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DEVELOPMENT OF S-13G-TYPE COATINGS AS ENGINEERING MATERIALS

Jet Propulsion Laboratory
California Institute of Technology
Pasadena California

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IIT RESEARCH INSTITUTE

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September 1, 1966 through August 31, 1968

JPL Contract 951737
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IITRI Project U6053

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FOREWORD

This is Report No. U6053-11 (Final Report) of IITRI Project U6053, JPL Contract 951737, Subcontract under NASA Contract NAS7-100, entitled "Development of S13G-Type Coatings as Engineering Materials." This report covers the period September 1, 1966 through August 31, 1968.

The research program was terminated in May of 1967 due to the exhaustion of available funds. An indefinite, no-cost-time extension was granted until May 1968 at which time additional funds were provided to complete the research program. Major contributors to the project during the course of the program were Frederick O. Rogers, project leader and principal investigator; Joseph Cherry, paint and pigment preparation; Henry DeYoung, reflectance measurements; John E. Gilligan, general consultation; George Kimura, space simulation testing and optical measurements; and Samuel Shelfo, paint and pigment formulation and preparation. Mr. Gene A. Zerlaut, Manager of Polymer Chemistry Research, provided administrative supervision and technical consultation.

The work reported herein was performed under the technical direction of Mr. William F. Carroll, Jet Propulsion Laboratory.

Data are recorded in logbooks Nos. C 18016, C 18966, C 19016, and C 19083.

Respectfully submitted,

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DEVELOPMENT OF S-13G-TYPE COATINGS AS ENGINEERING MATERIALS

I. INTRODUCTION

The objective of this program was the development of IITRI's S-13G thermal-control coating as an engineering material. The great initial promise of IITRI's S-13 thermal-control paint prior to the discovery of its "bleachable" infrared degradation, and the apparent solution to that problem provided by potassium silicate treatment of the zinc oxide (ZnO) pigment prior to its incorporation into the paint, are both well known at this time.[1] Indeed, the stabilized S-13 paint, which has been given the generic designation S-13G, has been successfully employed, while still in the development stage, on a number of spacecraft. It is currently being employed on ALSEP, ATM, LM, and EASEP, and is being considered for many other satellites and spacecraft.

The generic description S-13G has been used during the past two years to describe all variations and formulations of the stabilized S-13 zinc oxide-pigmented RTV-602 paints. All users of S-13G during its experimental development were at all times apprised of the changes incorporated into the pigment-treatment process. This communication, though by no means exhaustive in its treatment of the subject, is a comprehensive review of the status of S-13G and provides what we believe to be "working" specifications (presented in the Appendix) for the manufacture of the pigment and the manufacture and application of the S-13G paint as an engineering material. The generic description S-13G is retained and now specifically refers to the coating whose development and final formulation are described herein.

It was quickly realized during the course of the early studies that the development of stabilized ZnO-pigmented RTV-602 silicone paints is largely a process-related problem. Factors that had to be considered in engineering S-13G were:

(1) Initial ZnO-silicate reaction parameters such as 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

(5) Optimization of paint formula relative to pigment volume concentration (PVC), solvents employed, catalyst concentration, etc.

The two major problems that arose during the course of the research, both of which have been solved, were (1) decreased stability of S13-G compared to S-13 in the 385- to 450-nm wavelength region, and (2) intermittently poor shelf life of production batches that varied from 3 to 200 days. The techniques employed to solve these problems, as well as the more general processing problems encountered, are described in this report.

II. HISTORICAL ASPECTS OF S-13G

A. Ultraviolet Degradation of ZnO

Until 1965, zinc oxide (ZnO) was thought to be the most stable white pigment available in terms of the stability of its hemispherical spectral reflectance to ultraviolet irradiation in vacuum.[2-4] However, serious discrepancies in ZnO's behavior were reported between laboratory-simulation data and flight-experiment data obtained from the OSO-II[5] and the Pegasus[6] materials' experiments.

These data indicated that ZnO-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 beeen attributed to the formation of an easily bleached (oxygen) infrared adsorption band that cannot be observed by classical postexposure reflectance measurements in air. This band was first observed in the laboratory by MacMillan et al[7] during in situ measurements of the bidirectional reflectance of ZnO irradiated in vacuum. Confirmation of the bleachable infrared degradation of ZnO first noted by MacMillan et al was reported by Miller[8] and subsequently by Zerlaut et al.[9,10]

The effect of irradiation on IITRI's S-13 thermal-control coating, the ZnO-pigmented polydimethylsiloxane (General Electric RTV-602) paint that had degraded severely in flight tests,[6,7] is shown in Figure 1. The spectral data are plotted as a function of equal-energy increments of the extraterrestrial solar spectrum. The damage sustained by surfaces in the 400- to 700-nm region (visible), where nearly 50% of the solar energy lies, is more significantly and more accurately represented by graphical presentation of the data in this manner.

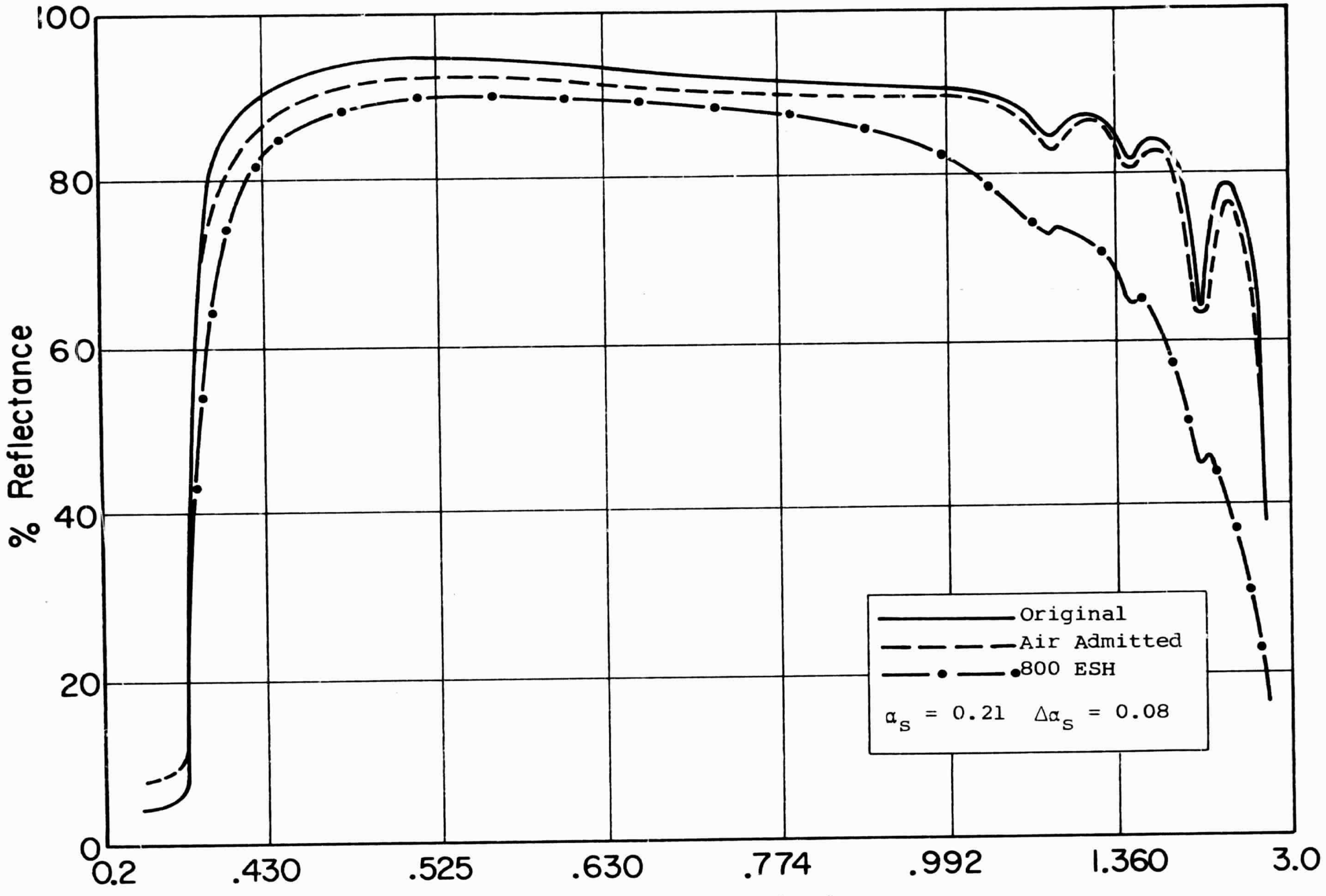

Figure 1: EFFECT OF UV IN VACUUM ON S-13 THERMAL-CONTROL COATING

S-13 exhibits a reflectance decrease of about 35% at 2000 nm (2 μ) after approximately 800 equivalent sun hours (ESH) of ultraviolet irradiation in vacuum, Figure 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 of exposure to air. The effect of 1000 ESH of ultraviolet radiation on "water-sprayed" SP500 ZnO is shown in Figure 2. These data show that the bulk of the solar absorptance increase exhibited by ZnO 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 ZnO and the abruptness with which air (oxygen) annihilates the absorption strongly indicate that the infrared phenomenon is associated with the photodesorption of adsorbed 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 ZnO can be explained on the basis of a free-carrier absorption mechanism. Gilligan,[11] in studies at IIT Research Institute for the Jet Propulsion Laboratory, concluded that the valence-band holes are attracted to the surface, where they discharge absorbed oxygen (and other absorbate gases) by capturing their electrons -- accounting for the accumulation of electrons in the conduction band. However, Greenberg et al,[12] in studies for the NASA-Marshall Space Flight Center, attributed the infrared band to bound donor states associated with oxygen vacancies at the surface.

B. Stabilization of ZnO to Ultraviolet Radiation

Of particular significance to the ensuing studies was the fact that IITRI's Z93 thermal-control coatings, an SP500 ZnO-pigmented potassium silicate paint, does not undergo the

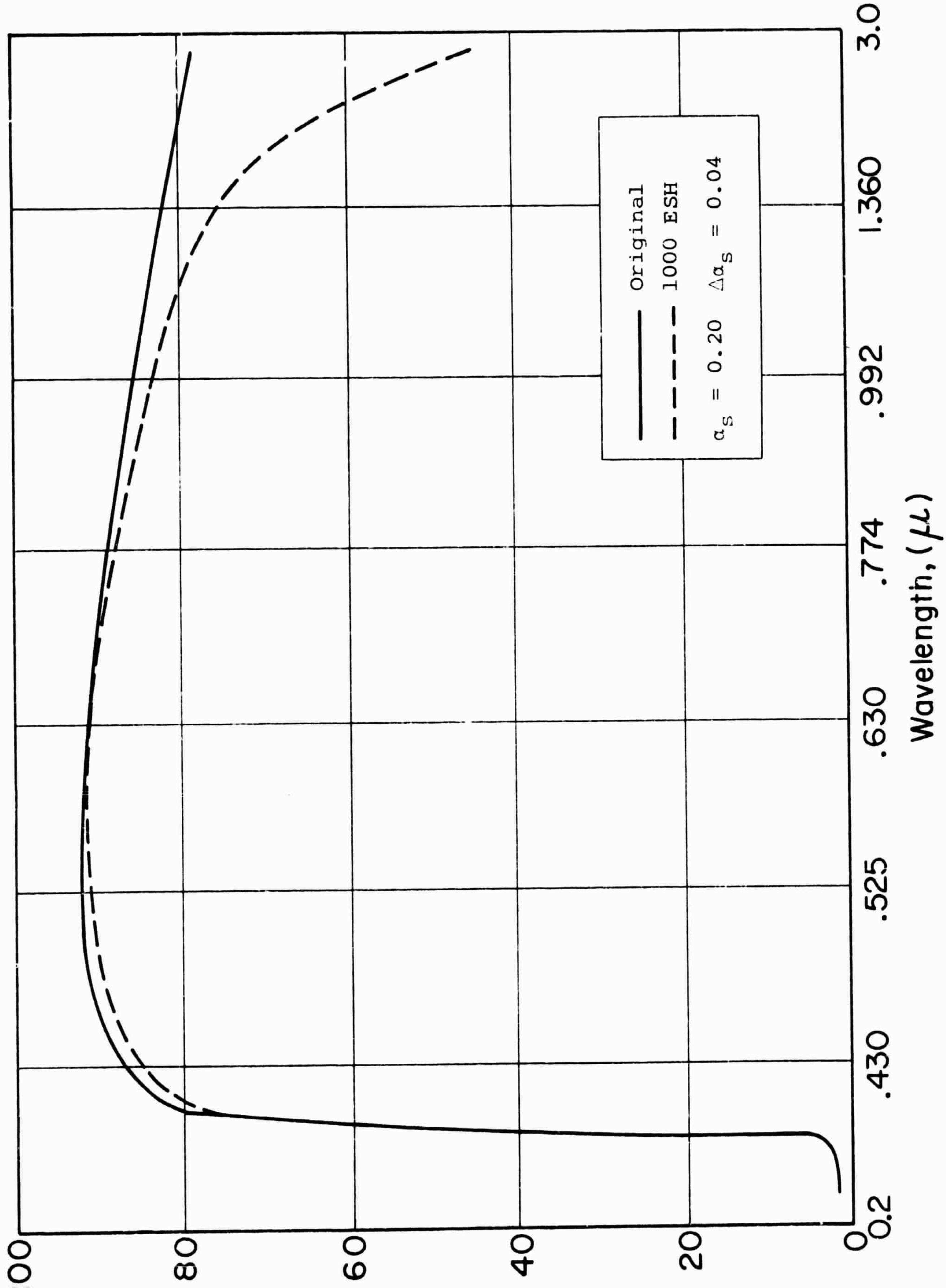

Figure 2: EFFECT OF UV IN VACUUM ON SP500 ZINC OXIDE

bleachable infrared damage exhibited by S-13G and pure ZnO. Figure 3 is a typical example of the spectra of irradiated and unirradiated Z93.

The absence of damage to ZnO-pigmented alkali silicate coatings suggested that the reactivity of ZnO with, for example, potassium silicate may have precluded the bleachable infrared degradation exhibited by ZnO powder and ZnO-pigmented silicone paints. The polydimethylsiloxanes do not "wet" the pigment particles and consequently we conjectured that they do not offer an effective barrier to photodesorption reactions on the surface of ZnO. We therefore performed a series of experiments in which ZnO was first reacted with potassium silicate and showed that a treated ZnO powder that does not exhibit infrared degradation can be prepared. The treated ZnO paints also do not exhibit infrared damage on irradiation in vacuum.[1] The reflectance spectra of an irradiated silicate-treated ZnO specimen are presented in Figure 4.

