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Final Report

PASSIVATION OF PIGMENT PARTICLES FOR THERMAL CONTROL COATINGS

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Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
HUNTSVILLE, ALABAMA

CONTRACT NAS8-21270



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PREFACE

The work reported in this final report was carried out under NASA Contract NAS8-21270, SRI Project 7083, and is based on our studies of surface redox couple additives and on plasma calcining of zinc ortho-titanate pigments. Earlier work on the project has been completely described in the following reports:

- Interim Final Report April 1974
- Interim Final Report June 1973
- Interim Technical Report No. 5 August 2, 1974
- Interim Technical Report No. 4 February 5, 1971
- Interim Technical Report No. 3 May 8, 1970
- Interim Technical Report No. 2 July 30, 1969
- Interim Technical Report No. 1 August 15, 1968

In addition a series of 33 letter reports, covering the period from May 24, 1972 to July 31, 1975, were issued, presenting our month-by-month progress.

In view of the extensive documentation of past work already presented to NASA, a brief background review has been deemed sufficient for the presentation of our current results. This review is found in Section II of the report.

ACKNOWLEDGMENTS

The authors are indebted to many people in government service, at IITRI, and at SRI for their participation in this research program. In particular we wish to thank both Daniel W. Gates (George C. Marshall, Space Flight Center) and William F. Carroll (Jet Propulsion Laboratory, California Institute of Technology) for their constructive suggestions and guidance during the course of the program.

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I INTRODUCTION

The emphasis during this final effort in the study on passivation of pigments was on preparation and testing of pigments and pigmented paints for evaluation of their photostability. The project was carried out under NASA Contract NAS8-21270, during the period from April 1974 to September 1975.

Our specific objectives in this effort were:

- To identify the most suitable redox couple additive for stabilizing a zinc orthotitanate pigment produced at the Illinois Institute of Technology Research Institute (IITRI) by coprecipitation of zinc and titanium oxalates.
- To investigate the additive concentrations and methods of application to the pigment surface to obtain an optimum passivated pigment.
- To evaluate the optimum conditions for plasma-calcining of the coprecipitated pigment provided by IITRI, and to plasma calcine a quantity of the pigment for additive treatments.
- To provide IITRI with a series of surface additive treated pigments for preparation of pigment and paint samples for electron spin resonance measurement (ESR) at SRI and space simulation tests.
- To assemble the results from the ESR and space simulation tests to evaluate (a) the efficacy of the redox additives for passivating pigments and paints, and (b) the potential of the ESR technique as used at SRI compared to spectral

reflectance measurements from space simulation tests for screening the photostability of thermal control pigments and paints.

- To evaluate the ESR technique for quality control of pigments and paints.

In Section II, we review the technical background for our current research. In Section III, the preparation of a matrix of 48 samples consisting of pigments and pigmented paints is described. The results obtained from testing these samples by ESR and by in situ spectral reflectance measurements in space simulation tests at IITRI are presented in Section IV. Our conclusions and recommendations for further research are given in Sections V and VI, respectively.

II TECHNICAL BACKGROUND

At the initiation of this program, zinc orthotitanate had been identified as a promising candidate pigment for thermal control coatings.^{1,2} The pigment can be made reasonably stable against damage under vacuum-ultraviolet conditions provided the surface is covered with a silicate coating or heated in a plasma-arc.³ Zinc orthotitanate that has been treated with potassium ferro-ferricyanide has also shown some resistance to proton damage.¹ The selection of the iron cyanide redox couple for zinc orthotitanate was based on work performed on ZnO, but it does not necessarily follow that the redox couple suitable for preventing ultraviolet damage in ZnO will be the most effective couple for proton or ultraviolet stabilization of zinc orthotitanate.

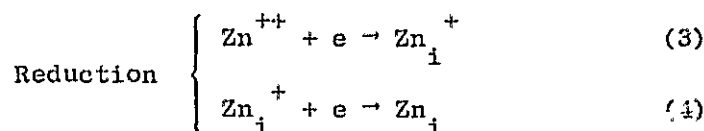
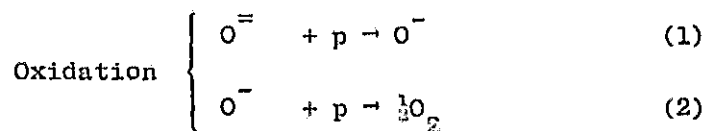
This research was therefore initiated to identify the optimum redox couple surface additive on zinc orthotitanate that will provide stability against ultraviolet radiation in vacuum.

The surface additive approach was originally developed for NASA to increase the stability of ZnO against damage under vacuum-ultraviolet conditions⁴ and to passivate the pigment against photointeractions with the polymer binder.⁵ This approach has also been used in an industrially supported program at SRI to passivate TiO₂ and to decrease chalking of paints containing this pigment.

Mechanism of Radiation Damage

Before discussing the mechanism of the protective action of surface additives, we will review the probable mechanism of radiation damage. In the case of ultraviolet radiation, photodamage to pigments is initiated by electronic charge carriers, electrons and holes, that are produced

when the semiconductor pigment absorbs photons of energy equal to or greater than the bandgap. The chemical damage ensues from interactions of the electrons and holes with the lattice ions. For example, in ZnO, the following reactions are believed to occur:



In reactions (1) and (2), the photoproduced holes p oxidize lattice oxygen ions O^{\equiv} to oxygen, which may leave the solid. In reactions (3) and (4), the photoproduced electrons e reduce the zinc lattice ions Zn^{++} and result in excess zinc, which becomes interstitial zinc, Zn_i^+ or Zn_i . The coloration of the pigment is believed to be caused by the excess interstitial zinc. First, the excess zinc ionizes to give conduction band electrons (grey color). Secondly, the excess zinc, which has limited solubility in the lattice, either causes mechanical strain in the lattice or it precipitates at defects, such as dislocations (yellow color).

In zinc orthotitanate, lattice titanium ions, Ti^{+4} , will be reduced by photoproduced electrons according to



and give rise to the Ti^{+3} color centers (or to the electrical equivalent, oxygen ion vacancies) with spectral absorption at about 0.9 nanometers (nm), and to color centers due to lattice imperfections with spectral absorption at about 0.4 nm. Because the photoproduced species Zn_i^+ and

Ti⁺³ are paramagnetic, their presence can be detected with great sensitivity by the electron spin resonance technique (ESR).

Mechanism of Surface Additive Protection

Inorganic surface additives increase the photostability of pigments by serving as recombination centers for the photoproduced charge carriers, which otherwise would produce chemical damage. The mechanism of the process of recombining electrons and holes can be illustrated by the ferro/ferricyanide (Fe⁺⁺/Fe⁺⁺⁺) redox couple that has been found effective in protecting ZnO.



No net change in the amount of the two forms of the additive occurs, and the photoproduced electrons and holes have been recombined and hence do not react chemically with lattice ions.

For a recombination center to be effective, the following requirements must be met: (a) the surface additive must be a one-equivalent redox couple and must be present in both valence states; (b) the oxidized valence state must have a high capture cross section for electrons; (c) the reduced valence state must have a high capture cross section for holes; (d) the surface state energy level of the additive must be in the forbidden gap of the semiconductor pigment; and (e) the additive must be chemically and photochemically stable and nonvolatile.

