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*Interim Final Report*

**PASSIVATION OF PIGMENT PARTICLES  
FOR THERMAL CONTROL COATINGS**

**CASE FILE  
COPY**

*By:* E. P. FARLEY K. M. SANCIER S. R. MORRISON

*Prepared for:*

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION  
HUNTSVILLE, ALABAMA

CONTRACT NAS8-21270



**STANFORD RESEARCH INSTITUTE**  
Menlo Park, California 94025 · U.S.A.



SCIENTIFIC RESEARCH INSTITUTES

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*June 1973*

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SRI Project PYU-7083

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PASSIVATION OF PIGMENT PARTICLES FOR  
THERMAL CONTROL COATINGS

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**PART I**  
**INDUCTION PLASMA CALCINING**  
**OF PIGMENT PARTICLES FOR**  
**THERMAL CONTROL COATINGS**

**E. P. Farley**

## SUMMARY

Five powders were received for plasma calcining during this report period. The particles of all five powders were too large to flow through the plasma facility. The large particle size may be the result of a reduction in the ball milling time from 24 hours to 1 hour. We therefore further reduced the particle size using a fluid energy mill, and obtained pigments that could be plasma calcined.

Pigment susceptibility to degradation can be monitored by observing the changes in the intensities of the ESR lines. Changes in the ESR spectra can be correlated with changes in plasma calcining variables, i.e., chamber pressure, plasma temperature, powder feed rate, and particle size.

Optimum results are obtained in the plasma calcining of zinc orthotitanate when finely dispersed particles are subjected to a calculated plasma temperature of  $1670^{\circ}\text{C}$  (see Equation 1).

Increasing the plasma calcining time by using multiple passes through the plasma stabilized the pigment to vacuum UV irradiation as evidenced by the resulting ESR spectra but slightly decreased the whiteness of the pigment. The observed darkening is apparently associated with the formation of  $\text{Ti}^{+3}$  color centers.

## INTRODUCTION

Zinc oxide (ZnO) is currently used as a pigment for thermal control coatings on space vehicles. Zinc orthotitanate ( $Zn_2TiO_4$ ) has inherent qualities, such as a lower frequency ultraviolet absorption shoulder, that enhance its potential as a pigment. Both of these materials lose reflectance during space flights or space flight simulations because of ultraviolet radiation in vacuum. To decrease susceptibility to damage from ultraviolet radiation, the zinc oxide is coated with an alkali silicate, then heat treated at low temperature. Zinc orthotitanate is formed at temperatures between  $900^{\circ}$  and  $1100^{\circ}$  C. Unfortunately, both of these heat treatments cause sintering and particle agglomeration, and a subsequent comminution processing step must be employed. The comminution results in zinc oxide particles that are not completely coated with alkali silicate in one case, and zinc orthotitanate that is mechanically damaged, in the other. Therefore, a heat treatment that does not result in agglomeration and sintering, thereby eliminating the need for subsequent comminution of the pigment particles, should provide materials with greater resistance to ultraviolet radiation under vacuum conditions.

The plasma technique is an attractive method of calcining fine particles without producing sintered agglomerates. The objective of this study is to determine the potential of employing induction plasma heating techniques for calcining pigment particles used in thermal control coatings. Fine particles of silicated zinc oxide and zinc orthotitanate were dispersed in a carrier gas of argon and oxygen and were heated by hot argon produced in an induction plasma.

Work during this report period was concerned with the effect of plasma

calcining time at temperature on an uncoated pigment. Samples of earlier pigment preparations were also plasma calcined and forwarded to NASA for flight testing.

## EXPERIMENTAL PROCEDURE

The experimental zinc orthotitanate ( $Zn_2TiO_4$ ) pigments used in this investigation were produced at IIT Research Institute under NASA Contract No. NAS8-26791. The original preparation of the  $Zn_2TiO_4$  pigments has been described in earlier reports.<sup>1-3</sup>

### Powder Preparation

The need for additional treatment of the new material supplied by IITRI became apparent when samples would not flow through the plasma system as before. The samples were passed through a series of screens and were found to contain a large portion of agglomerated particles. The powders were then subjected to milling using a fluid energy mill (Troost Mill) so that the agglomerates could be broken up with a minimum amount of contamination.

### Plasma Calcining

The plasma apparatus used in this study was described in detail in Interim Technical Report No. 1,<sup>1</sup> and the present operating conditions were described in Interim Technical Report No. 2.<sup>2</sup> The pigments were injected downstream from the plasma, and the constant gas flow rate employed produces a constant residence or heating time of about 1.1 seconds. The gas temperature in excess of ambient ( $\Delta T$ ) is calculated from the gas flow rate, the input electrical energy, and the heat capacity of the argon plasma gas, and is given by Equation (1)

$$\Delta T = 25 \frac{E_p I_p}{J} \quad (1)$$

where  $J$  is the total gas flow rate in liters/min at STP,  $E_p$  is plate

voltage, and  $I_p$  is plate amperage. The constant in this equation accounts for the conversion of units and the plasma efficiency. The plasma consisted entirely of argon, whereas the gases used to transport the pigment particles into the plasma apparatus contained equal amounts of argon and oxygen. The total resulting gas composition in the reactor was 80.7% argon and 19.3% oxygen.

The starting materials and the calcined products were analyzed by X-ray diffraction, scanning electron microscopy (SEM), Fisher subsieve analysis, and electron spin resonance (ESR) spectroscopy.

The ESR tests were run in the system described in Interim Technical Report No. 3<sup>4</sup> with a modification in the sample holder that prevents oxygen contamination as described in Interim Technical Report No. 4.<sup>5</sup> The ESR measurements were made before and after a vacuum UV irradiation time of one hour.

## RESULTS AND DISCUSSIONS

### Particle Preparation

The catalog of pigment powders (Appendix 1) shows that the common treatment of IITRI powders included a 24-hour ball milling period. This ball milling period apparently was decreased to one hour, as evidenced by the inability of the powders to flow through the plasma system. The five powders received during this research period were worse than any previously submitted samples and required fluid-energy milling to reduce agglomeration of the pigment particles. The mill and the cyclon separator were provided with rubber and plastic linings to eliminate contamination.

After milling, the product was slightly darkened. A change was also noted in the ESR spectra, and this change is probably associated with  $Ti^{+3}$  color centers. The physical effect of the milling on size distribution was the reduction of the agglomerate size from 100 micrometers to 5-10 micrometers. The material with the finer agglomerates flowed easily through the plasma system.

### Plasma Calcining

Several tests were run on silicate and phosphate coated pigments (Samples 17 and 20) in order to duplicate earlier results. A test was also run on a lithium coated pigment at a lower plasma temperature, but this procedure resulted in a very dark product.