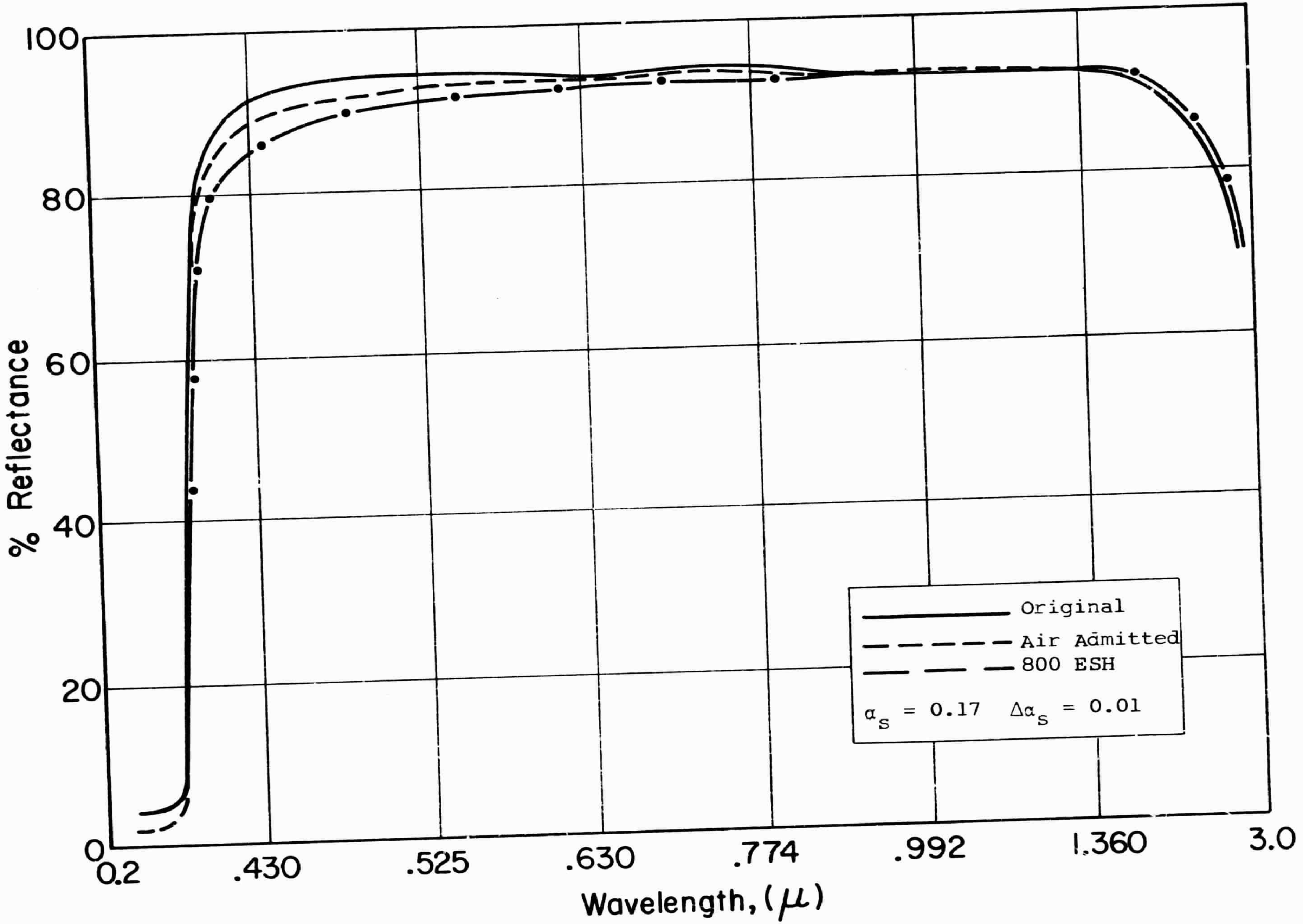

Figure 3: EFFECT OF UV IN VACUUM ON Z93

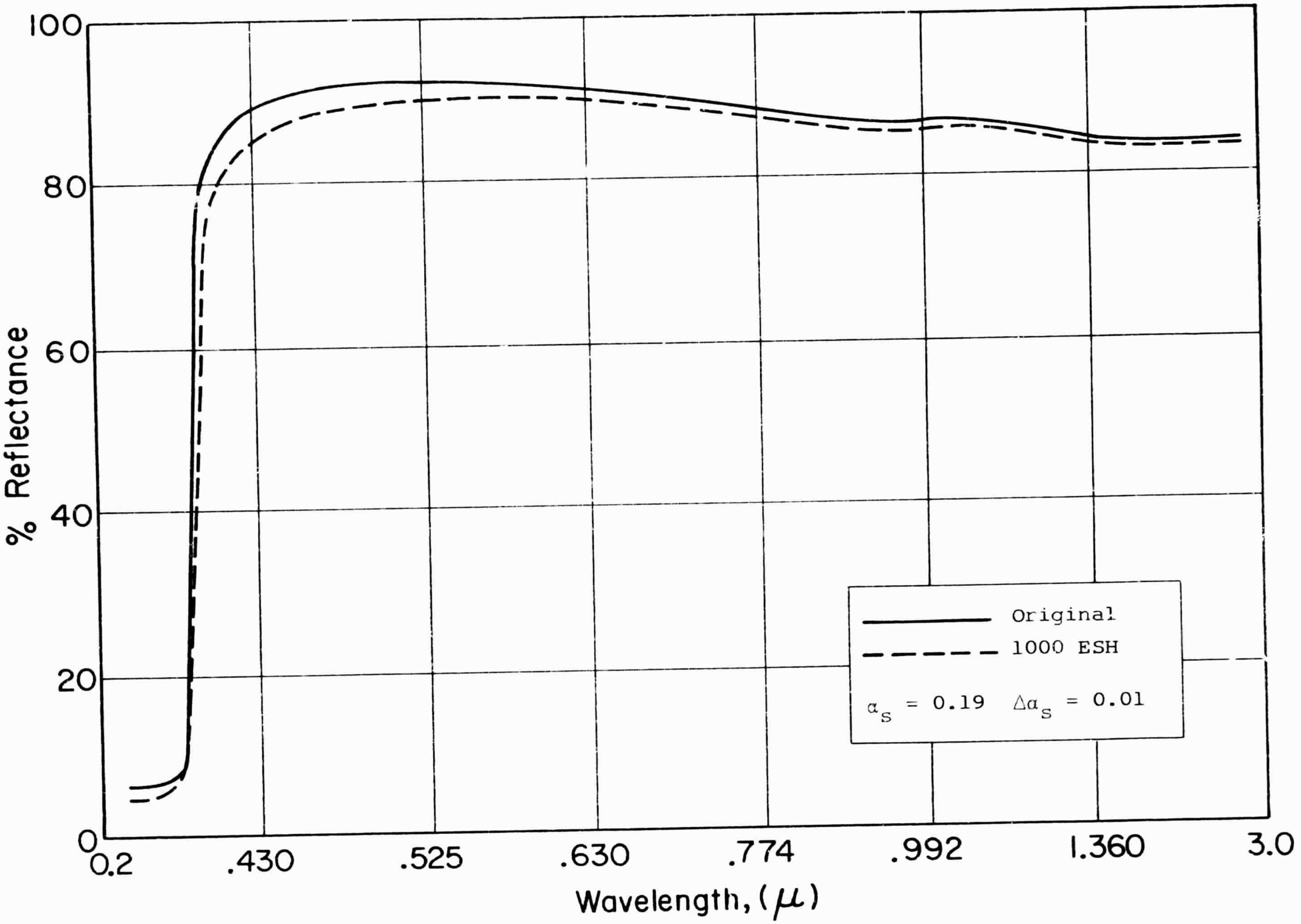

Figure 4: EFFECT OF UV IN VACUUM ON SILICATE-TREATED SP500 ZINC OXIDE

III. SPACE SIMULATION TESTING

Ultraviolet irradiation in vacuum was performed employing the IRIF-II space simulation facility and both 1000-watt mercury-argon (A-H6) and 5000-watt mercury-xenon (Hanovia) ultraviolet sources. The IRIF-II facility is shown in Figure 5; its predecessor, IRIF-I, has been described adequately elsewhere.[13] The total ultraviolet dose was determined as equivalent (space ultraviolet) sun hours (ESH) employing published manufacturers' data and an Eppley Model S wide-angle pyrheliometer. Irradiations were performed at nominal solar intensities of 6X for A-H6 radiation and 4X for Hg-Xe radiation. The Hanovia Hg-Xe is operated at 80% of capacity to maximize its lifetime. (The Hanovia burner is not shown in Figure 5 in order to more clearly present ITIF-II.)

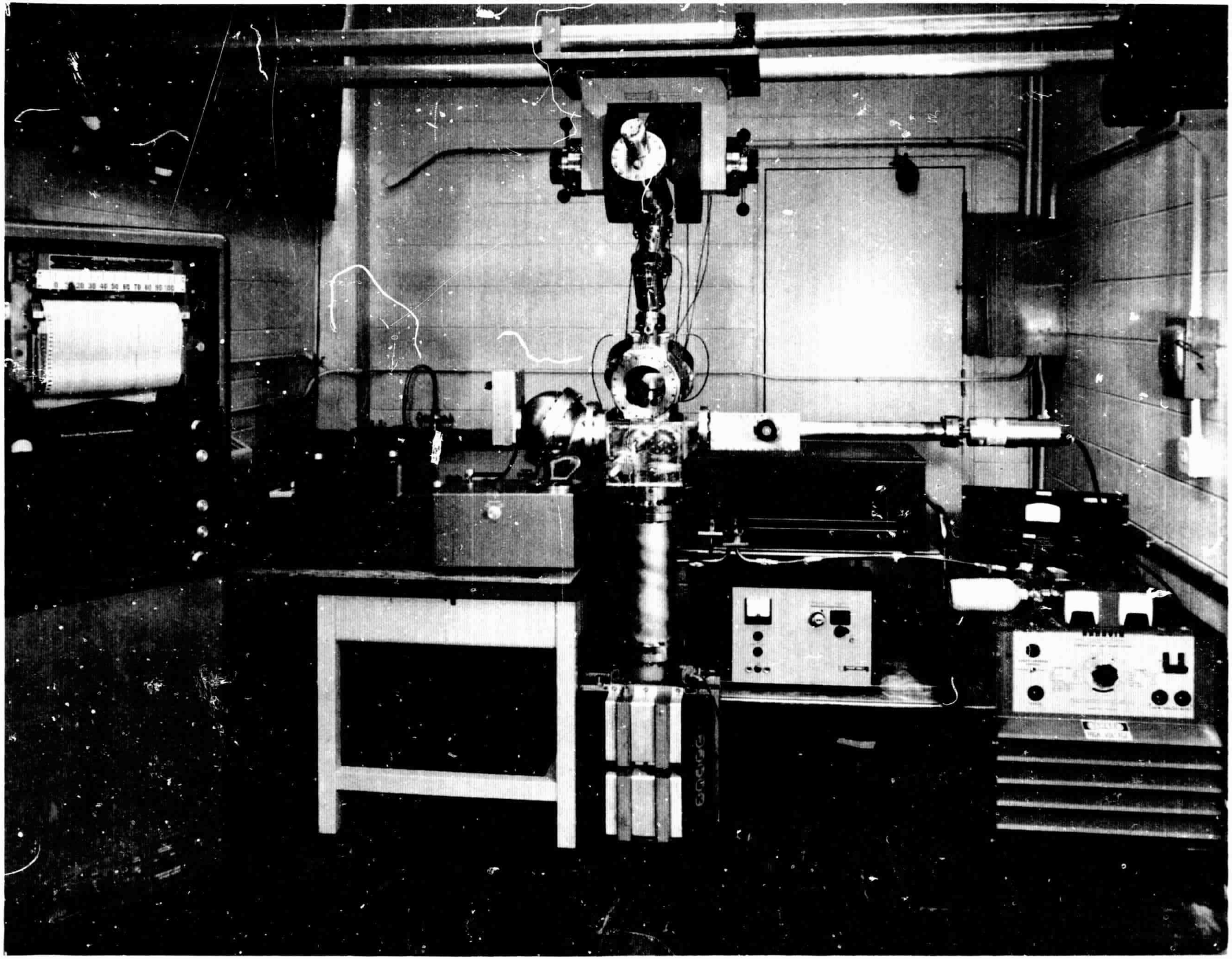

Figure 5: IRIF-II COMBINED RADIATION ENVIRONMENT FACILITY (CREF)

IV. OPTIMIZATION OF PIGMENT-TREATMENT PROCESS

A. General Laboratory Studies

The discussion in this section pertains largely to the initial studies that involved small laboratory-sized batches. Pilot production problems are the subject of the following section.

1. Cold-Process Treatment

The initial materials' ratio, a materials' balance still employed, was 1.7 parts PS-7 potassium silicate (Sylvania Electric Company) to 1.0 part SP500 ZnO (New Jersey Zinc Company). The reaction was carried out by ball-milling the mixture at room temperature for 0.5 hr and allowing it to stand sealed for 16 hr. The pigment was let down with distilled water, filtered through Buchner funnels, washed with distilled water, oven-dried at 100°C, dry-ground in a ball mill, and finally prepared as an RTV-602 coating at 30% PVC.

This cold-process pigment was very hard and brittle and required dry-grinding, or hand-milling, to reduce the pigment aggregates to a usable size. The resultant paint possessed the following characteristics.

(a) The pigment treatment did not offer complete protection against photodesorption-related infrared damage.

(b) The cured, virgin (unirradiated) films exhibited significant yellowing.

(c) The paint films exhibited more than twice the visible damage sustained by S-13 pigmented with untreated ZnO.

(d) The paints often gelled within 72 hr.

The severe yellowing of unirradiated and irradiated paint was ascribed to the vigorous grinding required to break the cold-process aggregates.

An attempt to use ethyl alcohol to dehydrate the moist pigment cake, and thus avoid much of the hard caking in the oven, resulted in a soft pigment that required no dry grinding. Unfortunately, the process tends to destroy the protective effect of the silicate treatment. The use of alcohol to azeotropically dry the pigment was therefore discontinued.

2. Hot-Process Treatment

The initial reaction temperature was increased from room temperature to approximately 77°C by employing a double boiler; the slurry was rapidly stirred at temperature for 30 min. The slurry was let down with distilled water, filtered, and redispersed twice more. This process resulted in a softer, whiter pigment that offered almost complete protection to degradation in the infrared.

The paints prepared from hot-process pigment still exhibited some degradation in both the visible and the infrared. The concept of "sweating," a process utilized in the organic-pigment industry, was subsequently employed with considerable success. This process involves sealing the wet filter cake from the first filtration in aluminum foil and allowing it to stand for 6 to 72 hr. The resulting pigment is exceptionally soft and white; it is easily dry-ground, easily milled into paints and does not yellow on curing.

A minimum of 6 hr of 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 resulted in unusable pigment. Paint milled from pigment that was sweated 48 hr was extraordinarily thixotropic and could not 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 6 presents the spectra of S-13G prepared from 16-hr-sweated pigment that was subjected to 600 ESH of ultraviolet irradiation. These data indicate that the infrared problem largely has been solved; the visible damage sustained by this S-13G specimen ($\Delta\alpha_s$ = 0.01) is little greater than that exhibited by S-13, Figure 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 increased with increasing reaction temperature and reaction time (sweat). Typical pigment analyses are presented in Table 1.

Table 1

COMPARISON OF SWEATED PIGMENTS
WITH HOT- AND COLD-PROCESS POWDER CAKES

Process	K_2O %	Silica, %
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

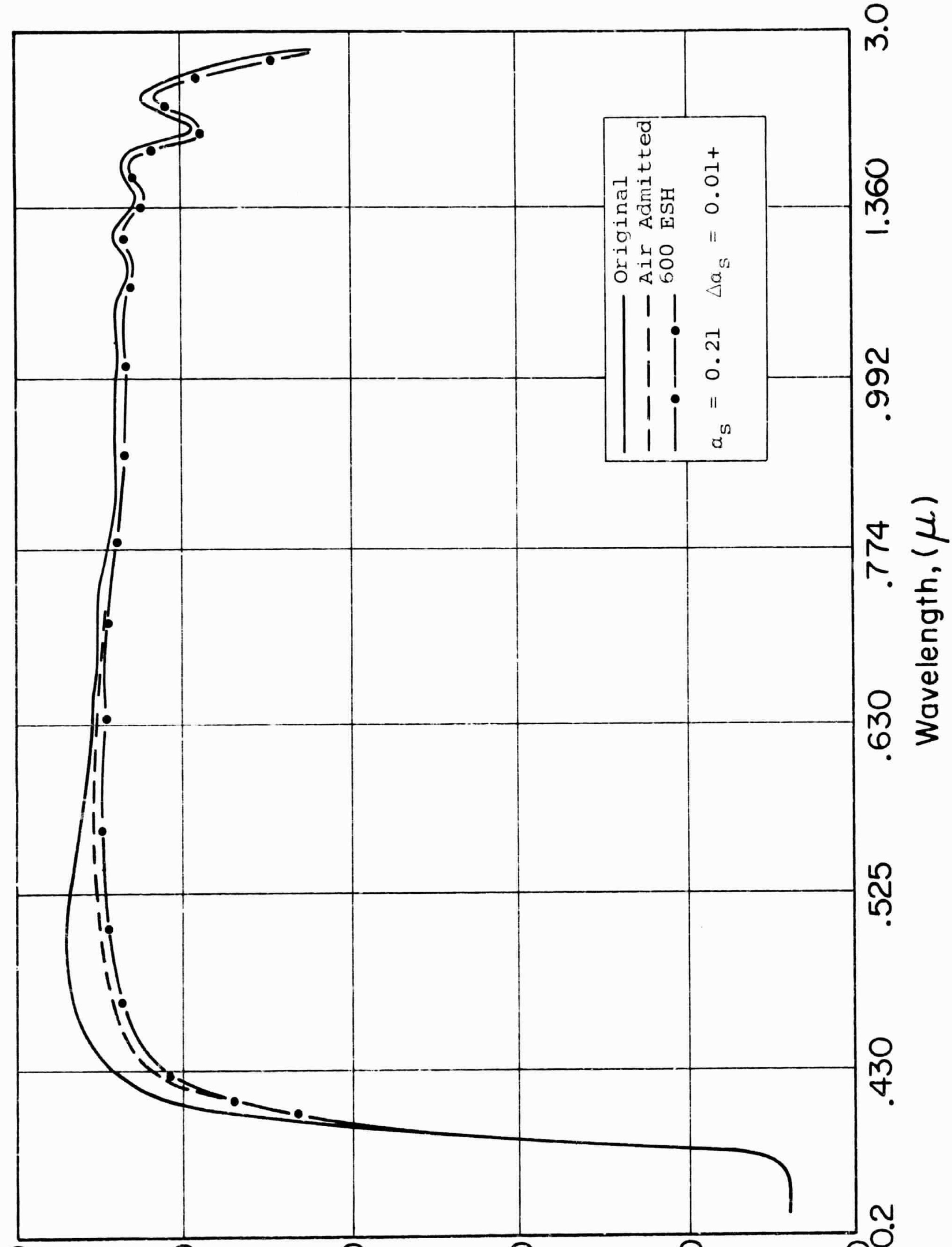

Figure 6: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; TOLUENE ONLY)

3. Heat Treatment of Silicated Pigment

Experiments to determine the effect of heat treating the sweated pigment were undertaken in the belief that the silicate "fixed" on the surface of the ZnO would be increased, thereby further improving stability to ultraviolet radiation as well as the shelf life.