In the case of ZnO, we tested numerous inorganic surface additives. We found that the iron cyanide couple satisfied the above list of requirements. We also found a correlation between the electron capture cross section and the standard redox potential of the additive couple.⁶ By

determining the surface state energies of the various additives on ZnO, we concluded that a favorable energy level for an effective additive, such as iron cyanide, is 0.1 eV below the bottom of the conduction band.⁶

Very low surface concentrations of a surface additive can provide protection against photodamage. In ZnO, significant protection was observed at 10^{-3} monolayers of the iron cyanide additive.⁷ The effective surface coverage is probably much lower than this value, since the iron cyanide is probably not completely dispersed but rather exists as surface agglomerates of much lower dispersion.

The high recombination efficiency at such low surface coverages of additives can be accounted for on the basis that the charge carriers have long diffusion paths, about one micrometer in ZnO. Since this distance is the order of magnitude of the diameter of most pigment particles, it is evident that large volumes of the crystal can be swept free of charged carriers.

Pigment-Binder Interactions

The surface additive also serves to decrease the photointeractions at the pigment surface between the photoexcited pigment and the binder of a thermal control coating. In particular, the electronic holes produced by irradiation tend to strongly oxidize some organic components of the binder.⁵ In the case of ZnO, we determined the relative oxidizability (hole capture cross section) of several solvents for the Owens-Illinois 650 resin (OI-650) because there was evidence that some impurity in the resin resulted in poor photostability of the coating. By use of electrochemical and ESR techniques, we showed that solvents, such as alcohol and dioxane, captured holes and enhanced ZnO photodecomposition, whereas ethyl acetate, acrylonitrile, and pentane were essentially stable.⁵ Moreover, we showed that the iron cyanide surface additive substantially decreased the damage caused by the presence of alcohol. The OI-650

resin has recently been modified to a more elastomeric resin, CI-650G, in which most of the terminal hydroxyl groups have been methylated. However, a paint made of the modified resin is still degraded in vacuum ultraviolet because of interaction of the resin with Zn_2TiO_4 .³

Degradation Measurement Techniques

The ESR technique is well suited for investigating the influence of surface additives on photodamage to pigments such as zinc orthotitanate. This technique permits study of the characteristic photodamage centers (Zn_i^+ and Ti^{+3}) in the pigment as powders and pigmented coatings.⁵⁻⁸

The ESR technique has also been used extensively in our laboratories to follow the effects of plasma-arc treatment on zinc orthotitanate² and charge transfer processes during reaction and chemisorption of gases.⁸ In zinc orthotitanate samples that we have examined, the ESR spectra contain two principal lines: one, at a g value of 1.94, associated with the donors (Zn_i^+ and/or conduction electrons) usually found in ZnO, and the other at a g value of 1.974 probably associated with the Ti^{+3} species.² As part of our study of the passivation of pigments, we have investigated the manner in which the intensity of these lines increases when the pigment is irradiated under vacuum. In an examination of the effects of plasma-arc conditions on the zinc orthotitanate product quality, we found that the intensity of these two ESR lines on ultraviolet irradiation showed some correlation with the reflectance properties of the product.²

Quality Control

Quality control is an important factor in assuring that the manufactured thermal control pigments and paints will perform as expected. Moreover, it is desirable that measurements of performance be made rapidly and inexpensively. It appears that the ESR technique is well suited to this application for (1) measuring photostability and (2) detecting certain kinds (paramagnetic) impurities.

III EXPERIMENTAL PROCEDURE

The preparation and testing of pigments and pigmented paints for evaluation of photostability was carried out in cooperation with IITRI according to an experimental procedure divided into six steps, as follows:

Step 1--Preparation of pigment LH-111(6-12) by IITRI.

Step 2--Plasma calcining of some of pigment LH-111(6-12).

Step 3--Surface additive treatment of the "as-received" and plasma-treated pigments with redox couple additives.

Step 4--Preparation of specimens at IITRI for evaluation of photodamage by space simulation tests at IITRI and by ESR tests at SRI.

Step 5--ESR evaluation at SRI of photodamage to pigments and pigmented paints.

Step 6--Space simulation tests at IITRI to evaluate photodamage to pigments and pigmented paints.

The six steps of the procedure are described in detail below.

Step 1--Preparation of Pigment

IITRI prepared the LH-111(6-12) Zn_2TiO_4 pigment using the following: Mixed oxalates having a mole ratio of 2.05 Zn:1.00 Ti were precipitated in an aqueous medium by reaction between a $ZnCl_2$ - $TiCl_4$ mixture with oxalic acid, at $90^\circ C$, over a 4-hr period. The precipitate was filtered by repeated hot water washing until the pH of the filtrate was 7. The powder was dried at $80^\circ C$ for 18 hr. The dried powder was precalcined

at 600°C for 2 hr to remove decomposition volatiles, i.e., CO, CO₂, and H₂O, and to achieve partial conversion to Zn₂TiO₄. The powder was then calcined at 1200°C for 2 hr by "flash" calcination, i.e., direct insertion of powder (fused quartz container) into a furnace at 1200°C, and removed from furnace. The resultant powder was hand-pulverized in a porcelain mortar and crucible to reduce the agglomerates. The precipitate was prepared in four batches of approximately 1200 g each, which was the capacity of the reaction vessel. These batches were designated LH-107, LH-108, LH-109, and LH-110. Precalcination (600°C) was conducted as two batches: LH-107 + LH-109 and LH-108 + LH-110. The final 1200°C calcination was done in one large batch to produce about 2000 g of Zn₂TiO₄ pigment. This pigment is designated LH-111(6-12).

Step 2--Plasma Calcining of Pigment LH-111(6-12)

The original application of the ultrahigh temperatures available within a plasma flame to the calcining of pigment particles, was intended to provide a short period of exposure to a very high temperature environment, for the purpose of annealing out defects without promoting further agglomeration and sintering. Ideally, an aerosol of pigment particles would pass through the reaction chamber without affecting the particle size distribution.

In our earlier work, the pigment material B-229 was supplied with a mean particle diameter very close to the optimum size for maximum light scattering ($\approx 0.5 \mu\text{m}$). The LH-111(6-12) pigment produced by IITRI under the above processing procedure is quite different in particle size. Figure 1 illustrates differences between the LH-111(6-12) and the earlier pigment material B-229. The effect of the larger particle size on surface area and settling rate are shown in Table 1.

Table 1

COMPARISON OF Zn_2TiO_4 PIGMENT PARTICLE SIZE

IITRI Pigment	Settling Rate (cm/sec)	Surface Area (m^2/g)	Average Particle Diameter (nm)
LH-111(6-12)	0.530	0.17	6.5
B-229	0.053	0.75	1.5

The ten times faster settling rate of pigment LH-111(6-12) necessitated major changes in the plasma calcining apparatus. Figure 2 illustrates these changes, which included the following: The particle dispenser was removed; the particles were allowed to exit at the bottom of the reaction chamber; a bag filter was replaced by a single cyclone separator; and the angle of the particle inlet tube was reduced to provide a longer residence period for these larger particles.

A series of runs were made at different chamber temperature (ΔT) to pinpoint the optimum treatment temperature for the LH-111(6-12) pigment powder in the modified apparatus. The resulting ESR peak intensity of the resonance line at $g = 1.974$ after UV treatment (Figure 3) was used as the criterion for choosing the optimum ΔT setting for the new pigment. The area between the solid and broken lines indicates the UV susceptibility of the 1.974-line. Our earlier work indicated that the most stable pigment material showed the least change after UV treatment. Within the test set of six treatment temperatures, the $\Delta T = 1620^\circ C$ material showed the smallest percent change in the 1.974-line. By coincidence, this was close to the optimum temperature ($\Delta T = 1670^\circ C$) for the earlier, smaller particle size pigment. Because of changes in configuration between these two plasma calcine chambers, the ΔT values are not strictly comparable.