The effect of time at temperature was investigated by passing the pigment material through the plasma calcining apparatus more than one time. The pigment was run through the plasma system at the reference temperature ( $T = 1670^{\circ}C$ ) and a sample was taken from the small condenser

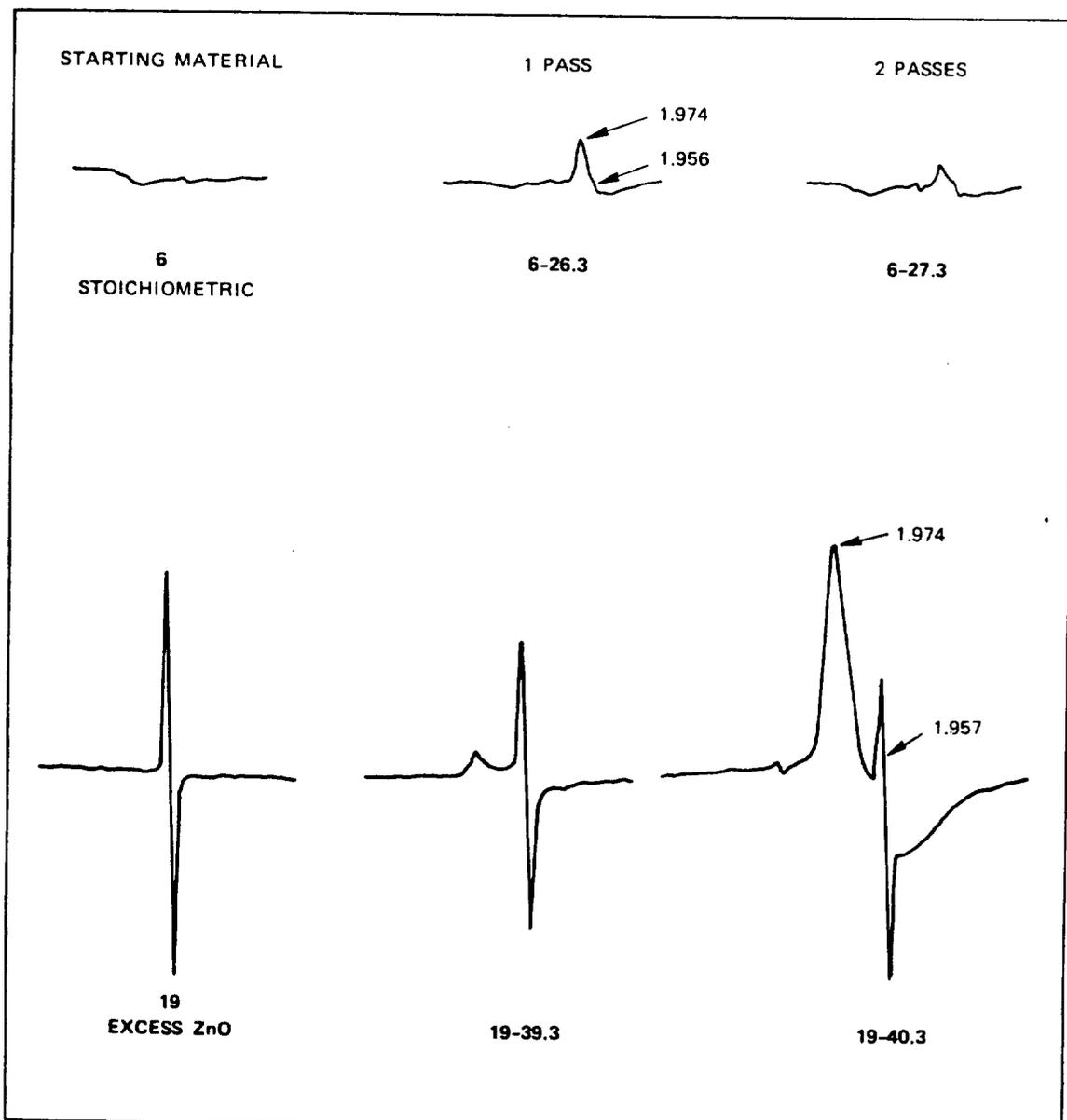
bank (19-39.3). The remainder of the small condenser bank material was then recycled at the reference temperature. A sample was again collected from the small condenser bank (19-40.3) and was submitted for ESR analysis.

Figure 1 shows the ESR spectra resulting from a sample containing excess ZnO (Sample 19) and from a stoichiometric sample (Sample 6). The intensity of the ESR line at  $g = 1.957$  is reduced slightly in Sample 19, but the intensity of the line at  $g = 1.974$  increases strongly with dwell time. The second pass on Sample 6 resulted in a decrease in the 1.974-line, and hardly any change in the 1.957-line.

If one considers the geometry of the plasma reaction chamber system with the powder inlet nozzle downstream from the plasma and just in front of the powder exit (see Figure 2), the actual dwell time for a particle is influenced by its mass. Agglomerates of any appreciable diameter will not exit from the reaction chamber but small particles will quickly reach the gas velocity and exit through the port. Another phenomenon noted in earlier reports is the coloration surrounding the powder within the flame at the exit of the inlet nozzle and reaching down to the vicinity of the exit port. This phenomenon could be due to vaporization and ionization of the coating or surface contamination of the powders, and would result in the distribution and redepositing of the volatile material on the surface of the dispersed powders. The effect of the coating resulting from this phenomenon may be more important than any other factor in the passifying of these pigment surfaces. To illustrate, Figures 3, 4, and 5 show the effect of chamber pressure, plasma temperature, and powder feed rate on the ESR spectra.

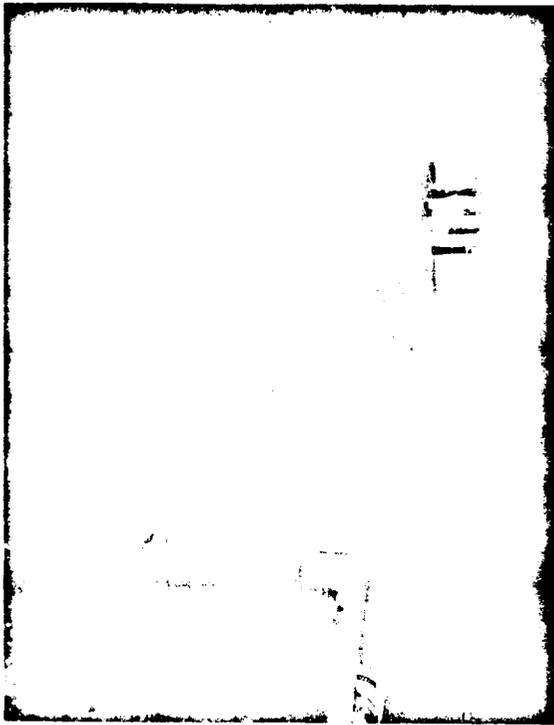
#### X-Ray Diffraction Analysis

The X-ray diffraction analysis of the powders shows no basic changes in structure as a result of plasma calcining. The only variation in phase distribution is associated with particle size differences.