The spectra of S-13G prepared from sweated pigment preheat-treated for 16 hr at 650°C is presented in Figure 7. The stability in the infrared was decreased by calcination, resulting in an increase in α_s from 0.01 (Figure 6) to 0.03 (Figure 7). These results are due presumably to the greater grinding required to reduce the calcined pigment -- thereby generating new, unprotected surfaces that are subsequently photodesorbed in the paint. Analogously, the greater infrared damage exhibited by paint prepared from unsweated, cold-process pigment is believed to be due to physical removal of the nonfixed silicate during the paint-milling operation.

4. Physical Sensitivity of Silicate-Treated ZnO

The sensitivity of pure ZnO to mechanical distortion has been discussed in numerous communications on the development of space-stable coatings. We examined the problem of mechanical distortion of ZnO in a program for the Jet Propulsion Laboratory (Contract 950746) in late 1965.[14] No detectable electron spin resonance signal was observed on SP500 samples that were mechanically yellowed. Damaged specimens were observed to possess a rather narrow, intense absorption band centered at about 375-nm wavelength.

In the studies cited as well as in both previous and later work, we have observed that mechanically yellowed specimens exhibit greater degradation when irradiated with ultraviolet in vacuum than samples that are not mechanically damaged. This is not surprising since the increased absorption also increases

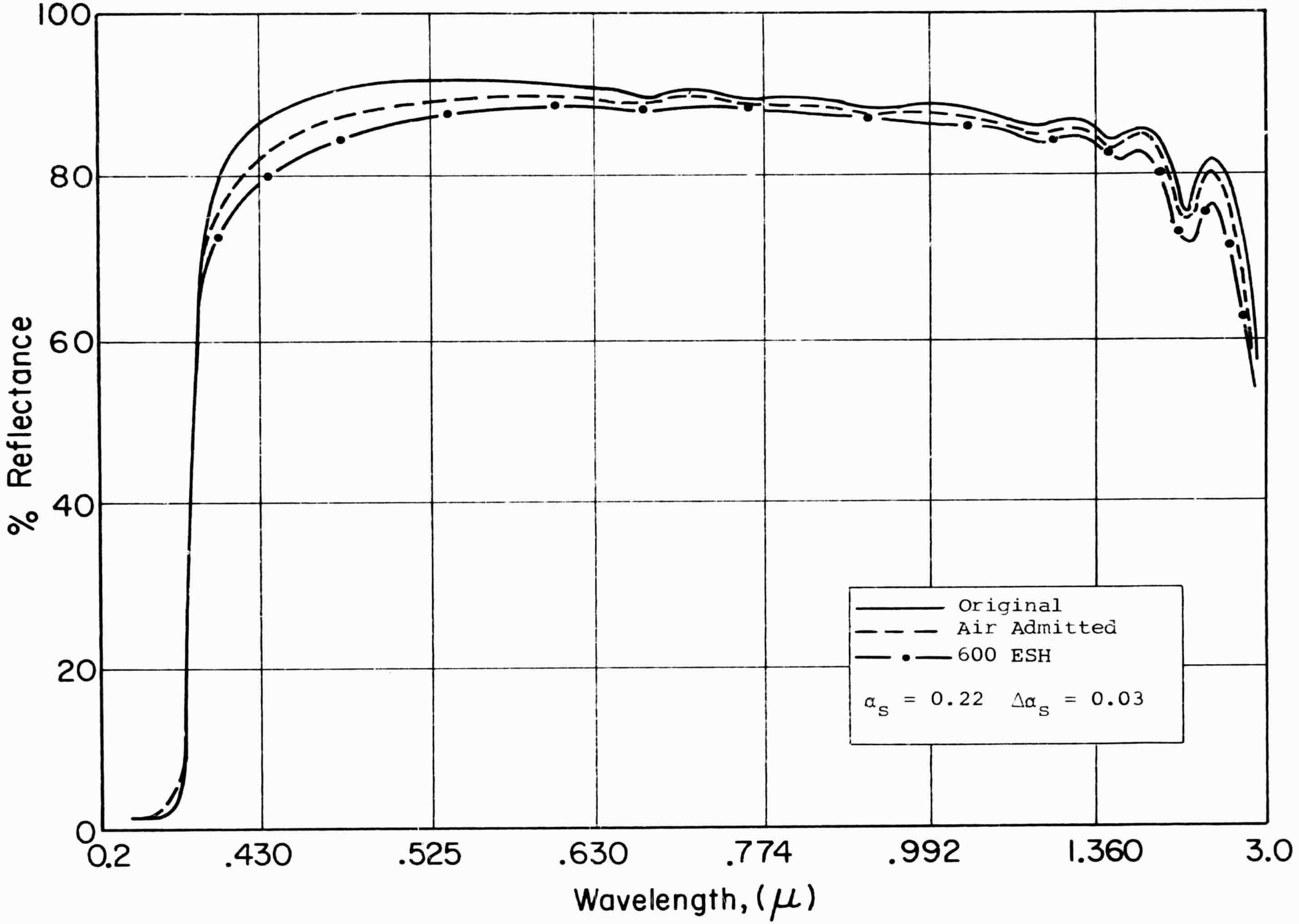

Figure 7: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; CALCINED)

the probability of the occurrence of photolytic effects. Although the mechanism is not well understood at this time, mechanically-induced yellowing has been attributed to the creation of interstitial zinc.

Our previous experience with the physical sensitivity of ZnO led us to examine the effect of grinding, and the physical distortion so produced, on the silicate-treated SP500 ZnO employed in IITRI's S-13G coating. A series of S-13G paints was prepared from the same batch of silicate-treated SP500 ZnO; the only difference was the manner in which the dried, treated powder was conditioned for grinding (manufacturing) into the paint. The data obtained are presented in Table 2. The spectra of paints 1 and 5 are presented in Figures 8 and 9.

Table 2

EFFECT OF GRINDING ON STABILITY OF S-13G IRRADIATED FOR 1400 ESH in IRIF-I (A-H6)

No.	Physical Treatment of Silicated ZnO	Paint Grind hr	Solar Absorptance α_s	Solar Absorptance $\Delta\alpha_s$
1	Sifted	3	0.24	0.01
2	Unsifted, unground	4	0,22	0.02
3	Dry-ground	3	0.22	0.03
4	Hand-mulled	3	0.26	0.05
5	Re-mulled	5	0.25	0.06

These data show that the stability to ultraviolet irradiation in vacuum is an inverse function of the shear stress applied to the dry, silicate-treated pigment prior to wet grinding. (Excessive wet-grinding is also known to decrease stability). A fivefold increase in damage, as measured by $\Delta\alpha_s$,

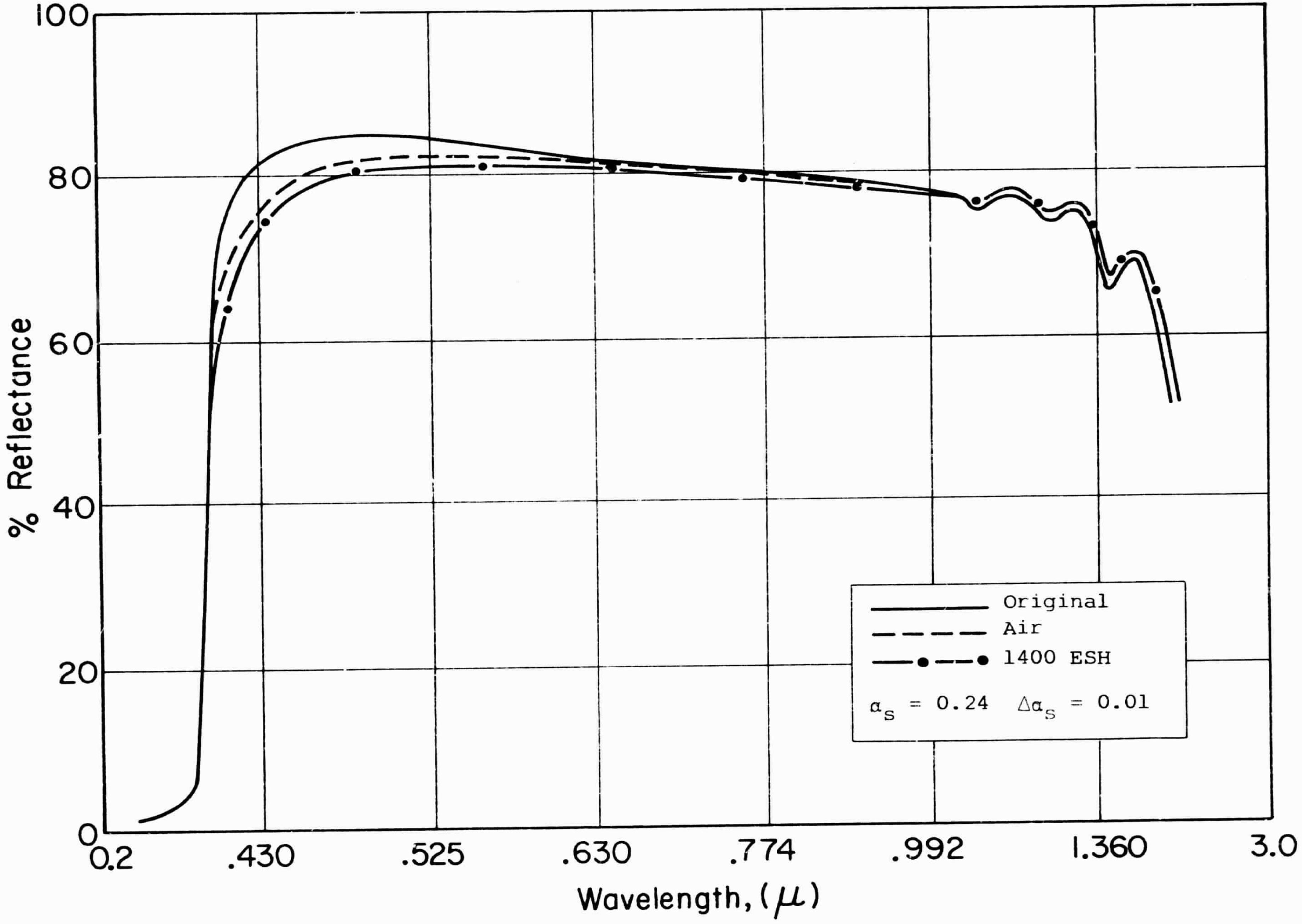

Figure 8: EFFECT OF UV IRRADIATION IN THE IRIF ON S-13G PREPARED FROM SIFTED PIGMENT (PAINT GRIND TIME = 3 hr)

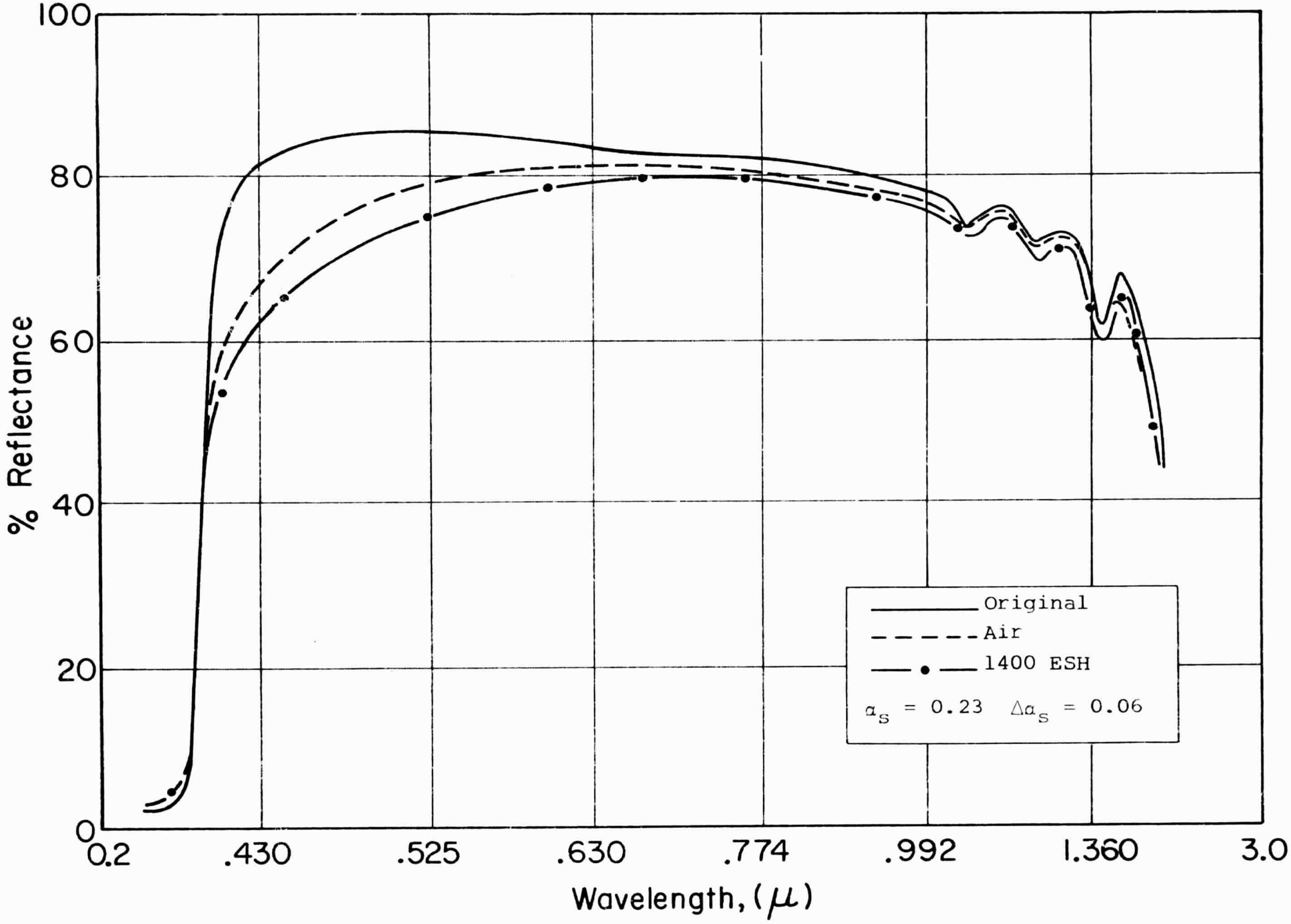

Figure 9: EFFECT OF UV IRRADIATION IN THE IRIF ON S-13G PREPARED FROM REMULLED PIGMENT (PAINT GRIND TIME = 5 hr)

was observed between the paint prepared from pigment that was only sifted and the specimen that was prepared from pigment that was hand-mulled prior to wet-grinding.

Hand-mulling procedures were originally employed in the manufacture of S-13G, but this procedure was terminated as a result of these studies. Sifting out the millable pigment is a highly inefficient and costly technique, even though it permits shorter wet-grinding times and therefore greater stability. We are therefore presently wet-grinding only, but for a slightly longer period. Paint prepared from the pigment that was neither sifted nor dry-ground (or mulled) exhibited a $\Delta\alpha_s$ of 0.02 in 1400 ESH, compared with 0.01 for the specimen prepared from the pigment that was sifted.

A specimen prepared from pigment that was first dry-ground for 30 min and subsequently wet ground for a short period exhibited a $\Delta\alpha_s$ of 0.03 in 1400 ESH. The specimen (Figure 9) prepared from pigment that was essentially remulled (too large to pass the seive) from the first hand-mulling operation exhibited a $\Delta\alpha_s$ of 0.06 in 1400 ESH.

5. Phosphating Studies on Silicated ZnO

Although the silicate treatment of ZnO was aimed at its incorporation into General Electric's RTV-602 polydimethylsiloxane elastomer, an obvious course of action was the preparation of silicate-treated zinc oxide paints based on the highly untraviolet-stable Owens-Illinois 650 resin. Unfortunately, the very chemical functionality of the 650 resin that allows it to be thermally cured at low temperatures without the use of catalysts causes nearly instantaneous gellation when mixed with silicate-treated zinc oxide. The highly alkaline surface of even the sweated, silicated pigment promotes rapid polymerization of the B-staged resin.

We therefore made two attempts to neutralize the triple-redispersed, sweated pigment prior to manufacture of S-13G. Figures 10 and 11 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. The data in Figure 10 show that the stability at most wavelengths was destroyed by neutralization with formic acid. On the other hand, the specimen prepared from the sodium acid phosphate-neutralized pigment, Figure 11, exhibited the greatest ultraviolet stability that has been observed for S-13G prepared from preheat-treated pigment.

We therefore reasoned that sodium acid phosphate might successfully be employed to neutralize the alkaline surface of the silicate-treated zinc oxide, thereby making it a useful pigment for the Owens-Illinois resin, without affecting the infrared stability of the pigment that is achieved by silicating. Experiments were accordingly performed to determine the effect of different methods of phosphate treatment of the silicated zinc oxide pigment.