Step 3--Surface Additive Treatment

Information on the redox couple additives, their concentration in the solutions, and their fractional surface coverage on the pigment are summarized in Table 2 under the heading "Additive."

The three additive redox couples studied were $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$, $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$, and $\text{Ce}^{+3}/\text{Ce}^{+4}$. The solution added to a pigment aliquot contained equal molar concentration of the salts in two valence states of a given redox couple, and the total concentration of both valence states at three concentration levels is listed in Table 2. The salts used were $\text{K}_4\text{Fe}(\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_3\text{IrCl}_6 \cdot 3\text{H}_2\text{O}$, K_2IrCl_6 , $\text{Ce}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$, and $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$; all were of reagent grade. The solutions of the iron cyanide [$\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$] and iridium chloride [$\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$] additives were at pH 6 or 7, while the solution of the cerium additive ($\text{Ce}^{+3}/\text{Ce}^{+4}$) was at pH 1 with perchloric acid so as to maintain the solubility of the cerium ions. Along with these nine additive solutions, the pigments were also treated with three other solutions: water and 0.1N HClO_4 as blanks, and 0.1N HF as an alternative acid.

These twelve solutions were individually applied both to the pigment LH-111(6-12) "as received" from IITRI and to this pigment after it had been plasma calcined. Just enough solution (12 ml) containing the dissolved additives was applied to the dried pigment (31 g) to produce a thick slurry, which was then dried for 3 hr at 150°C, unless otherwise specified. Thus, almost all the redox additives in the solution were deposited on the pigment surface. Preliminary tests had indicated that if not removed, the HClO_4 could oxidize the OI-650 resin paint binder during the curing process. Therefore, the pigments treated with solutions containing HClO_4 (Pigments No. 2, 4, 5, 6 in Table 2), were heated in air for 3 hr at 250°C to drive off excess HClO_4 .

The fractional monolayer surface coverage, θ , of additive in both valence states on the pigment was calculated from the amount of additive per gram of pigment and from the measured BET surface area of $0.17 \text{ m}^2/\text{g}$, by assuming that the surface site density on the pigment is $10^{15} \text{ sites/cm}^2$, and that the redox couple additive is uniformly dispersed on the pigment surface.

Step 4--Preparation of Specimens for Evaluation of Photodamage

Twenty-four additive-treated pigments were prepared at SRI: twelve pigments based on the "as received" LH-111(6-12) pigment, and twelve pigments based on the pigment after plasma calcining. These twenty four pigments were sent to IITRI, where samples of pigment powders and paints were prepared for evaluation of photodamage by ESR and space simulation tests.

a. Powdered Pigments

The twenty four pigments were individually slurried with water and sprayed onto hot aluminum coupons placed in the middle of a large heated petri dish. The pigment was essentially dry on contact with the hot surface. The pigment-covered coupon was used in space simulation tests at IITRI, and the excess dried pigment that adhered to the petri dish was scraped into vials for ESR examination at SRI. Thus, the loose pigment and that on the coupon are comparable in treatment and composition of the additives.

b. Paints

Paints were prepared by individually ball-milling each of the twenty four pigments into OI-650G silicone resin. The paints were sprayed onto aluminum coupons in a heated petri dish, baked at 160°C for 16 hr, and the excess paint on the petri walls was scraped into vials for ESR analysis at SRI.

Step 5--ESR Evaluation of Photodamage

ESR was used to measure the paramagnetic centers resulting from irradiation of pigments and pigmented paints in vacuum.

The pigments or paints were introduced into a quartz tube (3 mm ID) in a column about 4 cm high. This tube was fused to a Vac-Ion pump (Varian, 2 liters/sec) and to a roughing pump (oil diffusion with two traps in liquid nitrogen). The pigment was heated at 150^o C for 1 hr while pumping to about 10⁻⁵ torr, then the Vac-Ion pump was started, and the sample-Vac-Ion assembly was sealed off from the roughing pump.

The additive-treated pigments or paints were maintained at low pressure (10⁻⁶ to 10⁻⁸ torr) during UV irradiation. UV irradiation was carried out with a concentrated mercury arc (PEK Type 212 with quartz optics and a mirror with an aperture of f/0.5) at a distance of 24 in. During irradiation, the sample became only slightly warm to touch (< 40^o C). A single mercury bulb was used for all the irradiations, and its light output, which was measured at 360 nm, changed less than 5% during the irradiations.

The ESR spectra were measured with an X-band spectrometer (Varian E-12) equipped with a Fieldial and a dual cavity (TE₁₀₄) operated from the microwave bridge at a power level of 50 mW. The sample cavity was modulated at 10⁵ Hz with an amplitude of 1 Oe. The reference cavity contained a sample of 0.1% carbon in KCl (Varian) for monitoring cavity sensitivity and measuring g-value, and this cavity was modulated at 400 Hz. ESR measurements were made at 77^o K by use of a quartz dewar with liquid nitrogen into which the sample was placed. Because of slow temperature equilibration of the pigment at the low ambient pressure in the tube, the sample was precooled in liquid nitrogen for one hour before ESR measurements.

Step 6--Space Simulation Tests at IITRI

The pigments and paints on aluminum coupons were tested in two space simulation chambers, IRIF and CREF, in four separate runs. The total spectral reflectance data were measured at IITRI³ and were sent to SRI for evaluation of the photodamage.

IV. RESULTS AND DISCUSSION

All 48 samples of the matrix in Table 2 were analyzed by ESR. The priorities for the space-simulation tests were established by consultation between SRI staff members and the project monitors, but not all of these samples selected were measured.

Photodamage Parameters

The ESR spectra of the pigments as paints contained four main resonance lines:

- (a) Only the line with a $g = 1.974$ (line width of about 60 Oe at 77°K) increased on vacuum irradiation of the samples. It is generally accepted that this line results from Ti^{+3} centers.¹⁰⁻¹²
- (b) A narrow and weak line appeared with a g value of 2.003, and its intensity varied from sample to sample in a random way. The relevant paramagnetic center probably resulted from organic radicals arising from impurities introduced unintentionally during pigment preparation.
- (c) A broad resonance line was also observed at g value of about 2.1 and is ascribed to Cu^{+2} impurities in the original pigment.¹¹ The copper was probably introduced during pigment preparation at IITRI when the motor bearings of a stirrer burned out.
- (d) The resonance line generally ascribed to excess zinc at a g value of 1.94 was not observed in any of the 24 pigments listed in Table 2. However, this resonance line was observed when the LH-111(6-12) pigment was plasma calcined at the highest temperature (cf. Table 1).

The ESR results reported in Table 2 for the matrix of 48 pigments and paints include the following parameters: I_0 , the peak intensity of the 1.974-line before UV irradiation; I , the peak intensity of this line after vacuum irradiation for 3 hours; ΔI , the increase in peak intensity, e.g., $I - I_0$; and ΔI^* , the value of ΔI normalized for the intensity of the Cu^{+2} resonance ($g = 2.1$) whose spin density was assumed to be constant in the pigment. This normalization was desirable to correct for the amount of Zn_2TiO_4 pigment actually in the sensitive volume of the ESR cavity because of variable factors such as dilution by the paint binder, variations in density of the samples, or variations in the physical location of the sample in the ESR cavity. All the ESR intensity values have been normalized to an instrumental gain setting of 10^3 .

