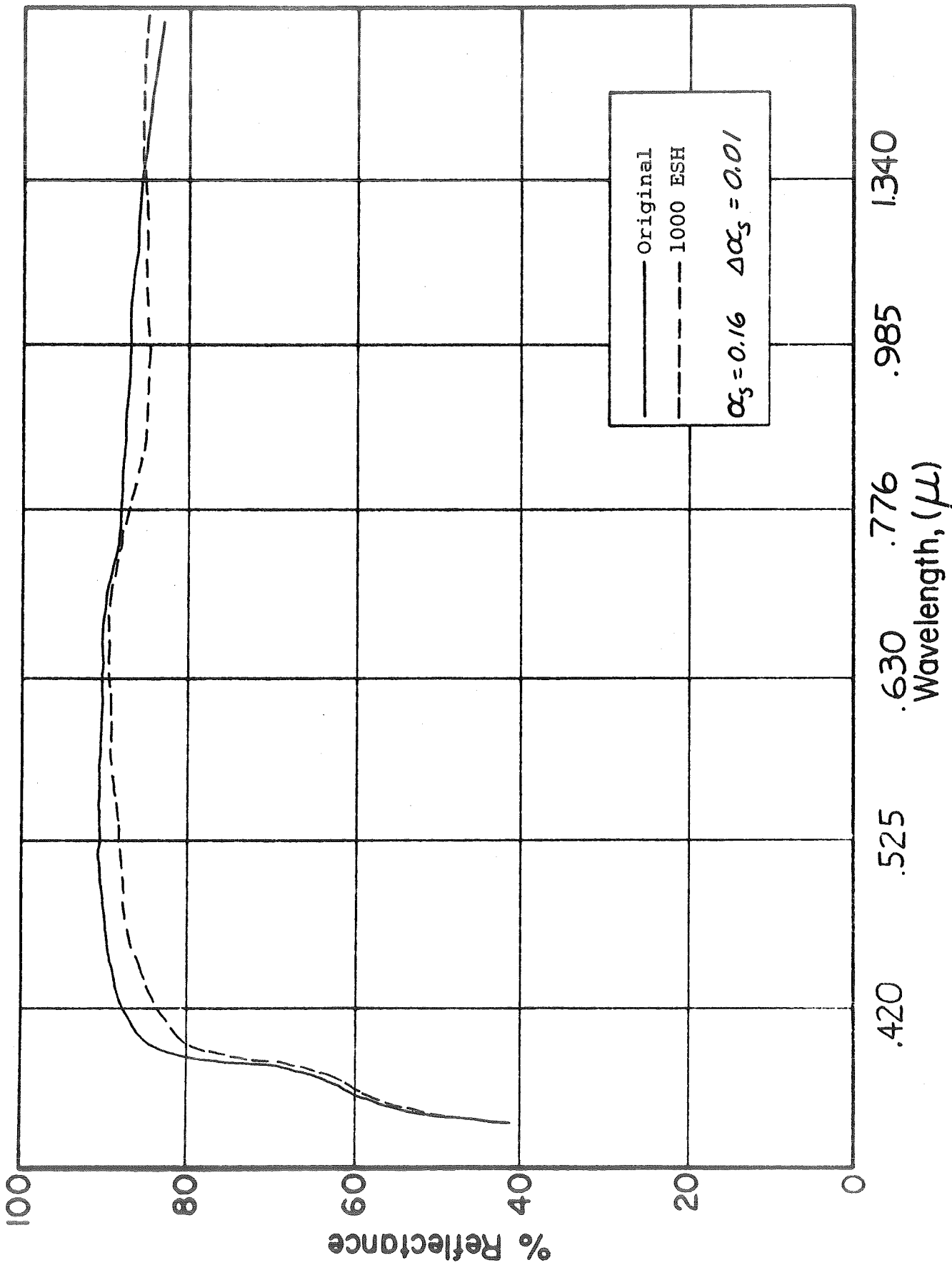


Fig. 20: EFFECT OF UV IN VACUUM ON ZINC ORTHOTITANATE POWDER (1050°C)