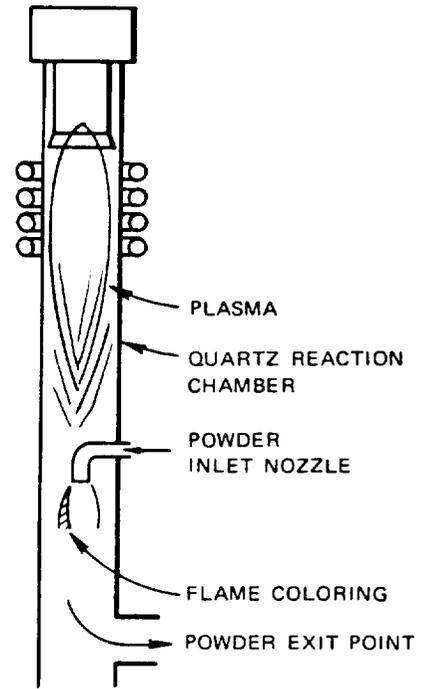


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FIGURE 1 EFFECT OF MULTIPLE PLASMA CALCINING PASSES ON ESR SPECTRA AT 1.3 g/MIN AND  $\Delta T = 1670^{\circ}\text{C}$



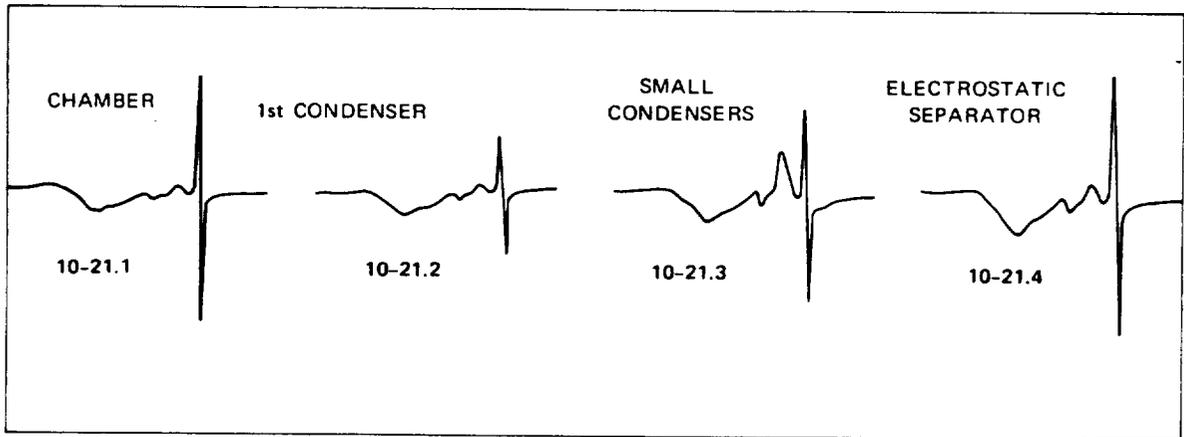
HEAD-ON VIEW



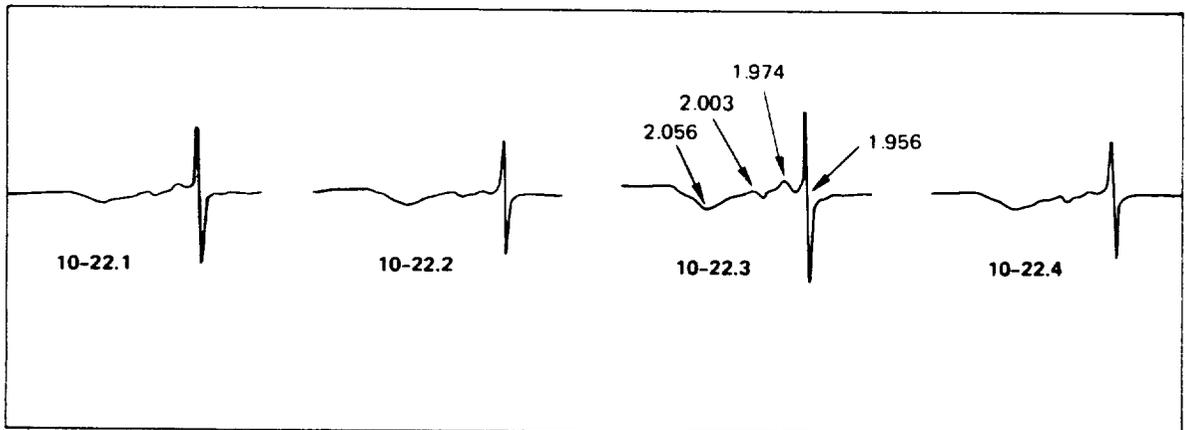
SIDE VIEW

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FIGURE 2 COLORING IN PLASMA TAIL FLAME DUE TO PRESENCE OF SILICATE AND PHOSPHATE COATING ON PIGMENT PARTICLES



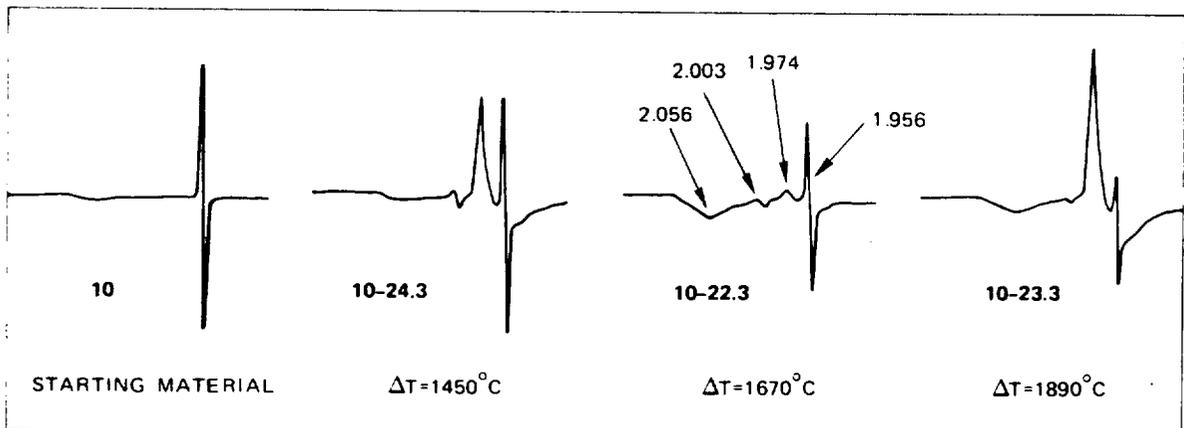
CHAMBER PRESSURE ( $P_2$ ) — 32 mm Hg



CHAMBER PRESSURE ( $P_2$ ) — 11 to 15 mm Hg

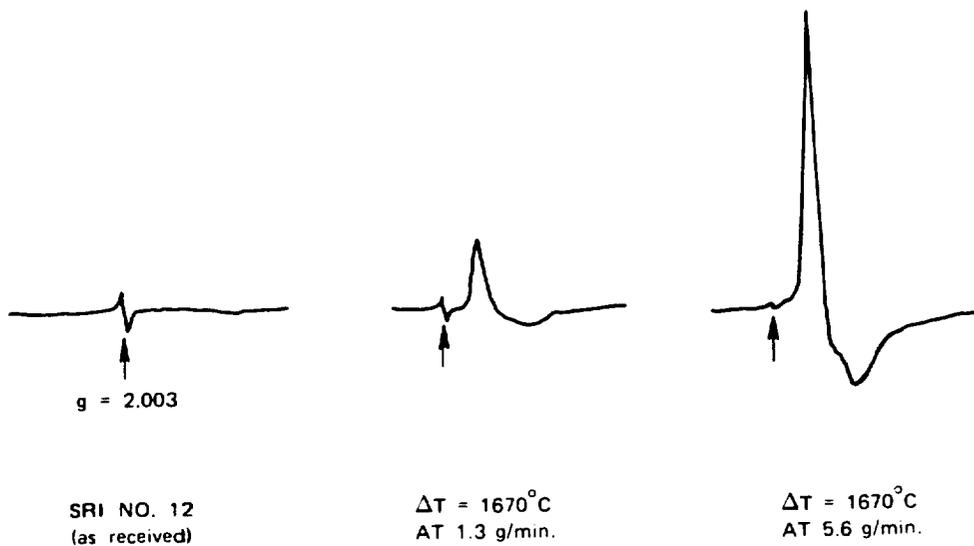
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FIGURE 3 EFFECT OF SAMPLE COLLECTION POINT ON ESR SPECTRA