The results of the space simulation tests run at IITRI are indicated by the values of the changes of spectral reflectance $\Delta R_{0.4}$ and $\Delta R_{0.9}$, at wavelengths of 0.40 and 0.93 nm, respectively, as measured from the spectral reflectance curves provided by IITRI and interpolated at 1000 equivalent sun hours (ESH). These wavelengths represent two types of optical damage centers in Zn_2TiO_4 : at 0.40 nm damage to the lattice, and at 0.93 nm damage resulting in Ti^{+3} color centers. The exposure chambers and run numbers of the simulation tests are indicated in the legend of Table 2.

The spectral reflectance lost on irradiation can be partially restored by an oxygen "bleach". The amount of the increasable change in spectral reflectance after the oxygen bleach has been measured from the reflectance curves and is included in parenthesis just below the value of $\Delta R_{0.4}$ and $\Delta R_{0.9}$.

The evaluation of the space simulation tests for the effects of redox surface additives on the photostability of paints was limited in scope because not all the paints that were given high priorities

were actually tested in a space-simulation chamber. As a consequence the data on the blank paints are not available, and also data on the effects of the redox surface additives on the photostability of paints based on the "as-received" pigment are limited to two paints. To approximate the behavior of a blank paint containing the "as-received" pigment we used the data from IITRI's space simulation results on paint LH-106 (6-12)/G.¹³ However, these spectral reflectance curves exhibited anomalous behavior and hence provided a poor basis for use as a blank.

The priorities for testing paints on the last space simulation test should have included the following paints for the stated reasons:

- (1) The two blank paints containing the "as-received" and the plasma-calcined pigments were included to provide a basis for judging the passivation provided by the redox couple additives.
- (2) The paints containing the "as-received" pigments that were treated with low concentrations of the two promising additives, $\text{Ce}^{+3}/\text{Ce}^{+4}$ and $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$, were included because these paints were less colored by the lower additive concentrations.
- (3) The paints containing the "as-received" pigments that were treated with HF and HClO_4 were included because the ESR results indicated that these treatments provided better passivation than the blank.

Photodamage Evaluation by ESR

The ESR results in Table 2 have been plotted to show the effects of the various redox couple additives on pigments (Figure 4) and paints (Figure 5). The logarithmic scale of the abscissas has been interrupted to indicated zero coverage of additives, i.e., the blanks.

Generally, we observe less photodamage for equivalent samples derived from the "as-received" pigment than from the plasma-calcined pigment. Also, among the three redox couple additives, the Ce^{+3}/Ce^{+4} additive appears generally to provide the greatest passivation for pigments and paints, but passivation by the $IrCl_6^{-3}/IrCl_6^{-2}$ additive is almost as good.

As the surface coverage of the surface additive is increased, the photodamage, ΔI^* , depends on the type of additive and on whether the sample is a pigment or a paint. For the pigments (Figure 4), an increase in coverage by the Ce^{+3}/Ce^{+4} additive generally results in less photodamage, except for the "as-received" pigment at $\theta = 0.03$ in Figure 4a. For example, with respect to the blank, the highest coverages of Ce^{+3}/Ce^{+4} results in a three-fold decrease in photodamage for the "as-received" pigment and about a 30-fold decrease in photodamage for the plasma-calcined pigment. An increase in the coverage of the other two additives results in an increase in photodamage, followed by a decrease in photodamage which generally becomes smaller than the blank at the highest surface coverages of the additives.

For the paints based on the "as-received" pigment, photodamage was decreased by higher surface concentrations of the additives (Figure 5a). However, the opposite occurred for the paints based on the plasma-calcined pigments for which the photodamage generally increased at higher surface concentrations of additives (Figure 5b). Note the decreased photodamage resulting from treating the pigment with only $HClO_4$ in comparison with water (except for the plasma-calcined pigment, Figure 4b). The passivating effect of $HClO_4$ is in agreement with that observed earlier¹⁰ for the B-229 pigment from which excess ZnO could be removed by dilute $HClO_4$ even after an acetic acid wash. However, the effect of exposing the pigment to an HF solution generally resulted in a large increase in photodamage.

The reproducibility of the ESR data in some instances is excellent but in other instances quite poor as indicated by the brackets under the columns marked ΔI^* in Table 2. This variation in the reproducibility of data may be explained in many ways; for example: (1) Very large variations may result from the presence of impurities that are not uniformly distributed in the sample. Such impurities may be introduced in any state of the handling of the pigment. For example, small segments of brush fibers are sometimes found in the plasma-calcined pigments as a result of the necessity of dislodging the pigment from the glass walls of the apparatus with a brush. If organic impurities are present, it is possible that during drying of the pigment at elevated temperatures, or upon irradiation, the organic molecules may be oxidized by holes from the pigment with the concurrent reduction of Ti^{+4} to Ti^{+3} .

(2) Samples were irradiated with a mercury lamp equipped with a parabolic mirror, and the mirror was usually adjusted so that the two images from the arc were in coincidence. However, this adjustment was difficult and variations of the irradiation flux among the samples may have occurred.

(3) The pressure above a sample was usually 10^{-6} torr or less before irradiation, but in some instances, when samples were evacuated overnight, the pressure was 10^{-7} or 10^{-8} torr. The effect of residual gas could have a strong effect on reversing photodamage, similar to the effects of oxygen bleaching observed in reflectance measurements.

Comparison of ESR and Space Simulation Results

One of the objectives of the program was to determine whether ESR could be used as a rapid technique to screen various pigments and paints for photostability. The matrix of results in Table 2 provides a comparison of photodamage as measured by ESR and spectral reflectance during space simulation tests.

A comparison is shown in Figure 6 by a plot of the ESR results of ΔI^* against the spectral reflectance results $\Delta R_{0.9}$, for the data on the paints in Table 2. The solid points refer to paints containing the "as-received" pigment; the open points refer to paints containing the plasma-calcined pigment. The error bars indicate the reproducibility of measuring ΔI^* for samples examined in duplicate. Comparable information is not available on the reproducibility of ΔR measurements.

The data in Figure 6 for the paints suggest that a correlation exists between ΔI^* and $\Delta R_{0.9}$. The corresponding data on the pigments shows little if any trend probably because the scatter of the data is about equal to the measured changes in photodamage, which are smaller for the pigments than for the paints. However, no correlation is found between ΔI^* and $\Delta R_{0.4}$ for pigments or paints.

It is reasonable to assume that a correlation will exist between ΔI^* and $\Delta R_{0.9}$, since both these parameters are ascribed to the Ti^{+3} color center. Such a correlation supports the model that ultra-violet irradiation produces electron-hole pairs in the pigment and the holes may oxidize either the lattice oxygen ions or the resin binder. The ESR results indicate that greater photodamage, e.g., greater values of ΔI^* , occurred when the OI-650G resin was present, therefore, the resin binder is involved in charge transfer with the irradiated pigment.

The correlation can undoubtedly be improved as the factors that give rise to the scatter in the data is better controlled. We have already discussed how the reproducibility of ESR results could be improved by controlling impurities, light intensity of irradiation, and ultimate pressure of the system before irradiation. Some errors in reproducibility probably also occur in the results from the space simulation chamber tests: for example, error may have been introduced by the use of two test chambers (IRIF and CREF), by taking data from

different runs in these chambers, by impurities, by using different light sources, thickness of the sample on the aluminum coupon, and incorrect registration of the infrared absorption spectral curves.