The starting point in all of these experiments was the first filter cake taken from the silicate treatment of the zinc oxide as regularly produced in the manufacture of pigment for S-13G paint. The acid phosphate treatments employed and the manufacture of the Owens-Illinois 650 resin-based paints are presented in Appendix A.

The results of shelf-life studies of "650 Resin"-based paints are presented in Table 3. Although the data were inconclusive, Table 3 shows that washing with sodium acid phosphate has an advantageous affect on the shelf life of the Owens-Illinois 650 paint. In the absence of definitive studies, we can only conclude that the "fourth" water redispersion of the

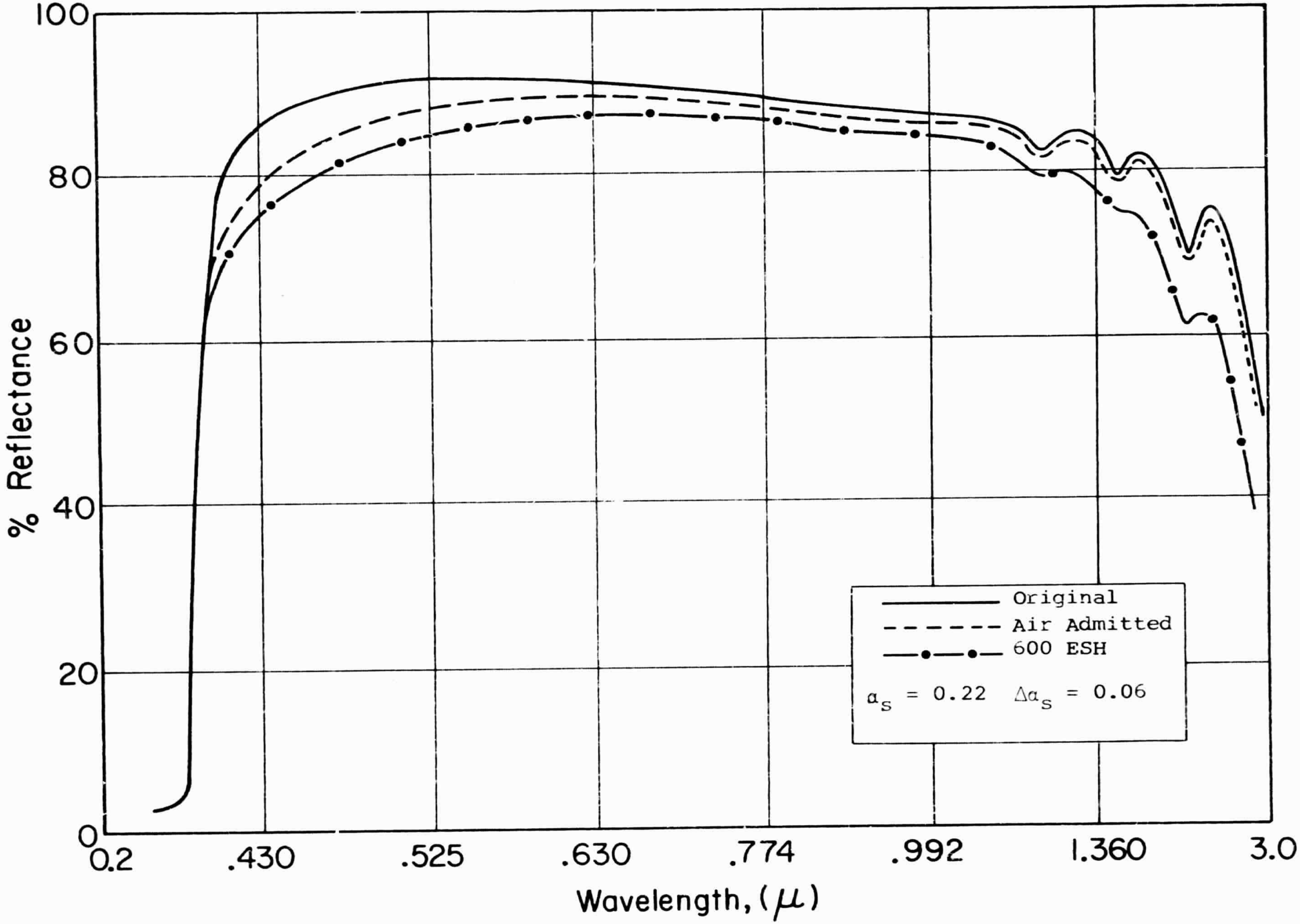

Figure 10: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; FORMIC ACID; CALCINED)

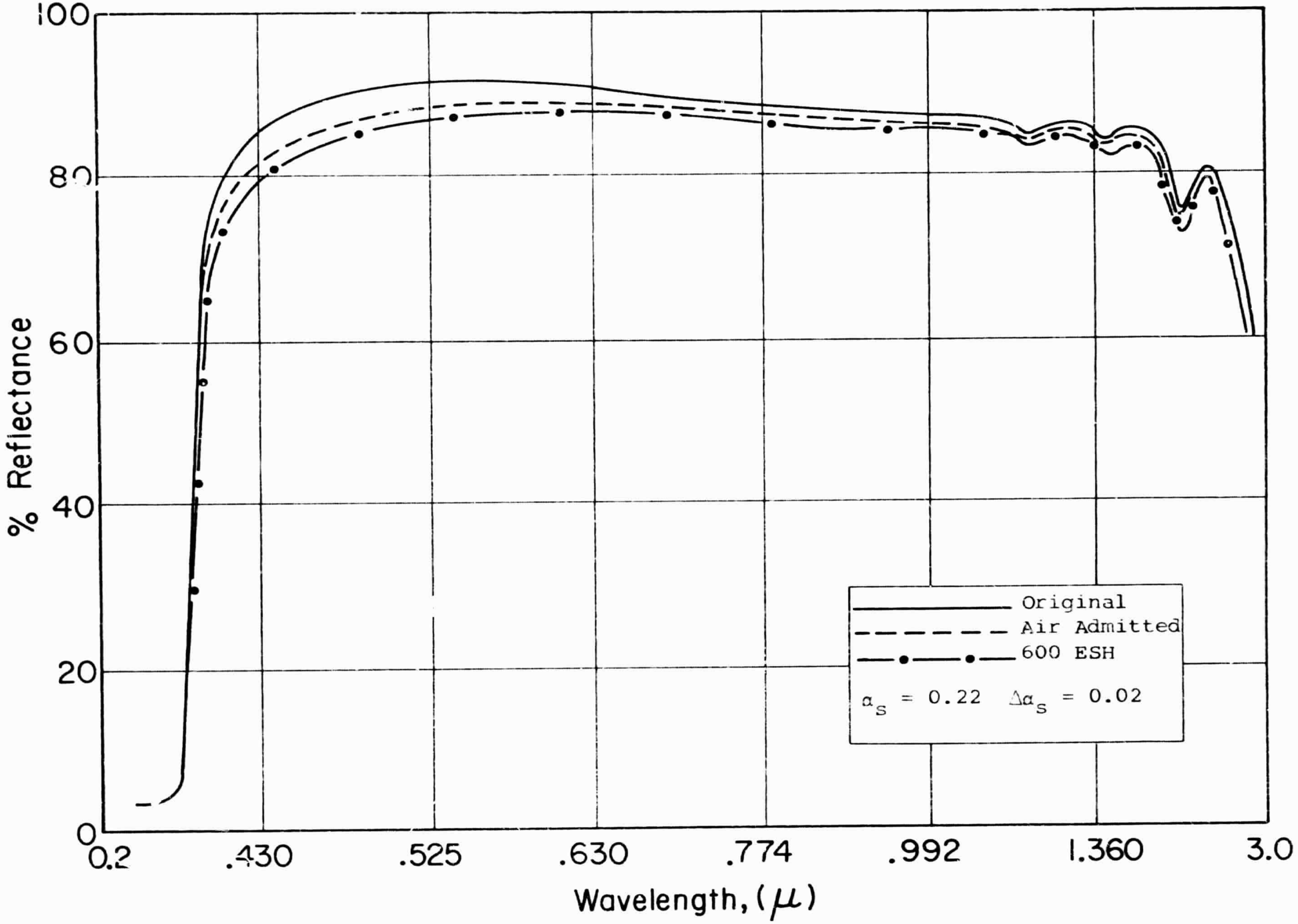

Figure 11: EFFECT OF UV IN VACUUM ON S-13G (SWEATED PIGMENT; ACID PHOSPHATE; CALCINED)

1% acid phosphate-treated pigment (A-413-4) removed the neutralizing influence of the acid phosphate and A-413-4 gelled due to alkaline polymerization of the polyfunctional 650 "silicone" resin. On the other hand, we hypothesize that the A-413-5 paint gelled by acid polymerization due to the 3% acid phosphate employed in the neutralization -- a factor which the additional water dispersion, employed in making pigment A-413-6, militated against. (It should be noted, however, that the acid phosphate was not "fixed" on pigments A-413-4 and A-413-6 by drying prior to the last redispersion in water).

Table 3

SHELF LIFE OF O-I 650/SILICATE ZnO PAINTS

Pigment No.	Description	Cake No.	Gelation Time, hr
A-413-1	Control	3	1.0
A-413-2	Control	4	2.5
A-413-3	1% Phosphate	3-P1	72.0
A-413-4	1% Phosphate*	4-P1	1.5
A-413-5	3% Phosphate	3-P3	4.0
A-413-6	3% Phosphate*	4-P3	72.0

*The last redispersion made in distilled water only.

The last two paints that possessed a 3-day shelf life were irradiated in IRIF-I. The specimen prepared from the 3%-acid phosphate-washed pigment was the superior of the two. Its spectra are presented in Figure 12. Indeed, this paint, designated A-413-6, gave the greatest stability to ultraviolet irradiation in vacuum yet achieved with a zinc oxide-polymethylsiloxane paint.

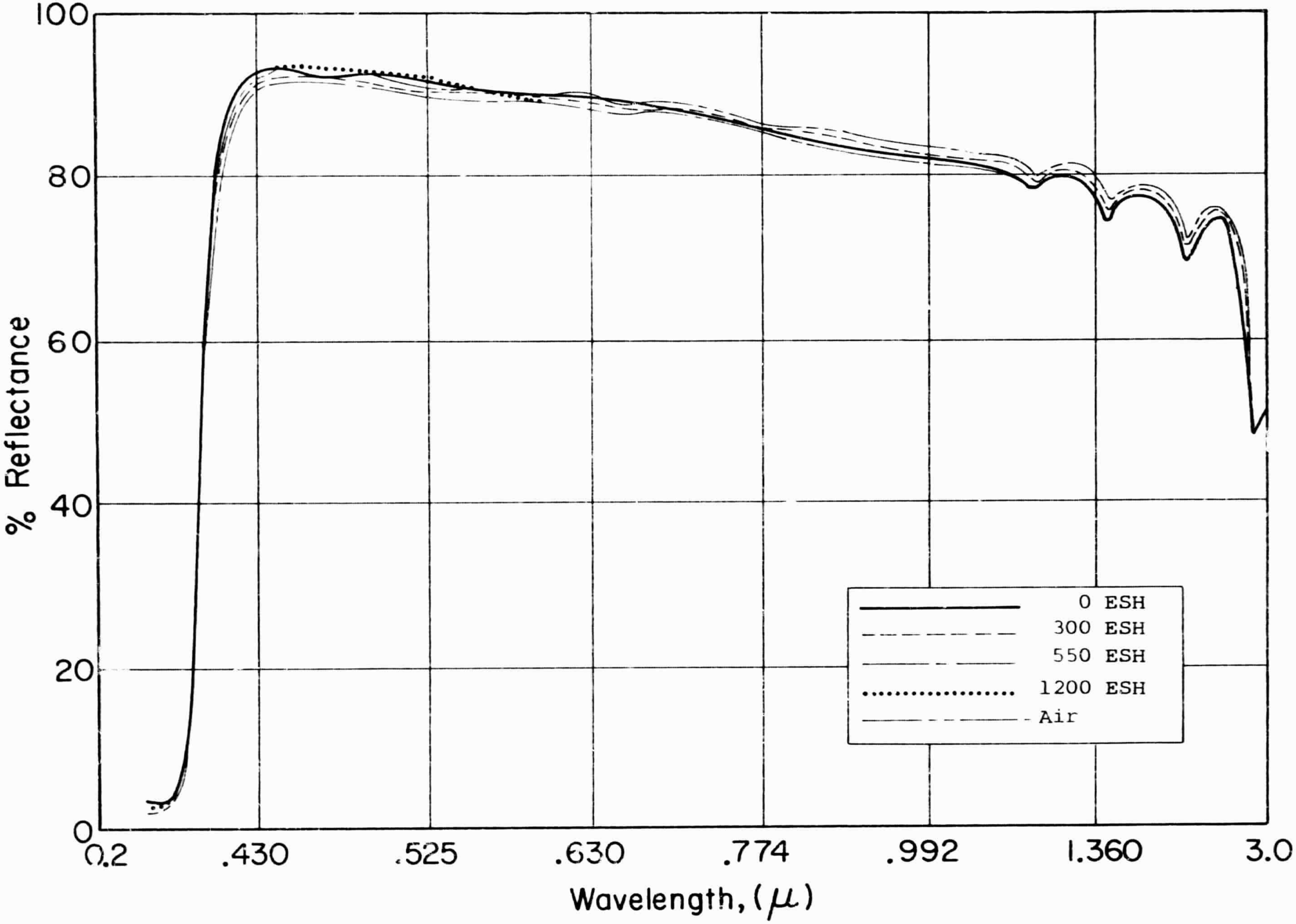

Figure 12: EFFECT OF UV IRRADIATION ON A-413-6 O-I 650 PAINT (SILICATED ZnO WASHED WITH 3% NaH_2PO_4)

B. Pilot-Production Scaleup Studies

Production scaleup of S-13G to 4-gal quantities was not only one of the objectives of the program but was required for application to ATM, ALSEP, etc. Quantity manufacture of S-13G necessitated the preparation of silicate-treated ZnO in 12- to 15-lb batches. The preparation of large batches of pigment posed process-related problems not encountered in the laboratory investigations that were described in the preceeding section. The preparation of large batches of pigment necessitated closer attention to temperature control during the silicate-ZnO reaction, but resulted in a severely diminished shelf life of the finished S-13G paint.

1. ZnO-Potassium Silicate-Reaction Temperature

The temperature employed was not at first closely controlled. Since a double boiler was employed for the laboratory process, the initial temperature could not have exceeded 100 °C and, since the laboratory batches were small, the heat of reaction was easily dissipated. A great increase in body results from the hot-process reaction, compared to the cold-process reaction, and analysis of the pigment produced from the first filtering (Cake 1) confirms this observation.

	%	
Process	SiO_2	K_2O
Cold	3	2.5
Hot	8	0.8

As long as the batch sizes for the pigment treatment were small, no trouble was encountered with the paint made from that pigment and the shelf life of the paint was in many cases as long as 8 mo.

With increasing batch sizes manufactured to meet an increasing demand for S-13G, however, a marked decrease in shelf life occurred. It was reasoned that in a large batch, heat from an exothermic reaction could not escape as readily as from a small batch, particularly when the slurry was of a thixotropic nature preventing convection. Hence, we reasoned that starting temperatures should be lower for the larger batches.

Comparisons were therefore made between a large batch with a starting temperature of 82°C and another batch of the same size with a starting temperature of 66°C, all other factors (mixing times, redispersion and filtration procedures) were kept equal. The pigment reacted at a starting temperature of 82°C resulted in a paint with a shelf life of 2 wk while the pigment started at 66°C produced a paint with a shelf life of 8 wk.

The temperature parameters were subsequently set at 82°C for the start of the reaction with the temperature at the close of the mixing period not to exceed 77°C, and preferably maintained below 74°C.

2. Pigment-Drying Temperature

During the period when poor shelf life was characteristic of the larger batches of S-13G, the theory was advanced that premature gelation of the S-13G paint was due to the presence of moisture in the pigment. Acting on this assumption, the drying-oven temperature was raised from 110°C to between 120 and 140°C and the drying continued for 2 days instead of 16 to 18 hr overnight. The pigment was stored in a dry box over phosphorous pentoxide until ready to use. The resulting pigment made a paint with an even shorter shelf life.

An experiment was conducted therefore to test the effect of heat on the S-13G pigment. A pigment was selected that had been dried overnight at 110°C and that had been formulated into a paint with 28-days shelf life without further treatment. Portions of the pigment were reheated at 130, 188, 288, and 650°C, respectively, with the results given in Table 4.

Table 4

EFFECT ON S-13G'S SHELF LIFE
OF POST HEATING THE PIGMENT

Pigment Reheating Temp., °C	Shelf Life of Resulting Paint, days
No reheating	28
130	17
188	6
288	3
650	43 (yellowed)

The temperature at which the acicular particles of SP5000 are converted to a less acicular, possibly nodular, state (permitting the pigment to be ground in PS-7 to make Z-93 and still possess flow which would not be possible with the acicular structures of untreated SP500) is 650 °C. However, the S-13G pigment did not withstand that temperature without yellowing.