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FIGURE 4 EFFECT OF CHAMBER TEMPERATURE ON ESR SPECTRA



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FIGURE 5 EFFECT OF POWDER FEED RATE ON ESR SPECTRA OF  $\text{K}_2\text{SiF}_6$  COATED  $\text{Zn}_2\text{TiO}_4$

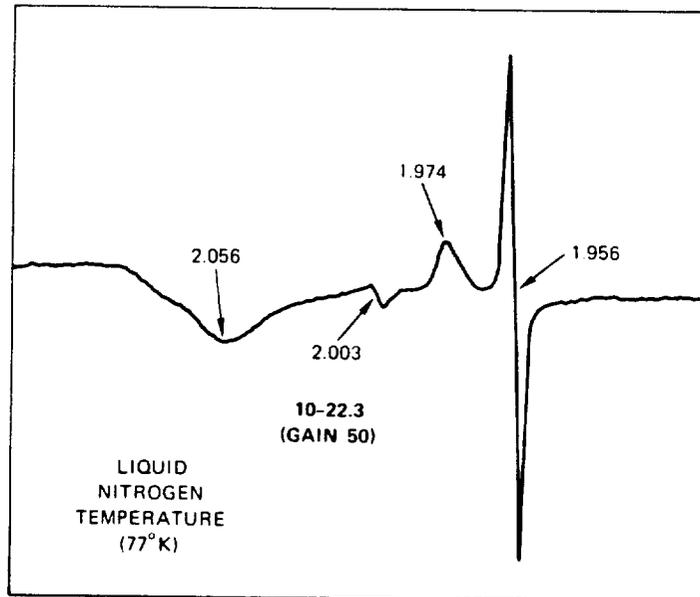
## Electron Spin Resonance

Figure 6 is the ESR spectra of the most stable plasma calcined zinc orthotitanate pigment powder produced. It was a silicate phosphate coated pigment and was calcined at  $\Delta T = 1670^{\circ}\text{C}$ . It withstood 2400 ESH hours of vacuum irradiation with the least degradation of any pigment powder tested.<sup>6</sup> The ESR line at a  $g = 2.056$  is probably due to iron contamination, and the other three  $g$ -values are characteristics of plasma calcined zinc orthotitanate.

## Effect of Vacuum UV Irradiation on ESR Spectra

When a comparison is made between changes in ESR resonance peak heights before and after UV irradiation, a correlation can be drawn between these changes and solar-simulation-induced changes in reflectance spectra. To illustrate the changes produced by vacuum UV irradiation in the ESR spectra, the peak heights were all adjusted to a gain of 50 and plotted in millimeters of height (Figure 7). A splitting of the plotted line for a given resonance is a direct reading of the degree of change produced by one hour of exposure to the mercury arc. Where the lines converge, there was no apparent effect of UV radiation on that particular ESR resonance.

Table I shows the effect of vacuum UV irradiation on three characteristic ESR line intensities of plasma calcined  $\text{Zn}_2\text{TiO}_4$ . Untreated stoichiometric (1:1) zinc orthotitanate develops a small 2.003-line and an increase in the 1.974-line. The reflectance spectra show a drop in reflectance at both ends of the spectrum (Figure 8). After the second pass through the plasma, the effect of irradiation becomes negligible. The first sample of untreated  $\text{Zn}_2\text{TiO}_4$ , formulated with 0.5% excess ZnO (Figure 9) was very stable under irradiation. In fact the 1.956-line drops in value. The second sample of untreated  $\text{Zn}_2\text{TiO}_4$  with excess ZnO required milling. The milling apparently increased the intensities both



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FIGURE 6 ESR SPECTRA OF STABLE PLASMA CALCINED  $Zn_2TiO_4$  PIGMENT