An attempt was made to determine whether a correlation exists between the ESR and the reflectance parameters by considering the part of the spectral reflectance that is not restored by oxygen bleaching. These data, which are inserted in parenthesis in Table 2 under columns marked $\Delta R_{0.4}$ and $\Delta R_{0.9}$, did not correlate as well as the data shown in Figure 6.

V CONCLUSIONS

The following conclusion can be drawn from the current study of the passivation of zinc orthotitanate pigments and pigmented paints:

- (1) Photodamage of pigments and paints as measured by ESR ($g = 1.974$) shows some correlation with photodamage as measured by change in reflectance at 0.93 μm ($\Delta R_{0.9}$); but additional work is required to improve the correlation. That such a correlation should occur is reasonable, since both the ESR line $g = 1.974$ and the parameter $\Delta R_{0.9}$ relate to the presence of the color center Ti^{+3} , which is formed by charge transfer during UV irradiation.
- (2) Plasma-calcining of the zinc orthotitanate pigment B-229 resulted in greater photostability,* but plasma calcining of pigment LH-111(6-12) resulted in less photostable pigments and paints. Therefore, the effects of plasma calcining are strongly dependent on the pigment history and plasma calcining procedure.
- (3) Photostability of pigments is increased by redox couple additives at sufficiently high surface coverage. Of the redox couple additives studied, the $\text{Ce}^{+3}/\text{Ce}^{+4}$ and the $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$ additives showed promise.
- (4) Photostability of paints is increased by applying redox couple additives to the "as-received" pigment. Again, the

* Paints were not prepared from pigment B-229.

Ce^{+3}/Ce^{+4} additive is superior to the other additives studied. However, paints based on the plasma calcined pigment are made less photostable by redox couple additives. These conclusions are tentative because the space simulation testing program did not follow the recommended priority for testing the paint samples. As a result, adequate information is not available on the photostability of the blank paints and on the effects of the redox couple surface additives on the paints containing the "as-received" pigment.

- (5) Perchloric acid treatment of the pigments significantly increased the photostability of pigments and paints (the plasma-calcined pigment is the only exception). The action of perchloric acid probably results in removal of excess ZnO from the pigment surface. However, according to ESR criteria, treatment of the pigments with HF increased the photodamage to the pigments.
- (6) The photostability of paints is generally less than that of pigments, indicating that photodamage in paints results partially from a pigment-resin photointeraction.
- (7) The ESR has demonstrated its potential as a tool for quality control. Certainly, the technique identifies very unstable paints. Also, an impurity such as Cu^{+2} can be readily detected.

VI RECOMMENDATIONS

With further work to reduce the scatter of data, the ESR method may be suitable for screening thermal control pigments and paints for photostability. At present it has the potential for quality control, for example to identify very unstable paints and to detect paramagnetic impurities. The costs and time requirements for the use of the ESR analysis of photostability are much less than those for reflectance measurements in space simulation tests.

Space simulation tests should be made on several paint specimens, which were given high priority, so that adequate evaluation of the effects of the redox couple surface additives can be made. The specimen to be included are the remaining paints based on the "as-received" pigment, and the blank paint based on the plasma-calcined pigment.

Further research is recommended to evaluate the passivating effects of acid treatments, such as perchloric acid which has shown great promise from results of the present study.

Also, the redox couple additives, $\text{Ce}^{+3}/\text{Ce}^{+4}$ and $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-4}$, which this study shows to have promise for passivating the zinc orthotitanate pigment, should be explored further.

To increase the photostability of paints, further work is required to develop a chemical barrier layer, such as aluminum hydrous oxide or sodium silicate, to be applied over the pigment surface after treatment with the redox couple additive. Such chemical barriers will decrease the amount of photointeraction of the resin with the redox additive and the pigment.

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ADDITIVE				PIGMENTS							
				AS - RECEIVED						PI	
No.	Type	Concn. ^a		I _o	I	ΔI	ΔI*	ΔR _{.4}	ΔR _{.9}	I _o	I
		Molarity	θ								
1	H ₂ O	-	-	7	48	41	37	0.06 (0.04)	0.08 ^e (0.07)	320 362 416 370	330 420 480 440
2	HClO ₄	0.1	-	10	32	22	18	0.08 (0.06)	0.08 ^e (0.02)	0	490
3	HF	0.1	-	0 0	530 190	530 190	} 300			17	1340
4	Ce ⁺³ /Ce ⁺⁴	4x10 ⁻³	0.3	3	10	7		6	0.05 (0.05)	0.05 ^e (0.02)	8
5	Ce ⁺³ /Ce ⁺⁴	4x10 ⁻⁴	0.03	0	84	84	78			0	400
6	Ce ⁺³ /Ce ⁺⁴	4x10 ⁻⁵	0.003	0	15	15	11			7	950
7	Fe(CN) ₆ ⁻⁴ /Fe(CN) ₆ ⁻³	4x10 ⁻³	0.3	0	14	14	13			285	530
8	Fe(CN) ₆ ⁻⁴ /Fe(CN) ₆ ⁻³	4x10 ⁻⁴	0.03	4	38	34	31			360	2380
9	Fe(CN) ₆ ⁻⁴ /Fe(CN) ₆ ⁻³	4x10 ⁻⁵	0.003	0	390	390	370			355 380	500 1720
10	IrCl ₆ ⁻³ /IrCl ₆ ⁻²	4x10 ⁻³	0.3	0 0	10 5	10 5	} 8	0.11 (0.10)	0.02 ^e (0.04)	375 340	400 390
11	IrCl ₆ ⁻³ /IrCl ₆ ⁻²	4x10 ⁻⁴	0.03	0	90	90		81			320
12	IrCl ₆ ⁻³ /IrCl ₆ ⁻²	4x10 ⁻⁵	0.003	0	1110	1100	890			340	1380

^a Additive Concn.: 12 ml of additive solution containing equal amounts of each val
θ - fractional monolayer surface coverage of additive in both valence states

^b ESR measurements at 77°K of line at g = 1.974; I_o = Peak intensity of g = 1.974
to the intensity of Cu⁺² resonance.

^c Spectral Reflectance: ΔR_{.4} and ΔR_{.9} are differences in spectral reflectance from
tests to 1000-ESH. Numbers in parenthesis correspond to the difference in spectra

^d Space Simulation Chamber: IRIF 70.

^e Space Simulation Chamber: IRIF 74

^f Space Simulation Chamber: IRIF 78

^g Space Simulation Chamber: CREF 17

SUMMARY OF DATA AND RESULTS

PHOTODAMAGE ^b																
PLASMA - CALCINED					PAINTS						PLASMA - CALCINED					
					AS - RECEIVED											
I	ΔI	ΔI^*	$\Delta R_{.4}$	$\Delta R_{.9}$	I_0	I	ΔI	ΔI^*	$\Delta R_{.4}$	$\Delta R_{.9}$	I_0	I	ΔI	ΔI^*	$\Delta R_{.4}$	$\Delta R_{.9}$
3300	2980	-	0.04	0.06 ^e	2	396	394	830	0.04	0.03 ^d	145	300	155	455		
428	66	81	(0.01	0.01)					(0.04	0.03)						
484	68															
440	70															
490	490	460			0	71	71	130			0	93	93	220		
1340	1330	1240			0	170	170	340			0	175	175	305		
21	13	12	0.04	0.06 ^e	4	47	43	63	0.06	0.05 ^e	0	835	835	2050	0.06	0.05 ^e
			(0.03	0.01)					(0.02	0.01)	0	808	808			(0.01
40	40	30			0	58	58	93			0	150	150	250	0.07	0.06
95	88	70			0	155	155	230			0	220	220	610		
530	245	440			0	130	130	215			65	1930	1865	12500	0.07	0.23 ^g
															(0.06	0.19)
2380	2020	2400			0	160	160	305			115	690	575	1740	0.05	0.09 ^g
															(0.05	0.06)
500	145	1600			0	310	310	595			135	425	290	1160	0.11	0.18 ^f
1720	1340														(0.08	0.12)
400	25	160	0.08	0.01 ^e	0	64	64	112	0.06	0.02 ^e	50	950	900	10700	0.07	0.22 ^e
396	56			(0.08	0.01)					(0.03	0.03)	60	1770		1710	
390	70	103			0	69	69	111			50	2000	1950	19500	0.07	0.16 ^g
															(0.06	0.12)
1380	1040	1240			0	260	260	500			135	315	180	1260	0.04	0.05 ^g
											138	588	450			(0.03

ch valence state of additive slurried with 31 g pigment LH 111 (6-12) and dried 3 hours at 150°C;