The only conclusion that can be offered is that until the critical temperature of 650 °C is reached, the effect of increased temperature of calcination of S-13G pigment may be to shorten the shelf life of the paint. The schedule presented in Table 4 was reconfirmed with the same results.

Because of this observation, the pigment cake is presently dried at 110 °C for 18 to 24 hr.

3. Effect of Retained Alkali and Acid in the Silicated ZnO

The possibility of greater retention of soluble alkaline residues in the larger filter cakes prompted the evaluation of this problem.

A series of samples were prepared to test this possibility and also to evaluate one method of coping with it, namely, the addition of NaH_2PO_4 -- previously found to be of value in treatment of S-13G pigment.

To a pigment found to make a paint with a shelf life of 26 days, increments of KOH were added to a top limit of 0.6% KOH (added) by weight of pigment. Likewise, small amounts of sodium acid phosphate, mono-basic, were also added in steps up to 0.20% by weight in a companion series.

The traces of KOH and of NaH_2PO_4 were carefully and intimately blended into the pigment samples which were then dried in an oven over a weekend before mixing into a paint. The resulting paints were stored for shelf-life tests and their stability to outer space environment was evaluated by testing them in IRIF-II. The data are presented in Table 5.

Table 5

EFFECT OF ALKALI ADDITIONS
ON SHELF LIFE AND STABILITY OF S-13G

Additions to Pigment	Paint Shelf Life, days	$\Delta\alpha_s$ (1000 ESH)
0.60% KOH	3	-
0.30 KOH	3	-
0.10 KOH	17	0.030
0.05 KOH	26	0.019
None, (control)	26	0.015
0.05% NaH_2PO_4	64	0.007
0.10 NaH_2PO_4	75	0.015
0.15 NaH_2PO_4	65	0.018
0.20 NaH_2PO_4	72	0.015

Table 5 appears to confirm the theory that the occlusion of free alkali in a large filter cake of pigment may well account for the loss of shelf-life of the resultant paint. The data also confirms previous work showing that treatment with NaH_2PO_4 is of definite advantage in improving the stability of S-13G.

4. Effect of Redispersion of Pigment on S-13G

In IITRI Report U6053-2, a monthly progress report dated November 21, 1966, the effect of the number of redispersions was studied; at that time, with the small laboratory-batch sizes then in use, three redispersions were determined to be the limit without risking the danger of causing a diminution in the protective efficiency of silicating as a prevention of bleachable infrared damage. The large loss in stability in infrared reflectance between the third and fourth redispersions was clearly obvious.

With the marked loss of shelf life in the very much larger batches subsequently used, a re-study of the process was undertaken, but using much larger batches than in the earlier investigation.

The results of the experiment with a 12-lb batch of PS-7-treated ZnO was very encouraging. Even five redispersions had no deleterious effect on the infrared stability of S-13G, while greatly extending the shelf life of the resultant coating. The data are summarized in Table 6. The table appears to confirm the theory that an increase in batch size requires certain process modifications, in this case an extra redispersion, to maintain the same results as were previously obtained with smaller batches. The data also show that a fourth redispersion is perfectly safe relative to the stability of S-13G after 1000 ESH, with a gain in shelf life of from 20 to 56 days. The spectral characteristics of the S-13G prepared from pigment that had received four redispersions is presented in Figure 13. Examination of the spectra shows that, although a slight

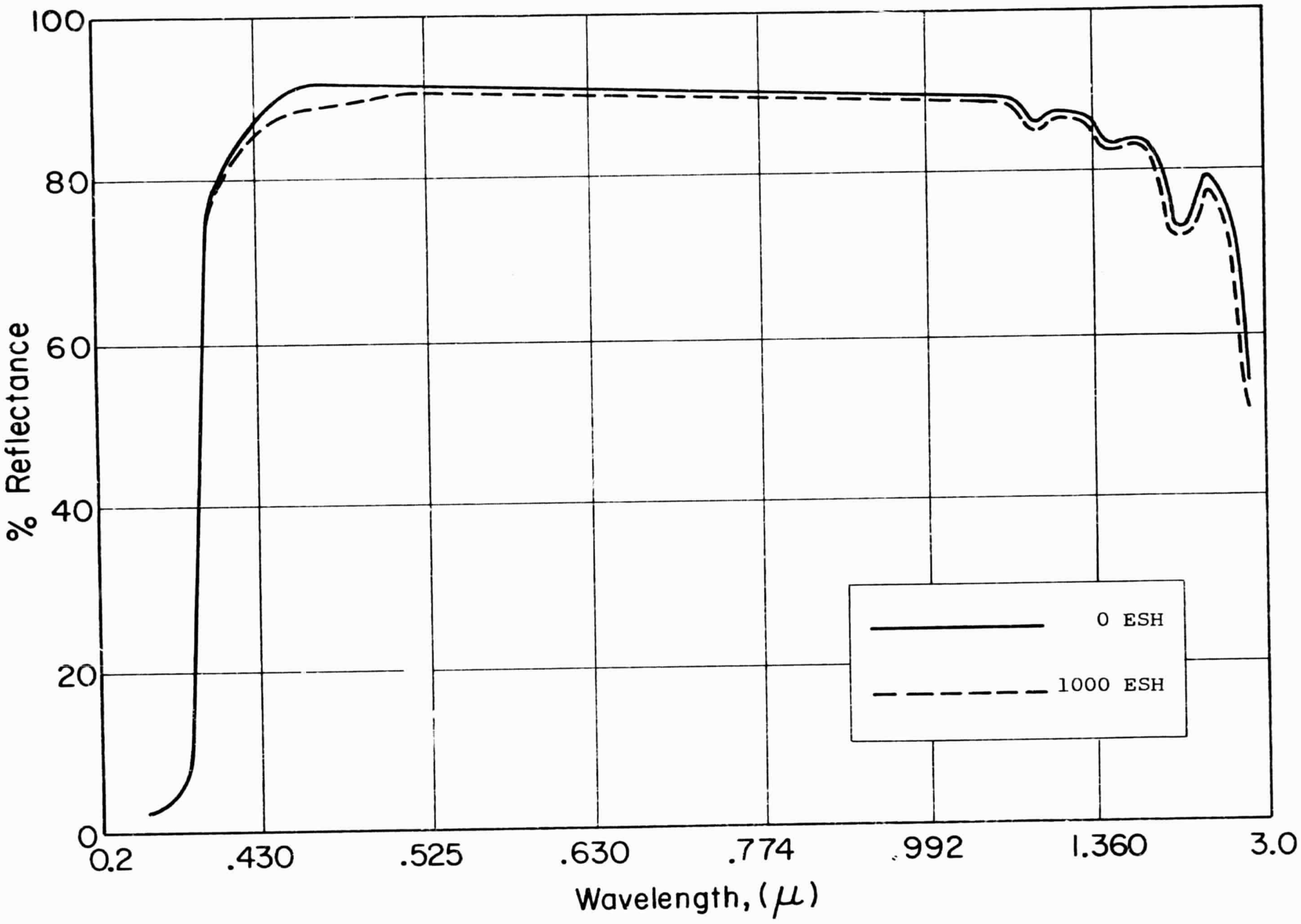

Figure 13: EFFECT OF UV IRRADIATION IN VACUUM (IRIF-II) ON S-13G PREPARED FROM PIGMENT THAT RECEIVED 4 DISPERSIONS IN WATER

decrease in reflectance occurred in the 2000-nm wavelength region, it was not bleached on admission of air to the space chamber. Four redispersions are therefore adjudged to be completely safe in terms of infrared stability.

Table 6

EFFECT OF REDISPERSION OF SILICATED ZnO
ON THE SHELF LIFE AND STABILITY OF S-13G
(BATCH A-938)

No. of Redispersions	Initial α_s	$\Delta\alpha_s$ (1000 ESH)	Paint Shelf Life, days
2	0.215	0.014	6
3	0.193	0.014	20
4	0.218	0.014	56
5	0.230	0.014	90

There well may be conditions where a still greater increase in the batch size may require a fifth redispersion with perfect safety (relative to the stability of the paint). However, current practice at IITRI is to prepare 12.5-lb batches of silicated pigment (required for 4 gal of S-13G) and four redispersions are employed, and are written into the process specifications contained in Appendix B to this report.

5. Effect on Shelf-Life of the Number of Redispersions Combined with Treatment with NaH_2PO_4

Since, singly, both the increase in the number of redispersions and the treatment with NaH_2PO_4 improved the shelf life of the paint made from silicate-treated pigment, tests were made of their combined effect on the shelf-life and stability of the coating. Shelf-life tests were performed accordingly on the pigments presented in Table 7.

Table 7

SCHEDULE OF PIGMENT TREATMENTS
EMPLOYED IN SHELF-LIFE STUDIES

Coating No.	Remarks	No. of Dispersions			
		1	2	3	4
B-042	Control (Std. 1967 basis)	H_2O	H_2O	H_2O	-
B-043	-	H_2O	H_2O	1% NaH_2PO_4	-
B-046	-	H_2O	3% NaH_2PO_4	H_2O	-
B-045	-	H_2O	1% NaH_2PO_4	1% NaH_2PO_4	-
B-037	-	H_2O	H_2O	H_2O	H_2O
B-038	-	H_2O	H_2O	H_2O	1% NaH_2PO_4
B-039	-	H_2O	H_2O	1% NaH_2PO_4	1% NaH_2PO_4

The pigments prepared according to the above schedule were, after drying under the same conditions, ground into an S-13G-type paint using the formula below; all pigments were ground the same length of time in identical jar mills with identical ball loads.

Formula: Pigment - 40% by weight
RTV-602 - 20% by weight
Xylene - 40% by weight

Xylene was selected as the solvent for this experiment since it permits the greatest acceleration of polymerization of RTV-602, and an accelerated test was required.

Figure 14 presents the changes in viscosity with age of each of the paints made from the pigments listed in Table 7. The shelf-life times are not to be considered as representative of the shelf-life of a batch of regular S-13G formulated from that pigment process. The regular formula with the new "mixed" solvent composition would have approximately three times the shelf-life of the samples shown above. The differences resulting from the different pigments preparation procedures are still maintained, however, and can be extrapolated to the optimum solvent composition.

The combination of four redispersions with the use of 1% NaH_2PO_4 solution in the last two, produces the pigment giving the longest shelf life of the series. This procedure has been adopted for production of S-13G, and comprises the process specification present in this report with one additional feature that is discussed in Section V.

6. Effect of Age of Prepared Pigment

Samples were prepared from pigment retains that were several months old (the shelf life of the paint made from the retain compared with that of the original paint batch) in order to determine the extent to which S-13G pigment deteriorates with age. In all cases, the older the pigment the longer its shelf life in the paint. The question of storage life of the silicate-treated zinc oxide pigment therefore was not considered further.

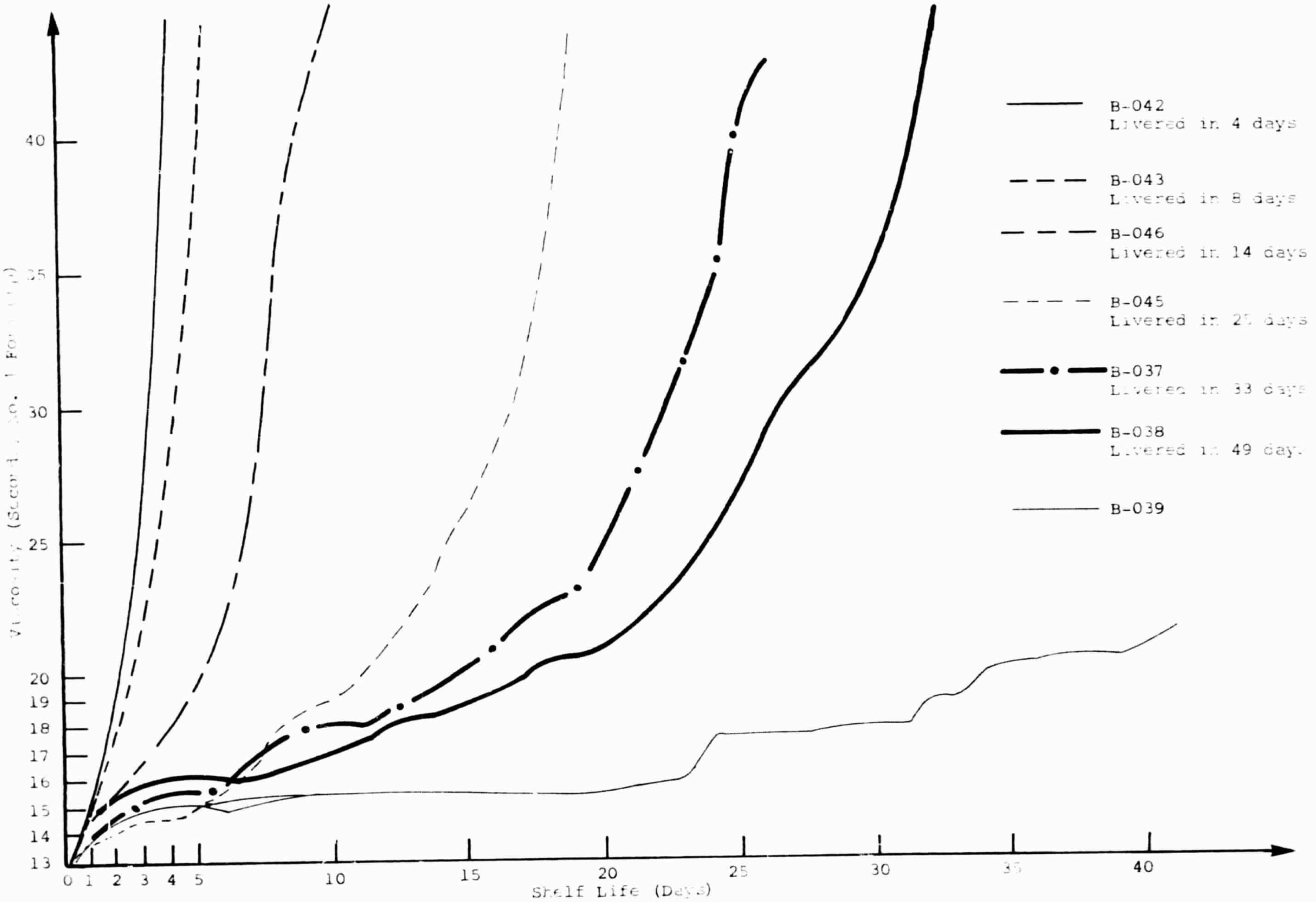

Figure 14: EFFECT ON SHELF LIFE OF RTV-602 PAINTS OF THE NUMBER AND TYPES OF DISPERSIONS OF THE SILICATED ZINC OXIDE PIGMENT CAKE

V. OPTIMIZATION OF S-13G PAINT MANUFACTURE

A. Early Studies on Effect of Solvent and Solvent Combinations

As originally formulated, only toluene was used as the organic volatile solvent in S-13G. Its use as the sole solvent in RTV-602 paints results in excessive spray dust due to its rapid evaporation; aromatic hydrocarbons also produce "orange peel" in RTV-602 films. In addition, S-13G paints formulated with toluene as the only solvent exhibit very poor shelf life.

Better application properties were obtained by replacing a portion of the toluene with 10% isopropanol and 5% butyl acetate by weight of total volatile solvent. This resulted in a more usable paint and an extension of the shelf life was observed.

The use of diluents as opposed to solvents is known to retard gelation of polymeric solutions that tend to undergo slow crosslinking polymerizations on aging. The highly alkaline surface of the silicate-treated ZnO actively catalyzes the polymerization of the RTV-602 polydimethylsiloxane binder employed in S-13G (and other silicones as well). In such cases, nonsolvating organic diluents can be effective in retarding gelation by the interposition of nonsolvent molecules between the reactive, solvated polysiloxane chains.

These considerations led to a series of controlled experiments to ascertain which chemical groups were responsible for the effect. (It is emphasized that these early tests were performed on S-13G paint prepared from pigment that was not sweated; paint prepared from sweated pigment is much less sensitive to solvent composition). The experiments involved replacing a portion of the toluene solvent with diluents and other solvents, while maintaining the total volatile always at 60% by volume. The viscosity in seconds, determined with a

No. 4 Ford Cup, was taken at the time of initial solvent addition, again on the following day, and then at regular intervals for up to several weeks.

The effect of replacing 5% of the toluene with organic diluents and other solvents is shown in Figure 15. It can be seen that the addition of cellosolve, diacetone alcohol and butyl acetate, all considered good solvents for silicones, has little effect in increasing shelf life. Indeed, in the case of cellosolve, the gelation of the paint is actually accelerated by the 95:5 solvent combination. On the other hand, the addition of ethanol, n-butanol and isopropanol all extend the shelf life. The effect of controlled addition of isopropanol to toluene is presented in Figure 16.

As a result of similar experiments that were performed employing xylene, n-butanol, and butyl acetate, an improved solvent composition was determined for early S-13G formulations, Table 8. It provides good spray, flow-out, and cure characteristics of the S-13G formulation.