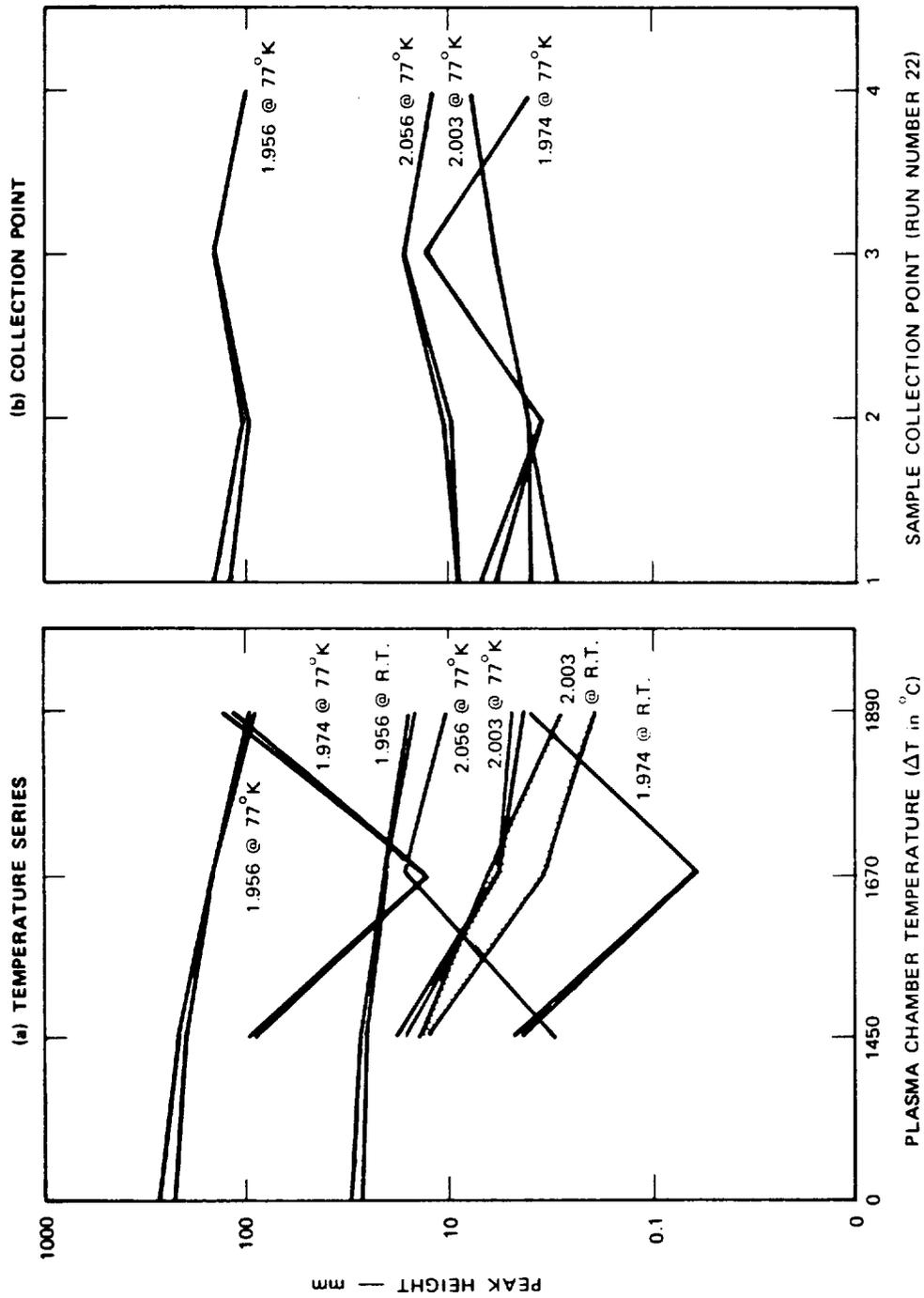
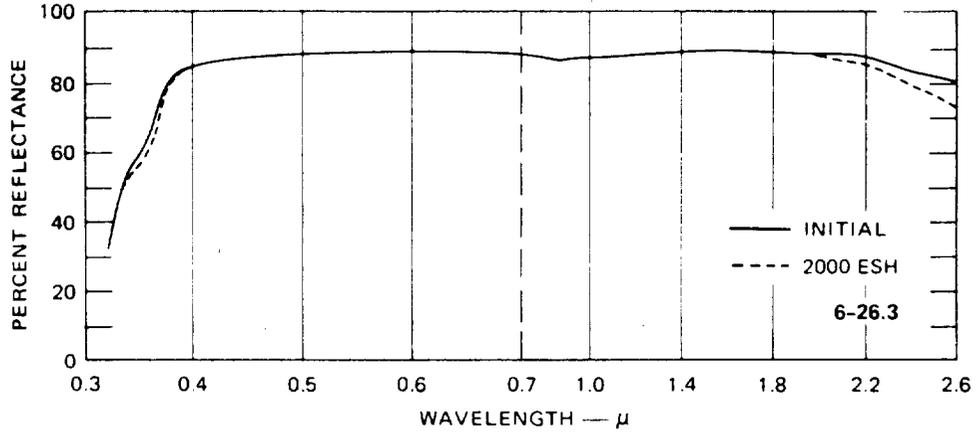


FIGURE 7 EFFECT OF VACUUM UV IRRADIATION ON ESR PEAK HEIGHT

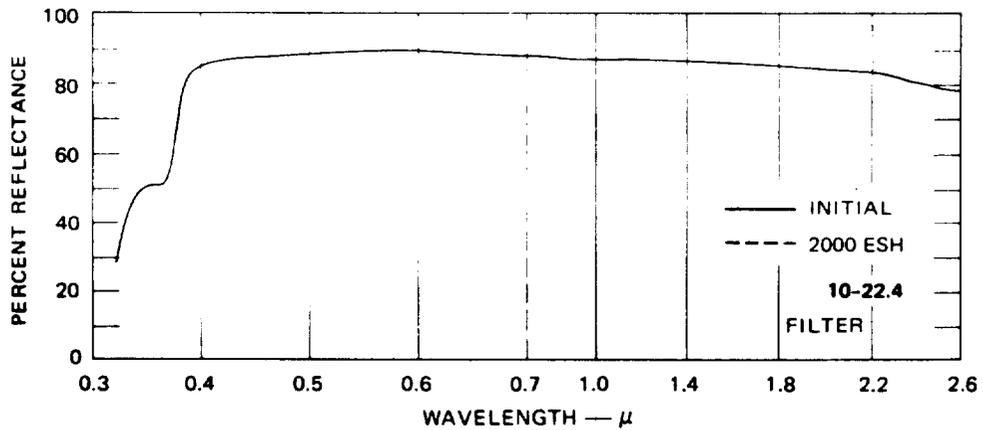
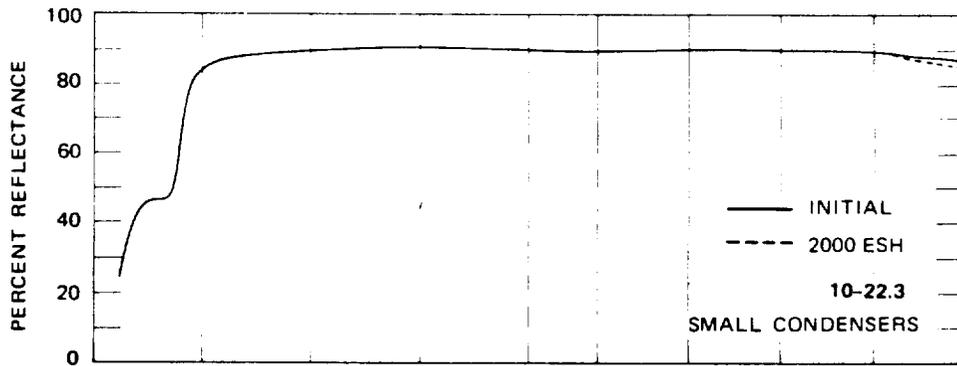
Table I  
 EFFECT OF VACUUM UV IRRADIATION ON THREE CHARACTERISTIC  
 ESR LINE INTENSITIES OF PLASMA CALCINED  $ZnTiO_4$   
 (in millimeters normalized to a gain of 50 at 77°K)

Pigment Description	Sample No.	g = 2.003		g = 1.974		g = 1.956	
		Before	After	Before	After	Before	After
Untreated (1:1)	6-26.3	0	2	40	52	2	2
Untreated (1:) (2nd pass through plasma)	6-27.3	6	7	20	20	14	14
Untreated (1:1 + excess ZnO)	9-25.3	11	10	10	10	610	555
Trost Mill (1:1 + excess ZnO)	19-39.3	9	10	66	94	1130	1140
Trost Mill (1:1 + excess ZnO) (2nd pass through plasma)	19-40.3	30	45	820	880	1250	1190
Silicate + Phosphate Coating (1:1 + excess ZnO)	10-22.3	6	6	13	13	144	143
$K_4Si_4W_{12}O_{40}$ Coating (1:1 + excess ZnO)	14-32.3	13	32	2480	2750	450	463



TA-7083-31

FIGURE 8 REFLECTANCE SPECTRA OF STOICHIOMETRIC  $Zn_2TiO_4$  PIGMENT CALCINED AT  $1670^\circ C$



TA-7083-22

FIGURE 9 EFFECT OF SAMPLE COLLECTION POINT ON REFLECTANCE SPECTRA BEFORE AND AFTER VACUUM UV IRRADIATION (2000 ESH EXPOSURE) ( $\Delta T = 1670^\circ C$ )

of the 1.974- and the 1.956-line. The second pass through the plasma increased the 2.003-line and greatly increased the 1.974-line but did not affect the 1.956-line. The irradiation effect on the second pass material again becomes negligible. Sample 10-22.3 of  $Zn_2TiO_4$  with the silicate and phosphate coating, which exhibits no appreciable change as the result of the irradiation, Figure 9, is included in the table to illustrate the magnitude of the line intensities for a perfectly stable pigment powder.