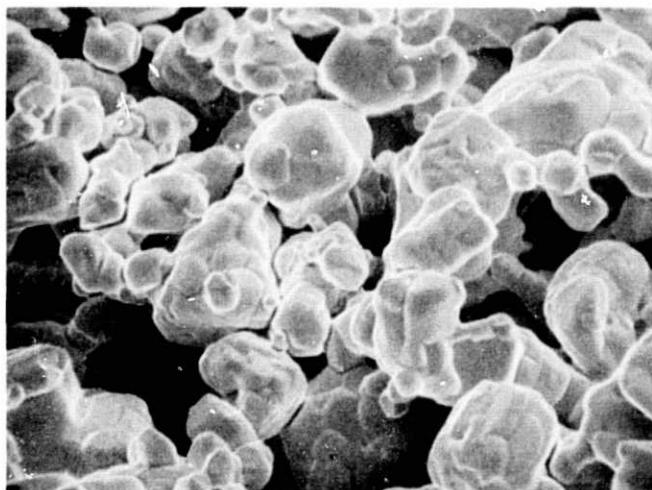
.974 line before UV; I = Peak intensity⁷ of g = 1.974 line after UV; $\Delta I = I_0 - I$; $\Delta I^* = \Delta I$ normalized

from initial conditions at 0.40 and 0.93 nanometers; data interpolated from IITRI's space simulation
spectral reflection at the given wavelengths between the reflectance and that after "oxygen bleach."