Table 8

X-99 THINNER

	Wt., %
Toluene	40
Xylene	20
n-Butanol	15
Isopropanol	20
Butyl acetate	5

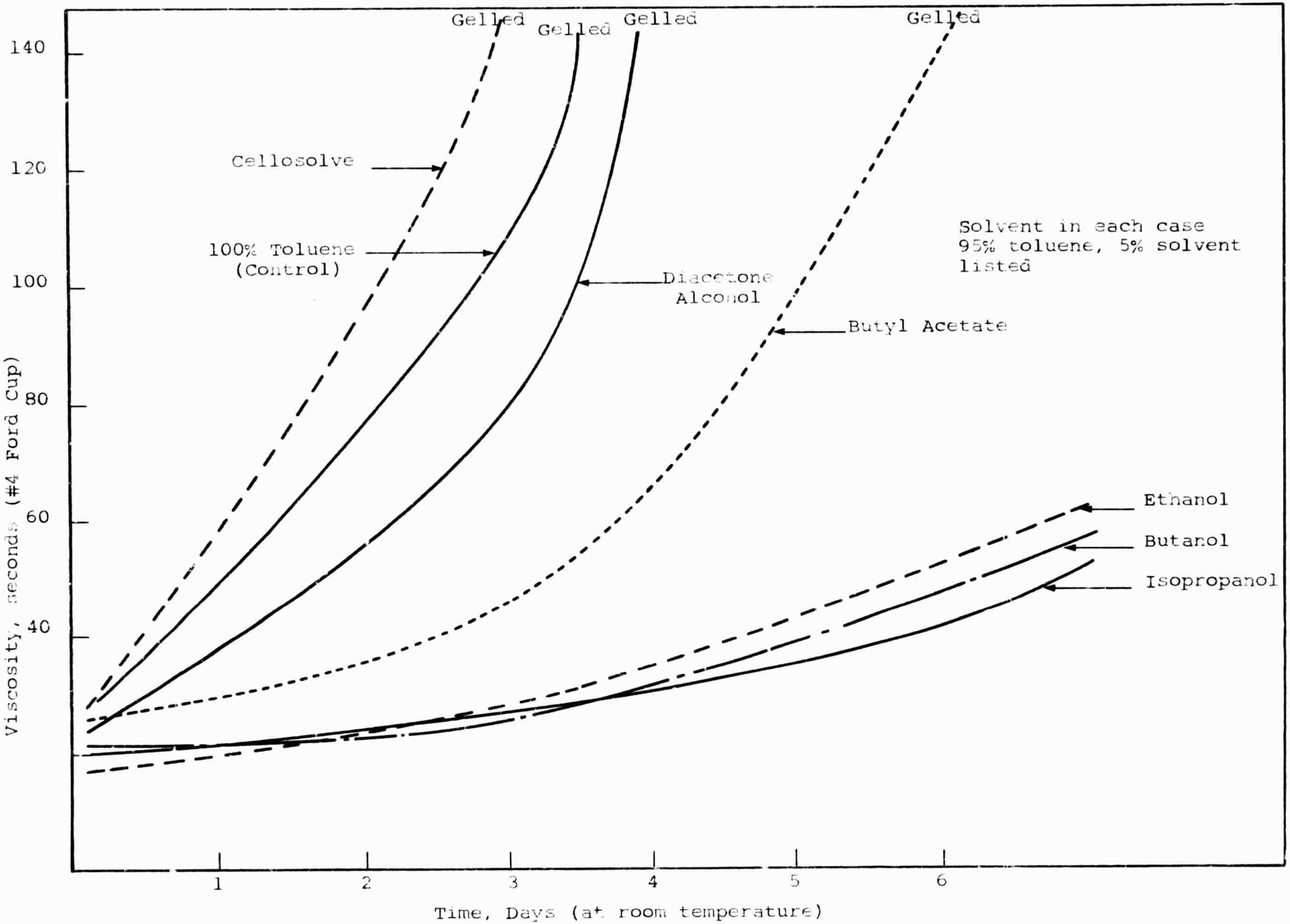

Figure 15: EFFECT OF SOLVENT COMPOSITION ON THE VISCOSITY OF S-13G

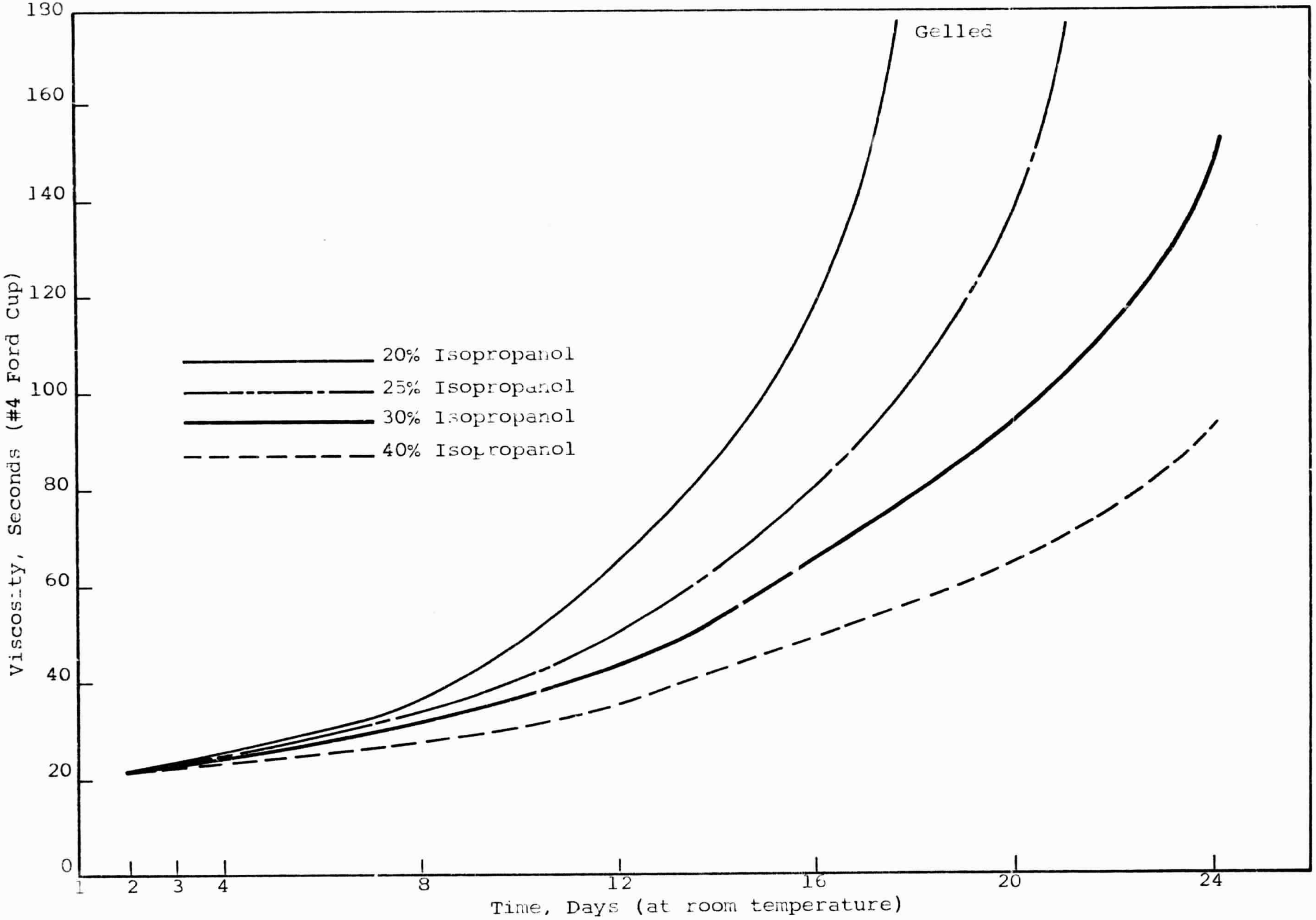

Figure 16: EFFECT OF TOLUENE-ISOPROPANOL SOLVENT COMPOSITION ON VISCOSITY OF S-13G

Of the many solvents examined, 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 increase in solar absorptance was 0.03 after 800 ESH, compared with a $\Delta\alpha_s$ of 0.01 for the identical paint employing toluene only.

B. Recent Studies of the Effect of Solvent Composition on Shelf Life

The effect of certain solvents on the shelf life of S-13G was clearly demonstrated in the preceeding section. The solvent combination X-99 was used in S-13G production throughout most of 1968. The solvent balance was designed to obtain the maximum leveling quality in the application of S-13G.

The period of poor shelf life led to a more careful investigation of the ingredients in the solvent mix with rather surprising results. Since RTV-602 is not soluble in some of the solvents studied alone, combinations of solvents had to be employed in several cases. Six variations in the solvent were made and, along with their effect on shelf life, are presented in Table 9; except for the solvents employed, all other factors were equal.

As a result of these tests, xylene and butyl acetate were removed from the solvent combination used in S-13G and are not included in the present formulation. They are, however, retained in the spray thinner X-99 where the hastening of cure might even be an advantage.

The behavior of commercial xylene in the above experiment led to the question of whether or not each of the pure xylenes behave in the same manner. S-13G-type paints were made using each xylene as the sole solvent; (all other factors were constant). The results of this experiment are presented in Table 10.

Table 9

EFFECT OF SOLVENT COMPOSITION
ON S-13G'S SHELF LIFE

No.	Solvent Composition, %		Shelf Life
1	Xylene	100	4 days
2	Butyl acetate Toluene	65 35	13 days
3	Toluene	100	26 days
4	Butanol Toluene	65 35	>4 months
5	Petroleum ether Isopropanol	65 35	Slightly stringy 4 months, yellows slightly
6	Isopropanol Toluene	75 25	>4 months

Table 10

EFFECT OF DIFFERENT XYLENES
ON S-13G'S SHELF LIFE

Hydrocarbon	Shelf Life, days
Toluene, (control)	24
Xylene, (commercial)	6
Xylene, pure ortho	10
Xylene, pure meta	6
Xylene, pure para	18
Ethyl benzene	10

As a result of these tests all hydrocarbons except toluene are omitted from the S-13G solvent composition.

A similar experiment utilizing various alcohols was performed employing, however, along with each alcohol, a proportion of xylene to accelerate the gelation test. The following alcohols were tested in admixture with xylene (75% alcohol, 25% xylene) as the volatile solvent portion of S-13G. The results of this experiment are listed in Table 11.

Table 11

EFFECT OF VARIOUS ALCOHOLS
ON S-13G'S SHELF LIFE

No.	Alcohol	Results, 2 months
1	200 proof ethanol	"Stringy"
2	i-propanol	Very "snotty"
3	n-propanol	"Stringy"
4	s-butanol	"Stringy"
5	i-butanol	"Stringy"
6	n-butanol	Very "snotty"
7	t-butanol	"Livered"
8	t-pentanol	"Livered"
9	i-pentanol	"Stringy"
10	MIBC (methyl isobutyl carbinol)	"Stringy"
11	901H (celanese higher alcohol mixture)	Very "snotty"

Of the list of alcohols shown in Table 11, those that are most conducive to long shelf life are:

n-propyl alcohol
s-butyl alcohol
i-butyl alcohol
i-amyl (pentyl) alcohol
MIBC

Those alcohols that promote tough S-13G films are:

- i-propyl alcohol
- s-butyl alcohol
- i-butyl alcohol
- t-butyl alcohol
- t-pentyl alcohol
- MIBC

Those alcohols that promote both long shelf life and a tough film are:

- s-butyl alcohol
- i-butyl alcohol
- MIBC

These may be combined with toluene in the proportion necessary to provide good spraying properties with the knowlege that long shelf life and a tough film will result.

C. Effect of Length of Grinding on Stability

An experiment was performed to determine the effect of small differences in ball-mill-grind time on the initial reflectance and stability of S-13G. It was known that long grinds, e.g., greater than 8 hr, cause discoloration of S-13G paint; dry-grinding of zinc oxide powder was shown to have a deleterious affect on reflectance and stability in earlier tests (reported in Section IV.A.4). However, the effects of small differences in wet grind time were not known. Samples from the same batch of S-13G were ground from 2 to 8 hr under identical conditions. The data are presented in Table 12. These data, while somewhat inconclusive, show only that initial reflectance (α_s) is a mild function of grind time whereas stability is essentially unaffected by grinding. However, in this experiment as well as in a confirming set of experiments, a curious decrease in stability occurred for specimens ground from 3 to

4 hr. In the absence of definitive studies, this loss in stability is associated with damage to the RTV-602 binder due to poor dispersion. The initial solar absorptance values show a trend that is consistent with their thicknesses. We usually grind for 5 hr in order to achieve a uniformly smooth, easily sprayed paint.

Table 12

EFFECT OF GRINDING TIME

Grind Time, hr	α_s	$\Delta\alpha_s$ (1000 ESH)	Thickness, mil
2	0.206	0.012	8
4	0.225	0.019	6
6	0.244	0.013	6
8	0.254	0.014	5

D. Effect on Stability of Premixing

The procedure in use for the grinding of S-13G paint through 1968 was to allow an hour of premixing, without the grinding balls in the mill, in order to allow the pigment aggregates to be broken and wetted and to thus prevent the impact of grinding balls upon dry pigment aggregates.

An experiment was accordingly performed in which the pigment portion of the paint was divided into several parts. One part was not premixed at all; i.e., the grinding media was placed in the mill at the very start. Another pigment portion was given the standard 1-hr premix before grinding. Other portions were premixed for increased times. The results are summarized in Figure 17. These data were confirmed in a second experiment. Although the shelf-life maxima of 12 days after 1 hr of premixing is puzzling, we have retained the 1 hr premixing step in the process specification.

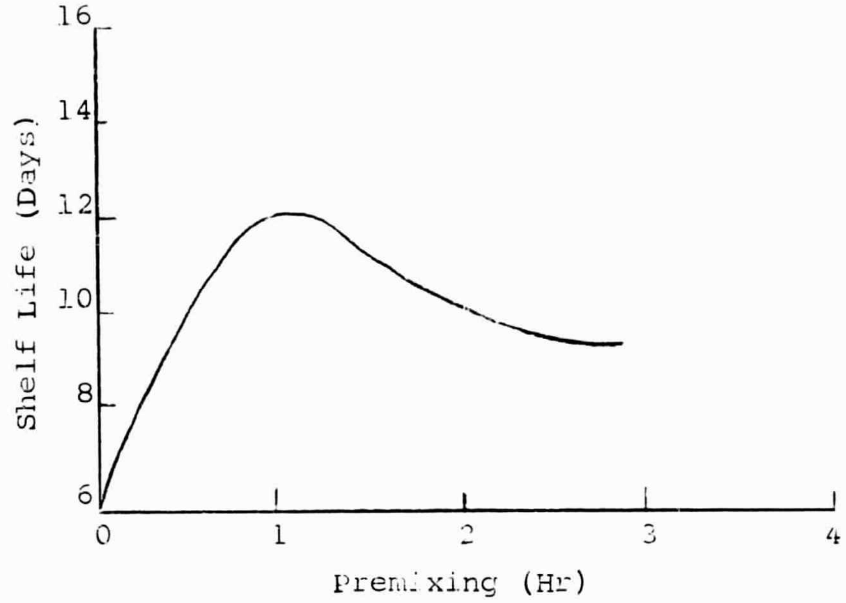

Figure 17

EFFECT OF PREMIXING ON S-13G'S SHELF LIFE

E. Effect of Addition of Silica to S-13G's Shelf Life

In order to determine whether or not traces of free silica deposited on the zinc oxide pigment (from the silicate treatment) might cause a loss of shelf life, samples of S-13G were treated with "Cab-o-sil" colloidal silica. These data are presented in Table 13.

The effect of the silica addition was to increase the shelf life rather than to reduce it. The thickening of the solution, however, ruled against its use as a component of S-13G and no ultraviolet stability tests were performed.

Table 13

EFFECT OF ADDED SILICA TO S-13G

Silica Added, %	Results
None	Shelf life, 28 days
2	Shelf life, 52 days
4	Shelf life, 52 days
8	No gelation but paste structure

F. Effect of Zinc Silicate on S-13G Shelf Life

The possibility that zinc silicate (whether formed by the silicate treatment of zinc oxide or present by direct addition as a pigment ingredient), might affect the shelf life and stability of S-13G paint had long been considered. Its possible use as a buffer had also been considered.

An experiment was performed in which various amounts of zinc silicate were added to the S-13G formulation. The effectiveness of zinc silicate in retarding gelation is shown in Table 14.

Table 14

EFFECT OF ZINC SILICATE UPON S-13G

Pigment, Wt. %	Shelf Life
None	28 days
2	> 4 months
4	> 4 months
8	> 4 months

The effect of 2% zinc silicate in extending the shelf life of S-13G from under 1 month to more than 4 months led to an immediate evaluation of its effect upon the physical strength of the film, the reflectance characteristics of the paint, and its ultraviolet stability.