There is a slight darkening of the second-pass product (19-40.3), which is probably associated with a  $Ti^{+3}$  color center. The second pass apparently produces more stability but a lower reflectance value. A similar increase in the 1.974-line intensity was found by plasma heating the  $K_4Si_4W_{12}O_{40}$  coated sample (14-32.3).

## V CONCLUSION

Increasing the residence time of the zinc orthotitanate pigment particles in the plasma during the calcining process increases the stability of zinc orthotitanate pigments to ultraviolet radiation damage. However, this increased stability is accompanied by a slight discoloration of the pigment.

## VI ACKNOWLEDGMENT

The author wishes to thank Kenneth M. Sancier for carrying out the ESR analyses and for all of his helpful suggestions in formulating this report.

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4. E. P. Farley, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 3, PYU-7083 (May 8, 1970).
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APPENDIX 1  
CATALOG OF PIGMENT POWDERS

SRI No.	Date Received	IITRI Number	Powder Formula	Synthesis Temperature (°C)*	Surface Coating	Hours of Ball Milling	Remarks	Plasma Run Numbers
1	5/7/68	?	ZnO	N/A	Silicate	6		18
2	5/7/68	5	Zn <sub>2</sub> TiO <sub>4</sub>	1050	None	None	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	15-17
3	5/7/68	6	Zn <sub>2</sub> TiO <sub>4</sub>	1050	None	24	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	1-6, 19
4	5/7/68	3	Zn <sub>2</sub> TiO <sub>4</sub>	925	None	24	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	7, 8
5	5/7/68	1	Zn <sub>2</sub> TiO <sub>4</sub>	925	None	None	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	11-13
6	5/7/68	4	Zn <sub>2</sub> TiO <sub>4</sub>	925/1050	None	24	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	9-10, 26-27
7	5/7/68	2	Zn <sub>2</sub> TiO <sub>4</sub>	925/1050	None	None	Leached with HC <sub>2</sub> H <sub>3</sub> O <sub>2</sub>	14
8	5/7/68	?	ZnO	N/A	Silicate	None		Not run
9	6/5/69	B-229	Zn <sub>2</sub> TiO <sub>4</sub>	925	None	12	Excess ZnO	20, 25
10	12/19/69	B-296	Zn <sub>2</sub> TiO <sub>4</sub>	925	Phos. & Sili.	(24?)	Excess ZnO	21-24
11	?	N/A	HfO + CaO	N/A	None	N/A		28
12	4/5/71	C-077	Zn <sub>2</sub> TiO <sub>4</sub>	925	K <sub>2</sub> SiF <sub>6</sub>	?	Excess ZnO	29-31
13	4/5/71	C-081	Zn <sub>2</sub> TiO <sub>4</sub>	925	K <sub>2</sub> Si <sub>2</sub> W <sub>4</sub> O <sub>12</sub>	?	Returned to IITRI	Not run
14	5/26/71	C-149	Zn <sub>2</sub> TiO <sub>4</sub>	925	K <sub>2</sub> Si <sub>2</sub> W <sub>4</sub> O <sub>12</sub>	?	Excess ZnO	32
15	?	N/A	ZnO	N/A	None	?		33
16	?	N/A	HfO	N/A	None	?		34
17	11/3/71	C-230	Zn <sub>2</sub> TiO <sub>4</sub>	925	Phos. & Sili.	1	Excess ZnO	35
18	11/3/71	C-235	Zn <sub>2</sub> TiO <sub>4</sub>	925	Li, Si, F	1	Excess ZnO	36
19	11/3/71	C-219	Zn <sub>2</sub> TiO <sub>4</sub>	925	None	?	Excess ZnO	38-40
20	12/16/71	C-229 & C-296	Zn <sub>2</sub> TiO <sub>4</sub>	925	Phos. & Sili.	1	Excess ZnO	37
21	2/23/72	C-330	Zn <sub>2</sub> TiO <sub>4</sub>	925	Phos. & Sili.	1	Excess ZnO plus Acid Neutralization	Not run

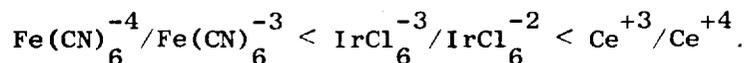
\* NA - Not Applicable

**PART II**  
**PASSIVATION OF ZINC ORTHOTITANATE**  
**THERMAL CONTROL COATINGS BY**  
**SURFACE ADDITIVES**

**K. M. Sancier**  
**S. R. Morrison**

## ABSTRACT

Zinc orthotitanate has been successfully stabilized against photo-damage by application of surface additives consisting of salts of one-equivalent redox couples. Electron spin resonance (ESR) techniques were used in two ways to measure the photoprotection provided by the additive. First, as a result of photolysis under vacuum, two ESR lines increase in intensity. These lines are attributed to interstitial zinc in an excess zinc oxide phase ( $g = 1.94$ ) and to  $Ti^{+3}$  ( $g = 1.97$ ). The surface additives inhibit formation of these point defects in the following order of increasing effectiveness:



In addition, an acid wash ( $10^{-2} N$ ) also imparts excellent photoprotection, presumably because excess zinc oxide is removed from the pigment.

Second, quinoline, an analog of a paint binder, is photooxidized on the zinc orthotitanate in the presence of oxygen. The photooxidation results in a stable free radical of quinoline that possesses an ESR signal at  $g = 2.003$ . The photooxidation of the quinoline is inhibited by the surface additives in the same qualitative order as found for vacuum photolysis, but not by the acid wash ( $10^{-2} N$ ).

Future research is outlined to provide a reliable pigment for thermal control coatings.

## INTRODUCTION

At the initiation of this program, zinc orthotitanate had been identified as a promising candidate pigment for thermal control coatings.<sup>1,2</sup> The pigment can be made reasonably stable against damage under vacuum-ultraviolet conditions provided that the surface is covered with a silicate coating or heated in a plasma-arc. Zinc orthotitanate that has been treated with potassium ferro-ferricyanide has also shown some resistance to proton damage.<sup>1</sup> 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.

A research program was therefore needed to identify the optimum surface additive on zinc orthotitanate that will provide stability against both ultraviolet radiation and proton damage. Stabilization of a pigment material by the surface additive approach is also dependent on the surface concentration of the additive, and therefore the research program includes a determination of the effective concentration of the surface additive.