FOLDOUT FRAME



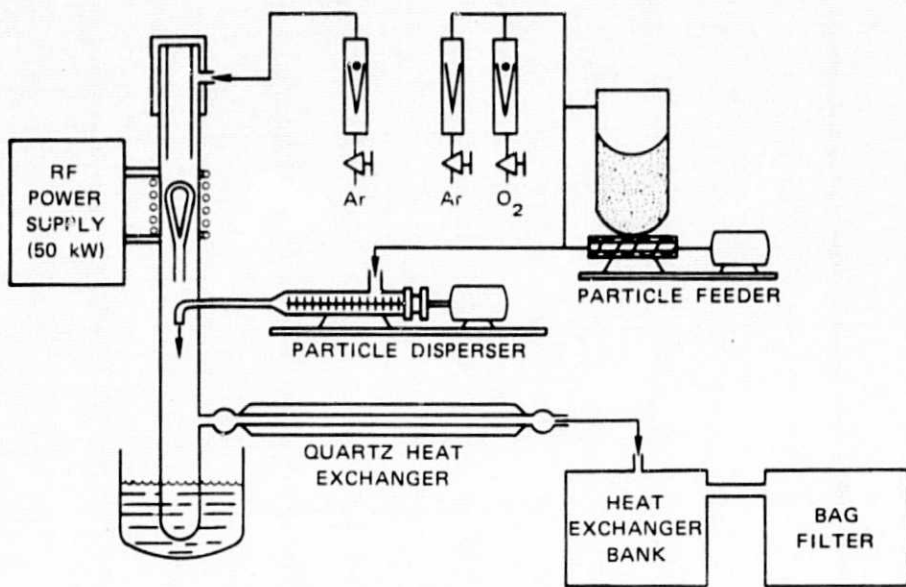
B-229 POWDER 2000X



LH 111 (6-12) POWDER 2000X

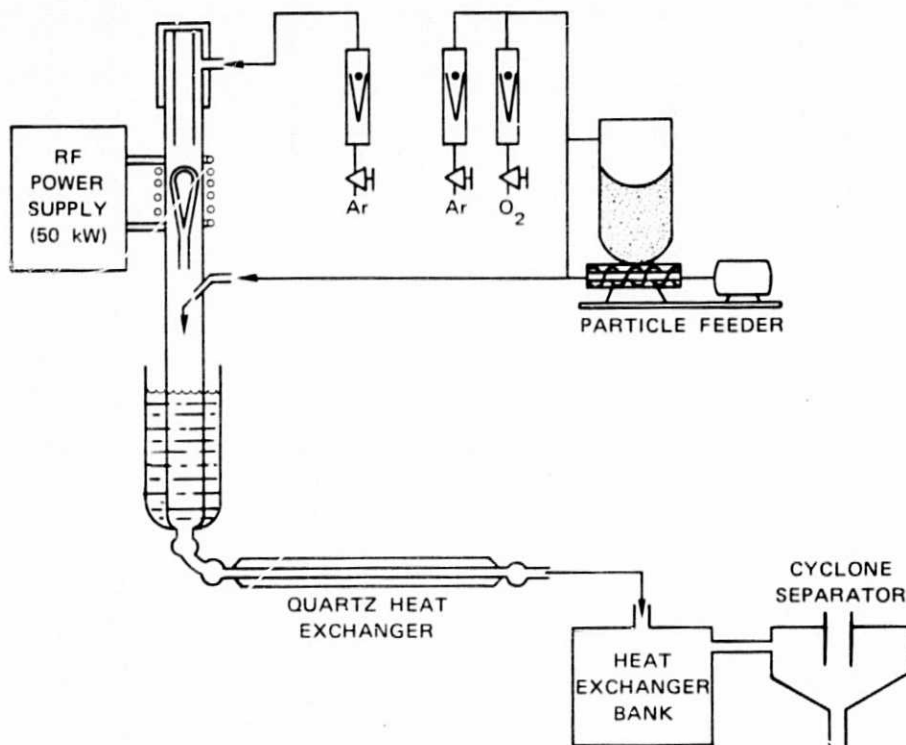
TA-7083-47

FIGURE 1 SEM PHOTOGRAPHS OF Zn_2TiO_4 POWDERS



(a) PLASMA APPARATUS FOR CALCINING FINE PARTICLE AEROSOLS

TA-7083-48



(b) PLASMA APPARATUS FOR CALCINING LARGE PIGMENT PARTICLES

TA-7083-49

FIGURE 2 PLASMA CALCINING APPARATUS

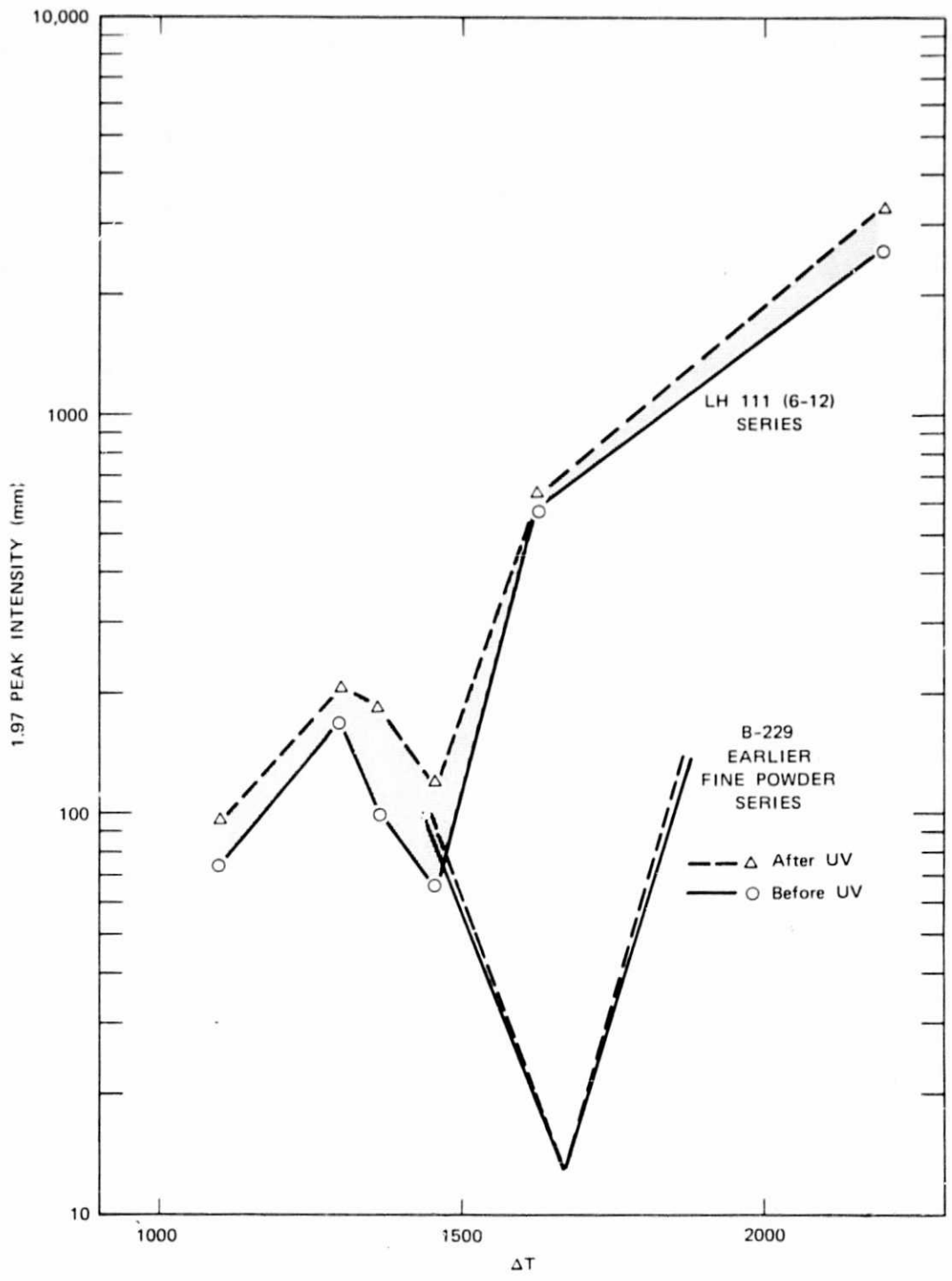


FIGURE 3 ESR PEAK INTENSITY VERSUS THE ΔT CHAMBER TEMPERATURE

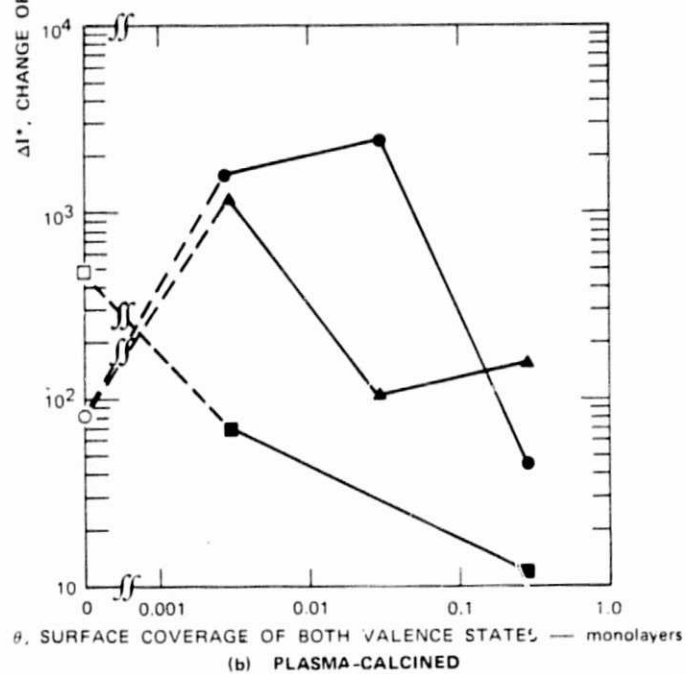
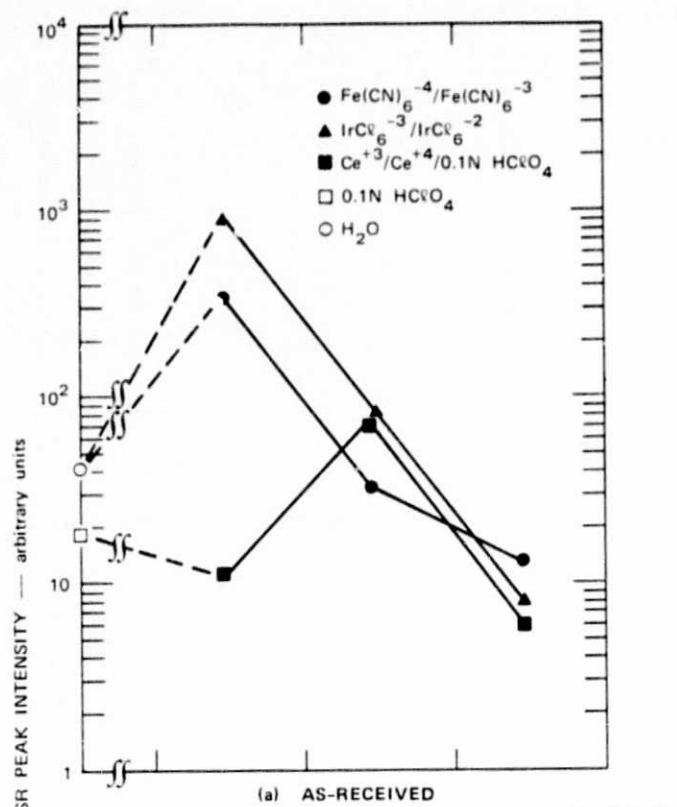
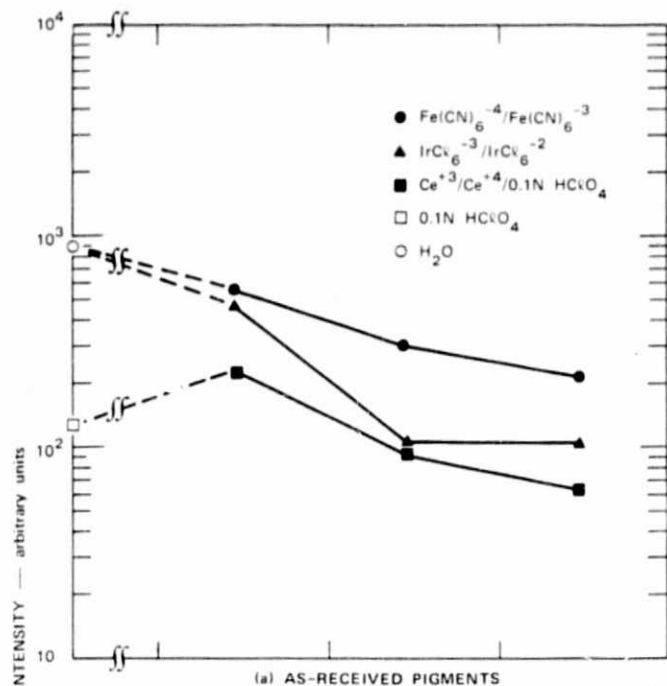
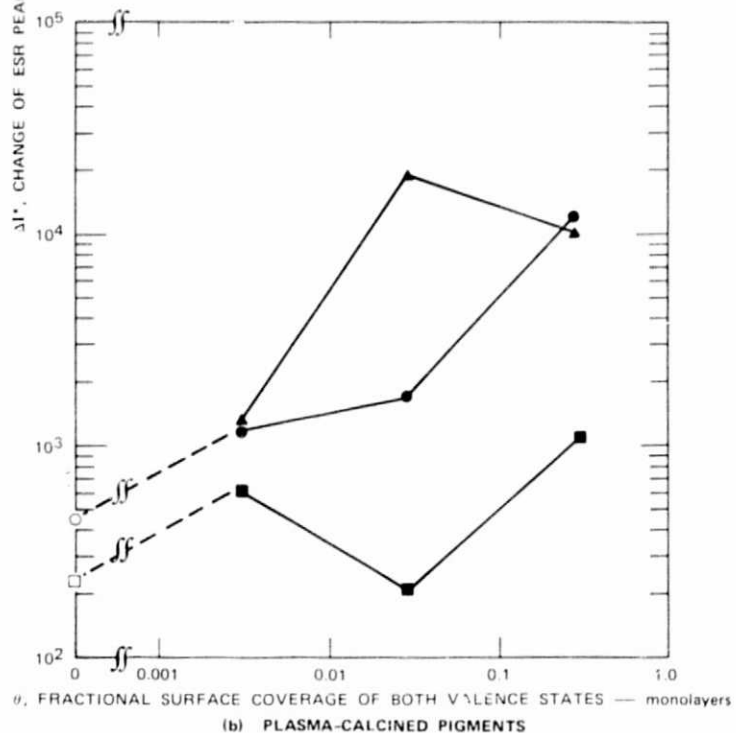