At 2% by weight (of silicated ZnO), the strength of the film was only very slightly impaired; at 4 and 8% by weight, the film was chalky and lacked strength. Since 2% was adequate for a great increase in shelf life, it was added in that concentration to pigment B-039 (which had shown the greatest shelf life, Figure 14). The resultant coating was exposed to 1000 ESH of ultraviolet irradiation in IRIF-II. The spectra are shown in Figure 18. The coating showed a $\Delta\alpha_s$ of only 0.009. A careful re-check of the effect of zinc silicate showed that the optimum concentration is 1% of the total pigment weight; larger concentrations result in impaired curing characteristics. One percent zinc silicate is the concentration employed in the process specification presented in Appendix B.

A number of laboratory batches and several 4-gal production patches of paint were sampled for the purpose of confirming the stability of the new process employing the additional (i.e., more than 3) redispersions of the silicated pigment and the use of 1% sodium acid phosphate and 1% zinc silicate.

Paint batch A-944 (a laboratory batch) utilized five redispersions and its stability is shown in Figure 19. It will be noted that no bleachable infrared damage occurred in 1000 ESH of ultraviolet irradiation (employing an A-H6 source and IRIF-I). Figure 20 is representative of the stability of all 4-gal production batches manufactured to date.

These data confirm the excellent space-ultraviolet-radiation stability of the new "specification" S-13G paint. The shelf life of production batches of the specification S-13G is greater than 4 months.

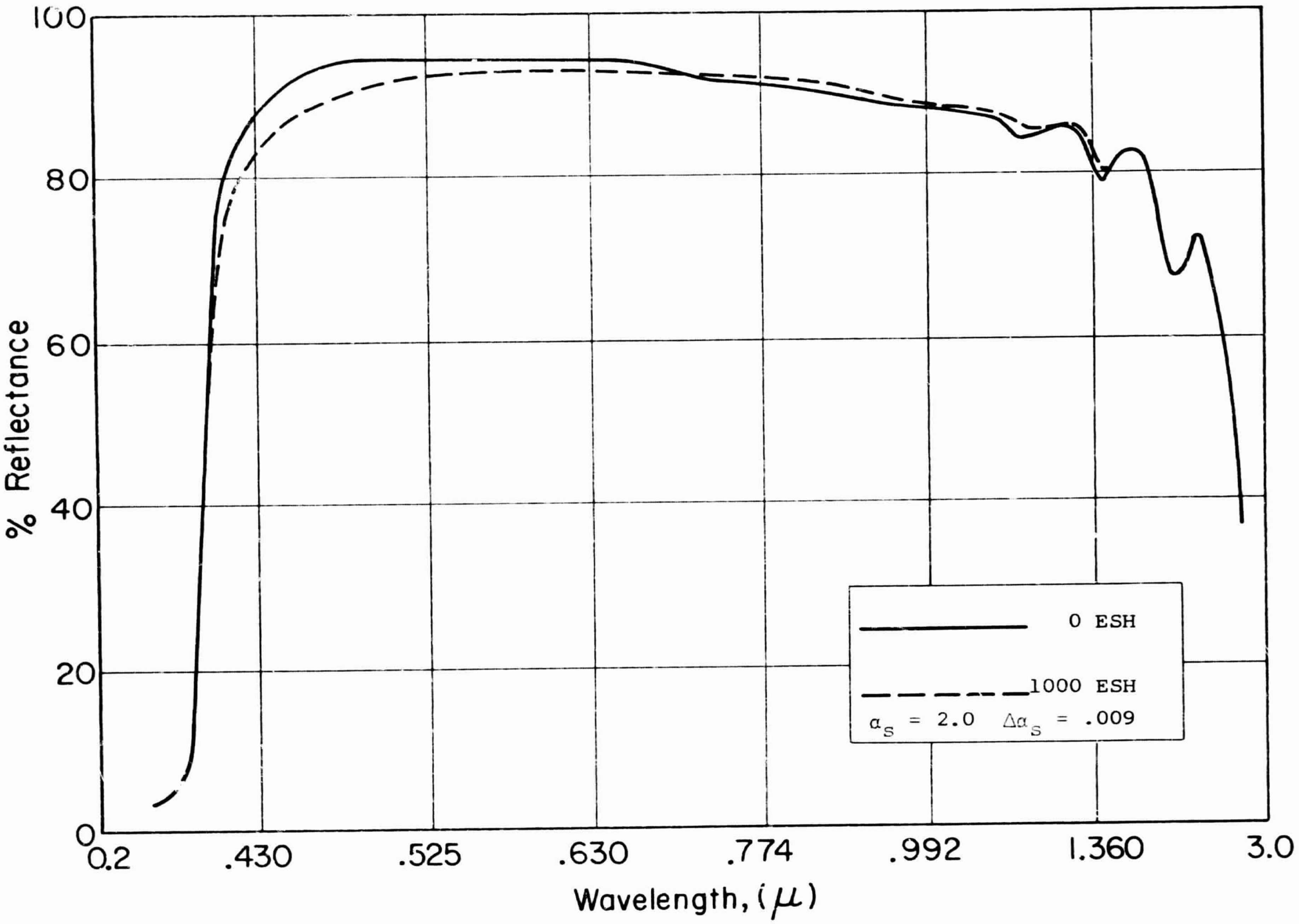

Figure 18: EFFECT OF UV IRRADIATION IN VACUUM (IRIF-II) ON S-13G CONTAINING 2% ZINC SILICATE (PIGMENT RECEIVED 4 DISPERSIONS

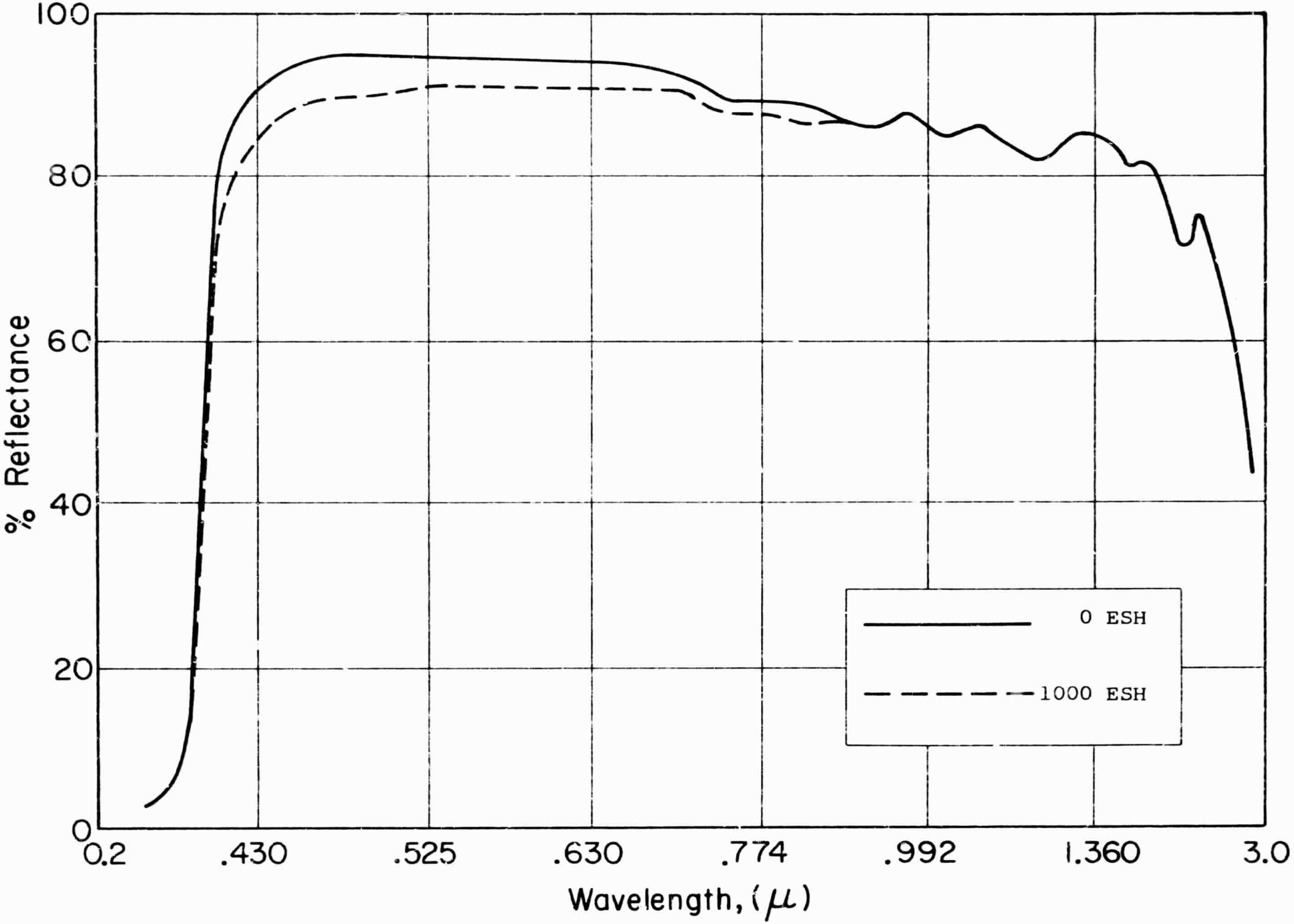

Figure 19: EFFECT OF UV IRRADIATION IN VACUUM (IRIF-II) ON S-13G PREPARED FROM PIGMENT THAT RECEIVED 5 DISPERSIONS (ZINC SILICATE WAS NOT EMPLOYED)

VI. SUMMARY

The thermal-control paint designated S-13G, developed at IIT Research Institute to replace the S-13 coating (which optically degrades in the infrared due to ultraviolet-induced damage), has been engineered to give a reliable, space-ultraviolet stable, thermal-control surface coating when manufactured in 4-gal production quantities. The shelf-life and optical-stability problems that plagued early production batches of S-13G have been solved by pigment- and paint-manufacturing process changes. These changes have consisted of the following.

(1) Employment of one additional (for a total of four) redispersions.

(2) The use of 1% solutions of sodium acid phosphate, NaH_2PO_4, as the wash in the last two redispersions.

(3) The use of 1% zinc silicate (based on weight of silicated pigment in the paint formula).

The resulting S-13G paint possesses a shelf life in excess of 3 months. It cures to an elastomeric adherent film when cured with General Electric's SRC-05 catalyst over their SS-4044 primer. Eight-mil films of S-13G have a nominal solar absorptance, α_s, of 0.20 and a nominal total hemispherical emittance, ϵ_h, of 0.88. An engineering value of $\Delta\alpha_s$ of 0.02 is recommended to account for the increase in solar absorptance as a result of 1000 ESH of space ultraviolet irradiation.

On the basis of a study undertaken for the Bendix Aerospace Systems Division, Ann Arbor, Michigan, we elucidated more fully the application parameters of S-13G, parameters that become critical when the coating is subjected to cryogenic temperatures in vacuum.

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APPENDIX A

EXPERIMENTAL

EXPERIMENTAL

Acid Phosphate-Treatment Procedure

Pigment A-413-1 (control): Ninety (90) g of Cake 1* was slurried with 50 g of distilled water for 15 min and filtered. The resultant Cake 2 was redispersed in 50 g of water, slurried 15 min, filtered and dried for 18 hr at 212°F. The product was designated Cake 3.

Pigment A-413-2 (control): Ninety (90)g of Cake 1 was treated identically to A-413-1 except that it received an additional redispersion in water. The final product was designated Cake 4.

Pigment A-413-3 (phosphate-treated): Ninety (90)g of Cake 1 was slurried for 15 min with 50 g of a 1% solution of NaH_2PO_4. The resultant Cake 2 was redispersed in 50 g of 1% NaH_2PO_4, slurried 15 min, filtered and dried for 18 hr at 212°F. The product was designated Cake 3-P1.

Pigment A-413-4 (phosphate-treated): Ninety (90)g of Cake 1 was treated with 1% NaH_2PO_4 identically to A-413-3 except that it received an additional redispersion in 50 g distilled water. The final dried product was designated Cake 4-P1.

Pigment A-413-5 (phosphate-treated): Ninety (90)g of Cake 1 was slurried for 15 min with 50 g of a 3% solution of NaH_2PO_4. The resultant Cake 2 was redispersed in 50 g of 3% NaH_2PO_4, slurried 15 min, filtered and dried for 18 hr at 212°F. The product was designated Cake 3-P3.

Pigment A-413-6 (phosphate-treated): Ninety (90) g of Cake 1 was treated with 3% NaH_2PO_4 identically to A-413-5 except that it received an additional redispersion in 50 g of distilled water. The dried product was designated Cake 4-P3.

Owens-Illinois 650-Resin Paints

Owens-Illinois 650-resin-based paints were prepared from each of the pigments described above by grinding 15 parts of the

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*Procedure used to silicate ZnO is given in Section IV.A.2.

28% O-I 650-resin solution in ethanol with 10 parts of pigment by weight (the PVC was approximately 32% in all six cases).

APPENDIX B

THE MANUFACTURE OF S-13G
THERMAL-CONTROL COATING

IIT Research Institute Specification
February 28, 1969

THE MANUFACTURE OF S-13G
THERMAL-CONTROL COATING

1.0 General Considerations

S-13G thermal-control coating is a dispersion of potassium silicate-treated zinc oxide (ZnO) pigment in a polydimethylsiloxane elastomer vehicle, with volatile solvents employed as required. A 4-gal batch of paint is chosen as appropriate to the current demand for the material, one that is sufficiently large to approximate the effect of mixing and milling upon even larger, industrial-sized batches, if required. The containers and apparatus specified are in the 5-gal range. The formulas and processes given in this specification are all in U. S. units.

2.0 Manufacture of S-13G Pigment

2.1 Materials and Sources

The ingredients required and their sources are:

- Zinc oxide (SP500 grade)	New Jersey Zinc Company Palmerton, Pennsylvania
- Potassium silicate (PS-7 electronic grade)	Sylvania Electric Company Tonawanda, Pennsylvania
- Sodium acid phosphate (monobasic NaH_2PO_4)	Any manufacturer of c.p. grade
- Distilled water	

2.2 Equipment and Sources

The following equipment, facilities, and apparatus are required (equivalent facilities are acceptable):

- Double boiler, stainless steel (Model K-7301, 7-qt capacity)	Edward Don & Company Chicago, Illinois
- Gas-fired burner (plate) heavy duty	Must withstand weight of about 60 lb)

- Motorized laboratory stirrer (stainless steel shaft & paddle, Model 3002)	Grenier & Company Chicago Ridge, Illinois
- Scale, capacity of 50 lb	
- Scale, laboratory balance capacity of 500 g	
- 4 Büchner funnels,* size 5, No. F-8220 (to fit 18.5-cm filter paper)	Coors Porcelain Golden, Colorado
- 4 Filter flasks,* 2-liter capacity, fitted with rubber collars	
- Vacuum pump, mechanical (for filtering) Cenco Hyvac 91105 or equal	
- 18.5-cm filter paper (Whatman 541 or S&S602)	
- 3/4-mil unplasticized Mylar sheet	
- Circulatory air oven (Blue M OV500 C-2, or equal)	

2.3 Silicate-Treatment Procedure

Twelve (12) lb of SP500 ZnO (bulking at 0.257 gal), 21 lb of PS-7 potassium silicate solution (bulking at 1.91 gal), and 3.25 lb (0.39 gal; 1500 ml) of distilled water are reacted together in a double boiler (see Note 1) in the following manner.

The ZnO and PS-7 potassium silicate are heated to 150 ± 5°F. The ZnO is then added slowly under high-speed agitation (see Note 2); high-speed mixing is maintained for 30 min. The heat is then removed and the hot water jacket is replaced by cold (tap). Exactly 13.25 lb (6-1/2 qt; 1.625 gal) of distilled

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*It is suggested that 4 vacuum filtering stations be constructed to operate from the one pump with an appropriate trap to protect the pump.

water is immediately added and the resultant slurry is mixed for 15 min with high-speed agitation. The slurry is then filtered through Büchner funnels (see Note 3).

The filter cake (Cake 1) is removed, wrapped in unplasticized Mylar, and allowed to "sweat" for 18 hr at 75 ± 8°F (see Note 4). After "sweating" for 18 hr, the cake is redispersed in 13.25 lb (6-1/2 qt; 1.625 gal) of distilled water, mixed with high-speed agitation for 15 min and again filtered through Büchner funnels.

The filter cake (Cake 2) is immediately removed and added to 13.25 lb (6-1/2 qt; 1.625 gal) of a 1% solution of NaH_2PO_4 (monobasic); it is then mixed with high-speed agitation for 15 min and filtered through the Büchner funnels.

The filter cake (Cake 3) is again redispersed in 13.25 lb (6-1/2 qt; 1.625 gal) of 1% NaH_2PO_4, mixed with high-speed agitation for 15 min and filtered through the Büchner funnels.

The filter cakes (Cake 4) are then spread on aluminum-foil sheets and placed in a circulating-air oven to dry for 18 hr at 230°F. After the treated-pigment cakes have partially dried in the oven (~1-1/2 hr), they may be easily crumbled to a powder by hand (use <u>clean</u> laboratory gloves) to facilitate drying.

The moisture content should be reduced to less than 0.1% (as determined by weight loss measurements after heating for 18 hr at 300°F). The potassium silicate-treated ZnO pigment should be stored in a thoroughly dry condition. It should neither be dry ground nor reheated to temperatures in excess of 230°F.