## SCOPE OF WORK

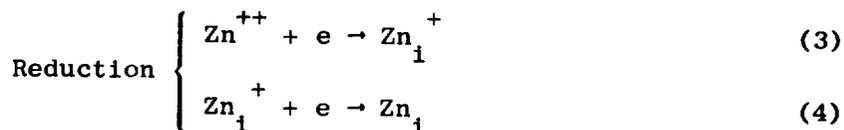
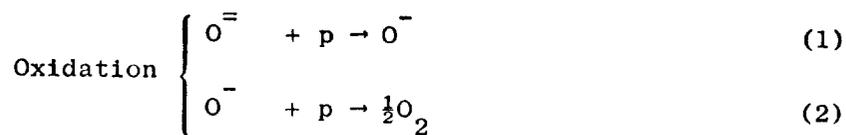
The objectives of the research program have been (1) to initiate studies of the passivation of zinc orthotitanate by means of surface additives with the ultimate goal of providing a pigment that will be stable under ultraviolet radiation in vacuum; (2) to investigate various surface additives in order to identify the one most effective in stabilization, and (3) to investigate the effects of concentration of additive and methods of application to the pigment surface in order to optimize the surface coating.

## BACKGROUND

The surface additive approach, developed for NASA, has been applied to increase the stability of ZnO against damage under vacuum-ultraviolet conditions<sup>3</sup> and to passivate the pigment against photointeractions with the polymer binder.<sup>4</sup> The approach has also been used in preliminary work sponsored by SRI to provide increased photostability of polymer films containing ZnO or TiO<sub>2</sub>.

### 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 the case of ZnO phase the following reactions are believed to occur:



In reactions (1) and (2), the photoproduced holes p oxidize lattice oxygen ions O<sup>=</sup> to oxygen, which may leave the solid. In reactions (3) and (4), the photoproduced electrons e reduce the zinc lattice ions Zn<sup>++</sup>

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 which has limited solubility in the lattice. This excess zinc either causes mechanical strain in the lattice or it precipitates at defects, such as dislocations.

In zinc orthotitanate it is expected that 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). It is of significance that the photoproduced species  $Zn_i^+$  and  $Ti^{+3}$  are paramagnetic. Thus it is possible to detect their presence with great sensitivity by the electron spin resonance technique (ESR).

In the case of proton radiation, the damage in oxide semiconductors may be divided into two processes: (1) displacement of lattice ions giving rise to defects which are color centers, and (2) massive production of charge carriers, along the proton track, which causes chemical damage as outlined above.

#### 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.



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

To be an effective recombination center, we have established that (a) the surface additive must be a one-equivalent redox couple and 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, numerous inorganic surface additives were tested. It was found that the iron cyanide couple satisfied the above list of requirements. A correlation was also found between the electron capture cross section and the standard redox potential of the additive couple.<sup>5</sup> The surface state energies of the various additives on ZnO were determined, and it was 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.<sup>5</sup>

Very low surface concentrations of a surface additive can provide protection against photodamage. In the case of ZnO, significant protection was observed at  $10^{-3}$  monolayers of the iron cyanide additive.<sup>6</sup> 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. It may be for this reason that protection against proton damage was observed for the iron cyanide surface additive on zinc orthotitanate; that is, those electrons and protons produced by ionization tracks of the protons are swept out of the bulk of the crystal by the additive. Of course, the damage caused by the displacement of atoms cannot be affected by the additive.

#### 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 oxidize strongly some organic components of the binder.<sup>4</sup> In the case of ZnO, we determined the relative oxidizability (hole capture cross section) of several solvents for the Owens-Illinois 650 resin because there was evidence that some impurity in the resin resulted in poor photostability of the coating. By employing 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.<sup>4</sup> Moreover, in that study we showed that the iron cyanide surface additive substantially decreased the damage caused by the presence of alcohol. In the present program, pigment binder interactions were investigated by use of quinoline as an analog of the binder.

#### 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 ( $Zn_1^+$  and  $Ti^{+3}$ ) in the pigment as powders as well as pigmented coatings.

The ESR technique has also been employed extensively in our laboratories to follow the effects of plasma-arc treatment on zinc orthotitanate,<sup>2</sup> and charge transfer processes during reaction and chemisorption of gases.<sup>7</sup> In the case of zinc orthotitanate samples that we have examined, the ESR spectra contain two principal lines: one at a g value of 1.956, associated with the donors ( $Zn_1^+$  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.<sup>2</sup> One part of the present program is the study of how the intensity of these lines increases when the pigment is irradiated under vacuum. In a study of the effects of plasma-arc conditions on the zinc orthotitanate product quality, the intensity of these two ESR lines upon ultraviolet irradiation correlated well with the reflectance properties of the product.<sup>2</sup>

Another part of the present program is an ESR study of the effects of surface additives on the passivation of the pigments toward quinoline photo-oxidation. In these experiments, quinoline is an analog of a paint binder, and the technique provides much faster evaluation of additives than the vacuum photolysis technique. The quinoline method has been developed on another program involving the use of rutile as a paint pigment.\*

In this method an oxidizable organic molecule, quinoline (Q), is applied to the pigment to be tested, and the ESR spectrum is measured during ultraviolet irradiation at room temperature with a gas flow of 0.4% oxygen in helium. The ultraviolet light produces electrons (e) and holes (p) in the semiconductor pigment ( $Zn_2TiO_4$ ), and the holes can oxidize the quinoline to a stable positive ion radical  $Q^+$ , which is detectable by ESR at a g value of 2.003,



The oxygen reacts with the excess electrons so that a space charge barrier does not form, i.e.,

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\* Industrial multiclient-sponsored program.



If a surface additive on the semiconductor is an efficient electron-hole recombination center, as it should be for efficient photostabilization of the pigment, then the steady-state concentration of holes is decreased and the intensity of the ESR signal due to the quinoline radical (i.e., by reaction (8)) will be decreased.

## EXPERIMENTAL DETAILS

### Pigment Preparation

The zinc orthotitanate pigment used in these studies is IITRI's batch C-219, which had been treated at 925<sup>o</sup> C to give formulation B-229. This material was dry-ground for 2.5 hours and screened to obtain the 20-mesh fraction. Unless otherwise specified, this pigment (100 g) was treated in 10% acetic acid (250 ml) for 36 hours to remove excess zinc.<sup>8</sup> The solid was repeatedly washed with deionized water, and the supernatant liquid of the settled slurry was removed by suction. The remaining solid was dried at 140<sup>o</sup> C for 15 hours under vacuum.

To apply the surface additives to the pigment, a slurry was made of the pigment (2 g) with a solution (4 ml) containing a known concentration of the appropriate inorganic salts. The slurry was centrifuged, the supernatant liquid poured off, and the solid was dried at 140<sup>o</sup> C for 15 hours under vacuum. Three additive redox couples were studied:  $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$ ,  $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$ , and  $\text{Ce}^{+3}/\text{Ce}^{+4}$ . The solution added to a pigment aliquot contained equal molar concentration ( $10^{-5}$  to  $10^{-2}$  M) of the salts of two valence states of a given redox couple. The salts used were  $\text{K}_4\text{Fe}(\text{CN})_6$ ,  $\text{K}_3\text{Fe}(\text{CN})_6$ ,  $\text{K}_3\text{IrCl}_6 \cdot 3\text{H}_2\text{O}$ ,  $\text{K}_2\text{IrCl}_6$ ,  $\text{Ce}(\text{ClO}_4)_3 \cdot 6\text{H}_2\text{O}$ ,  $(\text{NH}_4)_2\text{Ce}(\text{NO}_3)_6$ , and 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 that of the cerium additive was at pH 2 with perchloric acid in order to maintain the solubility of the cerium ions.