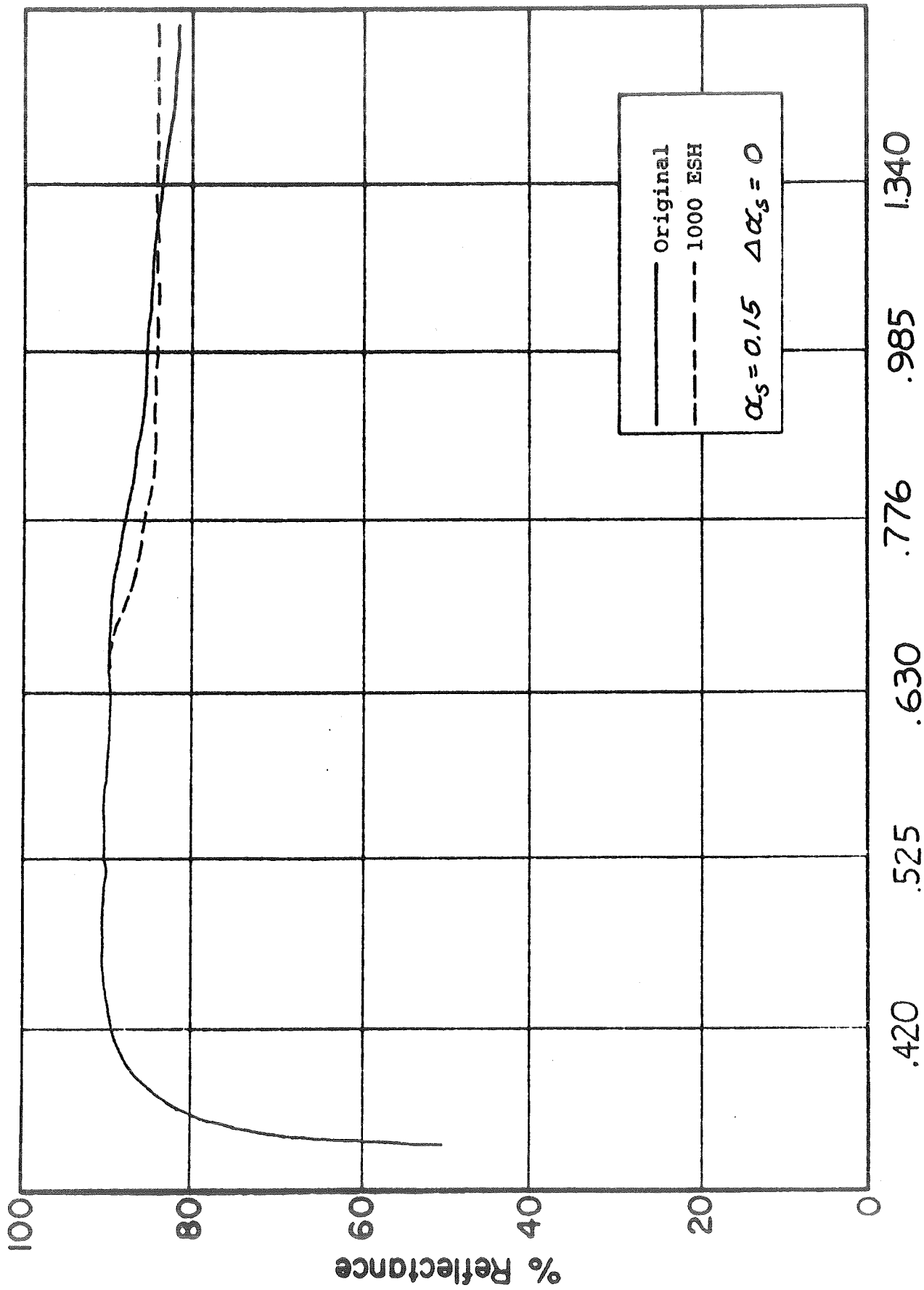


Fig. 21: EFFECT OF UV IN VACUUM ON ZINC ORTHOTITANATE POWDER (1050°C; EXTRACTED ACETIC ACID).