2.3.1 <u>Note 1</u>: The lower portion of the double boiler is filled with water sufficient to rise to the outside of the upper portion when in use. In the Model K-7301 double boiler, 7 liters of water are used to bring the water level to a 3-1/2 in. depth.

2.3.2 <u>Note 2:</u> The speed and location of the paddle should be adjusted to produce mixing without "dead spots."

2.3.3 <u>Note 3:</u> Four (4) Büchner funnels attached to 1 vacuum manifold are ideal. The filter cakes are built up until the funnel is half filled. The funnels are then emptied.

2.3.4 Note 4: The filtrate should be discarded and the equipment cleaned thoroughly to prevent hardening of the silicate/ZnO materials.

3.0 Manufacture of S-13G Paint

3.1 Materials and Sources

Silicate-treated ZnO pigment	Per paragraph 2.0, this document
RTV-602 Silicone potting compound	General Electric Company Silicone Products Dept. Waterford, New York
Zinc silicate SI-120	Alpha Inorganics Beverly, Massachusetts

Toluene
Isopropanol
Butyl acetate
Xylene
Butanol

Mixed thinners:

T-25	Toluene	40%	(by volume)
	Isopropanol	50%	
	n-Butanol	10%	
X-99	Toluene	40%	(by volume)
	Xylene	20%	
	Isopropanol	20%	
	n-Butanol	15%	
	n-Butyl acetate	5%	

3.2 Equipment and Sources

Scale, capacity of 50 lb
Liquid measures

Stainless steel containers, mixing, 5 gal capacity

Mill, ball, porcelain, 2 to 5 gal capacity; No. 3 jar, self contained unit, 8-gal gross capacity (4.8-gal net), 1/2 H.P., 3-phase motor; high density porcelain media, covers, gaskets, etc.	Paul O. Abbé

Mills, ball, porcelain, 1 pint capacity; No. OO B. F. jar with high density media, covers, gaskets, etc.	U. S. Stoneware
Variable speed, motor-driven rollers (for pint & quart batches)	Paul O. Abbé U. S. Stoneware
Paddle mixer (for premixing). A Sears Roebuck or Montgomery Ward drill press fitted with impeller will suffice.	

3.3 S-13G Paint Manufacturing Procedure (2-gal Batch)

The paint is prepared in 2-gal batches by milling in a Paul O. Abbé Company"s No. 3 jar mill. The grinding media consists of high-density porcelain balls that are charged to the mill at slightly less than 1/3 the apparent volume. The premixed paint is then added until the balls are completely covered (until the mill is charged with bulk to approximately 30% by volume). The premix is prepared as follows.

Twelve and one-half (12.5) lb of silicate-treated ZnO, 6 lb of RTV-602 and 2 pints of T-25 thinner are premixed in a "pony" mixer, dough mixer, or suitable heavy-duty paddle mixer to minimize the grinding required and prevent grinding of dry powder, and hence to optimize the initial reflectance and space-ultraviolet stability of the paint.

In the event that a suitable mixer is not available, the premix may be made by first removing the balls from the mill, adding the premix components listed above to the mill and running it without balls for 1 hr. This will adequately "wet" the pigment with the vehicle.

After premixing, the slurry is charged to the mill along with 4 pints of the T-25 thinner and 2 oz of zinc silicate. Add porcelain-ball charge to mill and grind at 60 rpm; (for No. 3 Abbé mill, 75% of critical speed for ball mills in general). The "grinding" is best controlled "by ear." The pebbles or balls should be heard "clicking" or "rolling" but never "crashing." If no clicking whatever is heard, more of the solvent portion of the total paint mix must be employed in the grind. The paint should be ground at as high a viscosity as the mill will permit and still have satisfactory flow, material transfer, and adequate shear. Count grid time from start of "clicking." Remove sample after the 4-hr grind and prepare specimen by rub-out, draw-down, or spraying. (Grind another hr if required).

Discharge contents of ball mill. Add 2 pints of the T-25 thinner to empty mill; grind 5 min and discharge contents to parent batch. Mix with "pony" mixer, or paddle mixer for 5 min. Determine viscosity with a No. 4 Ford Cup; if viscosity is greater than 30 sec, add T-25 thinner to a viscosity of 25 sec (should not require more than 5 fl oz). Determine weight/gal; if satisfactory, strain and package in glass containers using sheets of unplasticized Mylar between cap and container. Store in refrigerator at 42°F (or less).

4.0 Specifications

4.1	Pigment volume concentration (PVC):	32%
4.2	Weight/gal:	11.8 to 12.3 lb
4.3	Viscosity (fresh):	25 to 30 sec No. 4 Ford Cup (34 to 40 sec No. 2 Zahn)
4.4	Dried coating appearance:	Eggshell or semi-gloss, white, lightly stippled texture
4.5	Adhesion:	Requires use of a silane-coupling-type primer (General Electric"s SS-4044) applied at a dry film thickness of 0.05 mil to 0.5 mil, (not over 0.35 mil when hardware will be subjected to cryogenic temperatures).
4.6	Pot life:	Not over 1 hr when catalyzed with General Electric's SRC-05 in a ratio of 10 parts S-13G paint by weight to 1 part by weight of a 1% solution of SRC-05 in toluene (or 100 parts S-13G to 1 part of 10% solution SRC-05 in toluene).
4.7	Shelf life:	S-13G paint is usable as long as no gelation or "stringiness" is apparent in the paint. Paint 2 yr old has been successfully applied and shown to be stable to space ultraviolet radiation. A shelf life

of about 4 months is currently being achieved. Refrigeration greatly extends the shelf life of the S-13G coating.

4.8 Solar absorptance:	The solar absorptance of S-13G as a function of film thickness is shown in Figure B1. The data represent 28 measurements at thicknesses from 3-1/2 to 9-1/4 mils. The scatter in the data provides a general level of confidence as indicated by the graphical representation. The data will be accurate for correctly manufactured paint.
4.9 Total hemispherical emittance:	The total hemispherical emittance of S-13G films of 4-mils thickness or greater should be 0.88 ± 0.05 at a temperature of 300°K.

5.0 Application Procedure

5.1 Surface Preparation

The metal surface to which the primer is applied should in all cases be degreased. In the case of aluminum, etching with 5% NaOH, followed by rinsing, followed by de-smutting with 15% HNO_3, the process repeated until the surface is "break-free" to water, is required to ensure adhesion. Many aerosopace companies have standard "de-ox" processes of equal value. For magnesium alloys, complete Dow 17 treatment provides an excellent surface. For other metals, solvent cleaning after sanding is sufficient preparation.

Adhesion of S-13G to epoxy-fiberglass substrates is marginal (even when applied over the best of the silane-coupling-agent primers). (The loss of adhesion is between the substrate and the silane primer). Fiberglass substrates should be first lightly sanded and then solvent wiped; they should then be coated with 1 mil (± 0.25 mil) of MIL-P-23377A epoxy polyamide primer. After an overnight dry of the epoxy primer, SS-4044 is applied at a dry-film thickness of 0.05 to 0.35 mil and, after a minimum of a 1-hr air-dry, the S-13G may be applied to the customary thickness (8 to 10 mils).

5.2 Primer Application, General Electric SS-4044

A silane coupling agent is employed as the primer and is necessary for all applications of S-13G. General Electric's SS-4044 primer is the material routinely furnished for use under

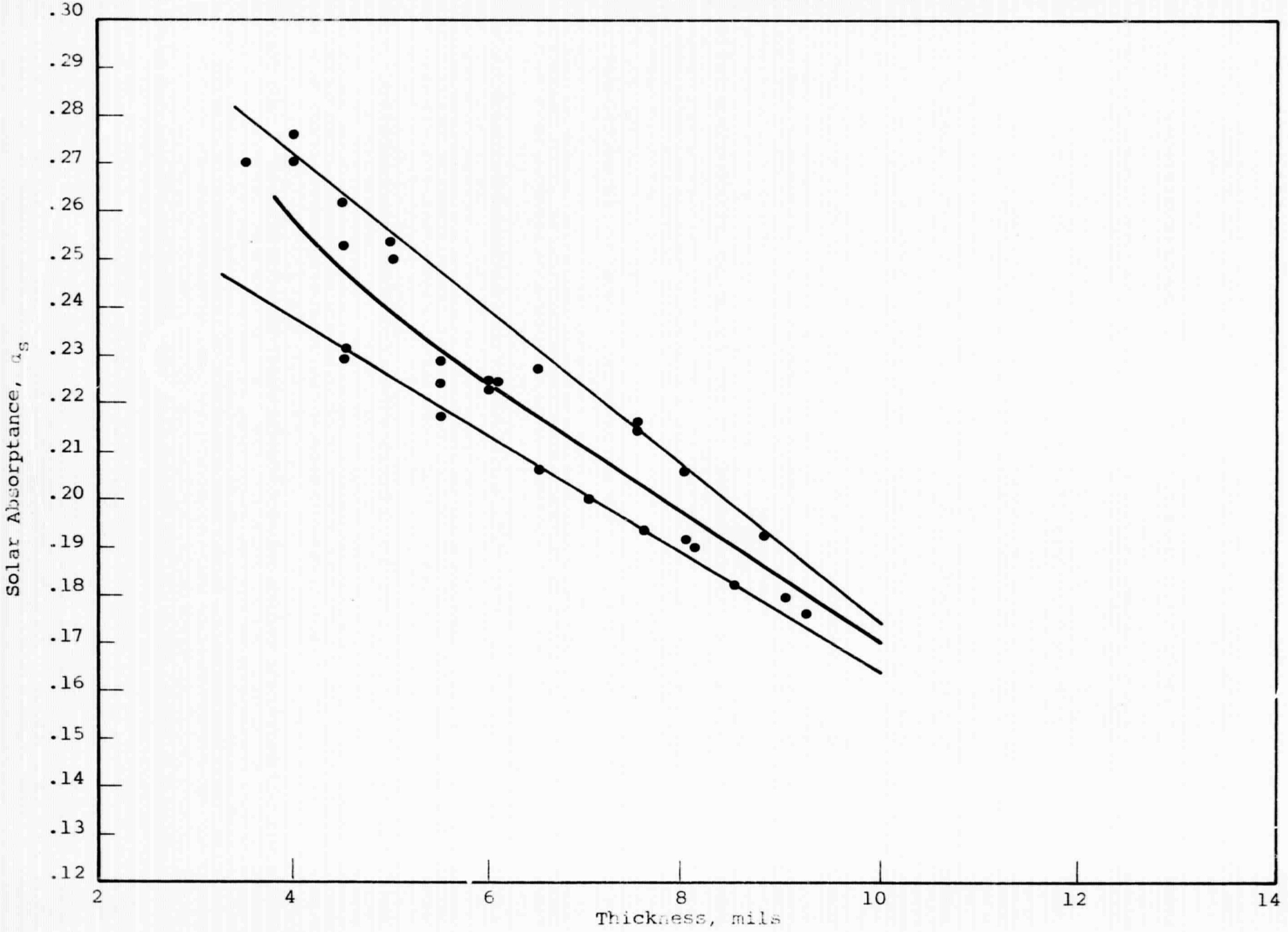

Figure B1: SOLAR ABSORPTANCE OF S-13G AS A FUNCTION OF THICKNESS

S-13G. It is applied with a spray gun fitted with a very small fluid jet. (For the Paasché AUT Air Brush, a No. 1 jet is used as compared with a No. 3 jet for application of S-13G). The SS-4044 should be applied from 0.05 mil to 0.35 mil in dry film thickness for optimum results. Over 0.5 mil can seriously impair adhesion in cryogenic applications. Other silane coupling agents such as General Electric's SS-4155 or Dow Corning's A-4094 will also serve as effective primers for S-13G. The same precautions against too thick a coating must also be observed with these materials. The primer must in all cases be allowed 1 hr of drying before application of S-13G; an overnight air-dry is preferred.

5.3 Cure of S-13G, General Electric SRC-05

S-13G paint requires the addition of an amine catalyst in order to cure. General Electric's SRC-05 catalyst is supplied and is diluted with toluene as either a 10% solution or a 1% solution. The 10% solution is added to the S-13G in the ratio of 1 part by weight of catalyst to 100 parts by weight of paint. The 1% solution is used in the proportion of one part by weight of catalyst to 10 parts of paint. This more diluted form of catalyst is recommended for touchup work where only a small amount of paint is used at any one time.

After catalyzing, S-13G is best reduced with X-99 thinner (see Section 3.1) to a viscosity of 15 to 18 sec No. 4 Ford Cup (24 to 30 sec No. 2 Zahn Cup) in order to obtain as smooth a spray application as possible. However, no more paint should be catalyzed than can be applied in 1 hr. The optimum cure is obtained if an induction period of 15 min after catalyzing is allowed before beginning the spray application. This leaves only 45 min of actual spray time after the induction period.

5.4 S-13G Paint Application

Once the application of S-13G is undertaken it should be applied to its full thickness within 5 hr time or, if impossible to complete in a 5-hr period, allowed to cure 72 hr before adding any further coating. The tendency of the polymer is to swell on recoating before complete cure and thus sets up strains in the dried film. With a 72-hr dry, the cure is complete to the point where swelling is not observable.

6.0 Typical Silicated-ZnO Pigment Prep Sheet

Materials	Weight	Remarks
SP500 Lot No. ____	12 lb	Preheat liquids to 150°F Add ZnO, mix 30 min
PS-7 Lot No. ____	21 lb	Final temperature, ____°F
H_2O, distilled	1500 g	Remove heat

CAKE 1

Change lower boiler to cold water jacket.
Add H_2O, distilled -- 13 pints, mix 15 min, filter.
Wrap filter cakes in Mylar for overnight "sweat", (16 hr)

CAKE 2

Add sweated cake to H_2O, distilled -- 13 pints, mix 15 min, filter.

CAKE 3

Add filter cake No. 2 to 1% NaH_2PO_4 -- 13 pints, mix 15 min, filter.

CAKE 4

Add filter cake No. 3 to 1% NaH_2PO_4 -- 13 pints, mix 15 min, filter.

Place filter cake No. 4 on aluminum foil in circulating oven.

Break up well with clean hands while still slightly moist.

Dry overnight at 230°F.

Store in clean dry area.

Record yield.

Identify batch.

Pigment density (by pycnometer) 38 lb/gal.

7.0 Typical S-13G Paint Prep Sheet (2-gal Batch)

Item	Volume	Weight	Remarks
S-13G Pigment Lot No. ____		12-1/2 lb	Mix pigment, vehicle and thinner without balls for 1 hr.
G.E. RTV-602 Lot No. ____		6 lb	
T-25 Thinner	2 pints		
T-25 Thinner	4 pints		Add balls, begin grind. Listen for grind "clicking." Count grind time from start of "clicking."
Zinc Silicate		2 oz	
Check grind with draw-down or spray-up.			Grind 4 hr to first test. (Possibly another hr needed for adequate grind).
Empty into mixing pail place under paddle.			
To mill, add			
T-25 Thinner	2 pints		Grind 5 min only, then add this rinse to the main batch Mix paint 5 min. Determine viscosity with No. 4 Ford Cup over 30 sec. Add T-25 thinner until viscosity is about 25 sec, (i.e., about 5 fl oz). Determine wt/gal; if O.K., strain and fill.

Package the paint in glass jars with a sheet of unplasticized Mylar between the cap and the jar.

APPENDIX C

RESULTS OF STUDY OF S-13G CRYOFAILURE AT BENDIX AEROSPACE SYSTEMS DIVISION

RESULTS OF STUDY OF S-13G CRYOFAILURE AT BENDIX AEROSPACE SYSTEMS DIVISION*

This study was undertaken as a result of the catastrophic loss of adhesion suffered by S-13G (primer/substrate failure) when cycled at LN_2 temperatures in vacuum. Because of its cogency to the study work reported herein, the results of the cryo-failure study are presented here.

(1) The major factor in the loss of adhesion during cryovac tests at nitrogen temperatures is the thickness of the primer employed. We advise a primer thickness of 0.25 ± 0.10 mil when General Electric's SS-4044 primer is employed. The primer should be air-dried 24 hr prior to application of S-13G.

(2) Our recommendation is that S-13G be applied to full thickness within 5 hr maximum total coating application time; if not completed in that time, a full three days of cure time should be allowed before repainting.

(3) The adhesion of S-13G paint films definitely improves with age; only a slight, if not significant, gain is achieved by aging the primer coating. The final coating system should be aged not less than 7 days prior to thermal (cryogenic)-vacuum simulation tests. Longer aging is required for applications involving primer thicknesses in excess of 0.35 mil. For example, 90 days of aging of S-13G is required if the primer thickness exceeds 0.6 mil and if cryo testing is required.

(4) The use of other "primers" e.g., General Electric's SS-4155, Dow Corning's DC4098 and Z6020, with S-13G

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*IITRI Project U6056, Bendix Contract SC-0265, Subcontract under NAS9-5829.

results in good performance but no real improvement over General Electric's SS-4044 primer when a thickness of 0.25 mil is maintained.