FIGURE 4 PIGMENTS: EFFECT OF FRACTIONAL SURFACE COVERAGE OF ADDITIVES ON CHANGE OF ESR PEAK INTENSITY OF 1.974-LINE UPON VACUUM PHOTOLYSIS OF Zn_2TiO_4 PIGMENT



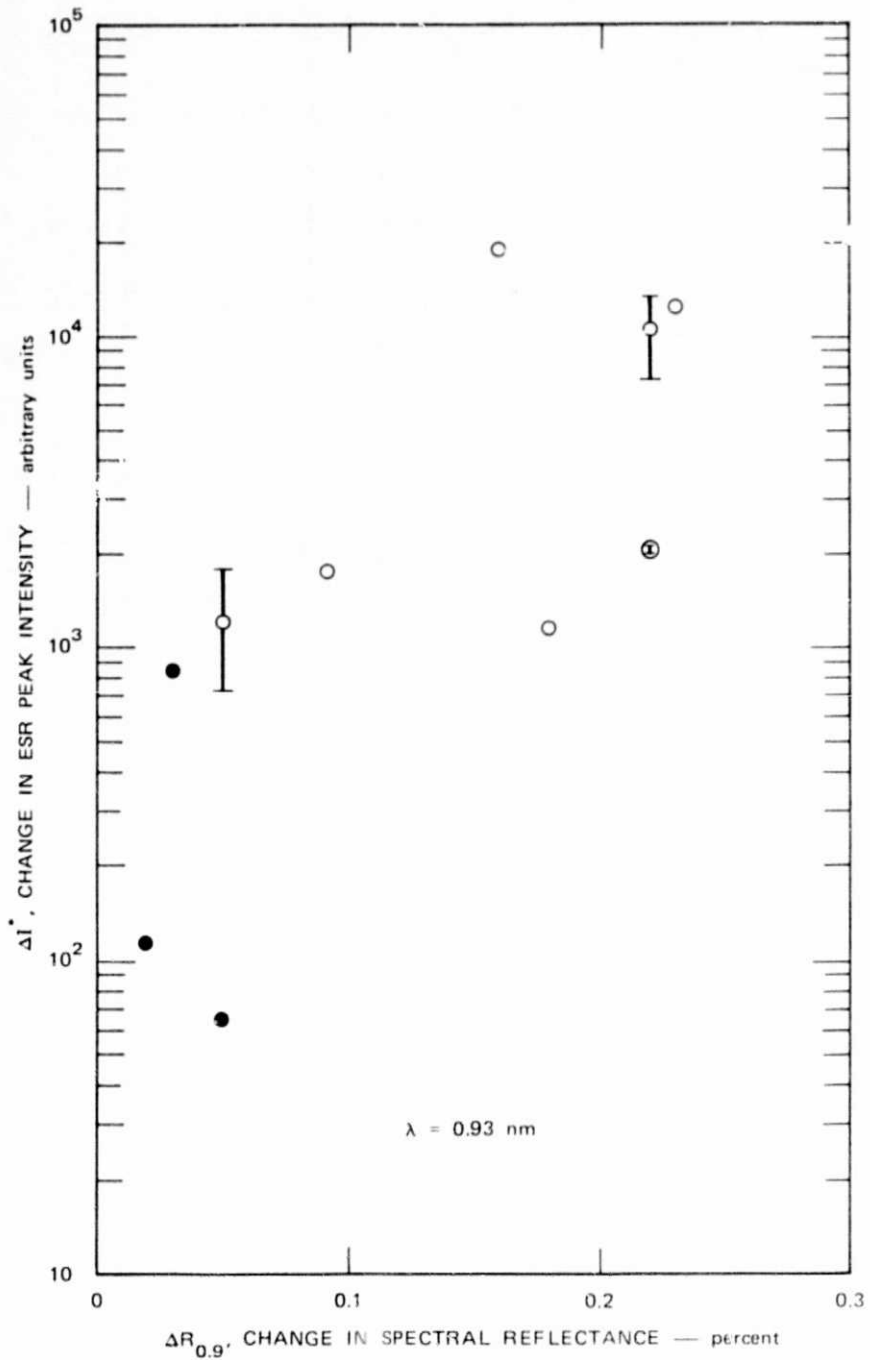
TA-7083-53



TA-7083-54

FIGURE 5 PAINTS: EFFECT OF FRACTIONAL SURFACE COVERAGE OF ADDITIVES ON CHANGE OF ESR PEAK INTENSITY OF 1.974-LINE UPON VACUUM PHOTOLYSIS OF PAINTS WITH Zn_2TiO_4 PIGMENTS

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TA-7083-56

FIGURE 6 COMPARISON OF ESR AND SPACE SIMULATION RESULTS FOR PAINTS CONTAINING AS-RECEIVED PIGMENTS (●) AND PLASMA-CALCINED PIGMENTS (○)