The surface coverage of additive on the pigment was calculated from the solution concentration, the hold-up of the solution after centrifuging

(0.35 ml/g pigment), the surface area of the pigment (about  $10^2 \text{ m}^2/\text{g}$ ), and with the assumption of a surface site density of  $10^{15} \text{ sites/cm}^2$ . Calculation of the surface coverage  $\theta$  in monolayers of the additive in each valence state shows it to be equal numerically to twice the molarity of the additive in each valence state in the solution used to treat the pigment. This calculation assumes no preferential removal by the pigment of either valence state.

#### Vacuum Photolysis

The additive-treated pigments were maintained at low pressure ( $10^{-7}$  to  $10^{-8}$  torr) during ultraviolet irradiation. The pigments were introduced into a quartz tube (3 mm i.d.) in a column about 4 cm high. This tube was fused to a Vac-Ion pump (Varian, 2 l/sec) and to a roughing pump (oil diffusion with two traps in liquid nitrogen). The pigment was heated to  $125^\circ\text{C}$  for 1.5 hours 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.

Ultraviolet irradiation was carried out with a concentrated mercury arc (PEK Type 212 with quartz optics of f/0.5) at a distance of 24 inches. Irradiation was at room temperature, and the sample became only slightly warm to touch ( $< 40^\circ\text{C}$ ).

#### Quinoline Photolysis

The pigment was situated in a special quartz tube (3 mm i.d.) which was held vertically in the ESR cavity. The bottom of the tube was constricted (1 mm opening), and a plug of quartz wool at the bottom of the tube supported the pigment column (4 cm high). The top of the tube was attached to a gas supply, 0.4 vol% oxygen in helium, which was passed over the pigment at 50 cc/min. The ESR spectrum was recorded before, during, and after ultraviolet irradiation (same PEK lamp as used in vacuum

photolysis study).

The quinoline was applied to the additive-treated pigments in the following way. After a pigment was placed in the quartz tube, the tube was immersed in a solution of quinoline in chloroform (0.25 wt% quinoline) to wet the pigment. The tube was then withdrawn from the solution, and the oxygen/helium gas was passed through the tube for about 5 minutes to evaporate the chloroform. Finally, the tube with the quinoline-treated pigment was mounted in the ESR cavity.

#### ESR Equipment

The ESR spectra were measured with an X-band spectrometer (Varian V-4502) equipped with a dual cavity, 12-inch magnet Fieldial, and a dual cavity ( $TE_{104}$ ) operated from the microwave bridge in the low power mode. The tube containing the pigment was situated in the cavity with a screen window through which the ultraviolet light was focused. This cavity was modulated at  $10^5$  Hz with an amplitude of 10 Oe. The other cavity contained a sample of 0.1% carbon in KCl (Varian) for monitoring cavity sensitivity and measuring g-value. This cavity was modulated at 400 Hz.

For the vacuum photolysis study, ESR measurements were made at  $77^\circ\text{K}$  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, it was necessary to precool the sample in liquid nitrogen for one hour before ESR measurements.

For the quinoline photolysis study, ESR measurements were made at room temperature by scanning the magnetic field repeatedly once a minute over a 250-Oe range with the center of the range at about  $g = 2.00$ .

## RESULTS AND DISCUSSION

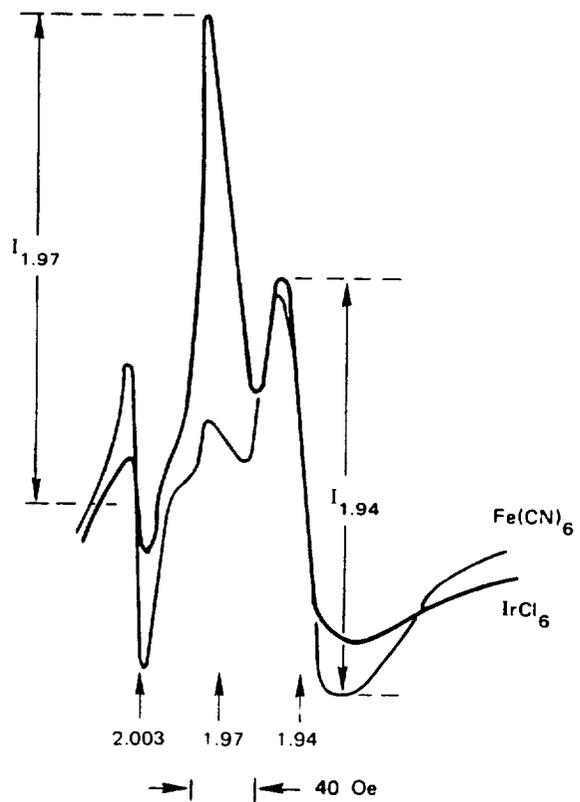
### Vacuum Photolysis

#### Iron Cyanide and Iridium Chloride Additives

Before ultraviolet irradiation of zinc orthotitanate, the ESR spectra exhibit a weak line at  $g = 2.003$  (probably a carbonaceous impurity) and a broad line at about  $g = 2.1$  (probably due to ferric ions). Neither of these features was altered significantly by ultraviolet irradiation.

The two spectral features that result from irradiation are at  $g$  values of 1.97 and 1.94, and typical spectra are shown in Figure 1. It is assumed that these ESR lines correspond to those observed at 1.974 and 1.956,<sup>2</sup> respectively, of plasma-annealed zinc orthotitanate pigments. The intensities of these two ESR lines, presumably due to the paramagnetic centers  $Ti^{+3}$  and interstitial  $Zn_i$  in the excess ZnO, depend on the time of irradiation, the type of redox couple additive, and the surface coverage  $\theta$  of the additive. The ESR line at  $g = 1.97$  has been observed in plasma-annealed zinc orthotitanate pigments and has been ascribed to the  $Ti^{+3}$  damage center.<sup>2</sup> The ESR line at  $g = 1.957$  that is present in the pigment before the treatment with 10% acetic acid is not observed, evidently because the acid removed the excess ZnO phase and its interstitial zinc  $Zn_i$  centers that gave rise to the resonance. The origin of the ESR line at  $g = 1.94$  is not known, but may be due to a form of interstitial zinc in a type of excess ZnO phase. Because the two lines appear to be overlapped, their intensities are measured as shown in Figure 1.

The dependencies of the intensity of these lines upon time of irradiation and as a function of concentration of two additive redox couples



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FIGURE 1 EFFECT OF IRON CYANIDE AND IRIIDIUM CHLORIDE REDOX COUPLE ADDITIVES AT  $\theta = 10^{-3}$  ON THE ESR SPECTRA OF  $Zn_2TiO_4$  PHOTOLYZED IN VACUUM FOR 3.5 HOURS

are shown in Figures 2 and 3. The predominate ESR lines for each additive are used to record the photodamage.

In general the photodamage increases with time of irradiation, and the photodamage is decreased by higher concentrations of the surface additives. For the iron cyanide additive, there appears to be an initial rapid photodamage followed by a slower one (Figure 2). For the iridium chloride additive, the photodamage is almost linear with time of irradiation (Figure 3).

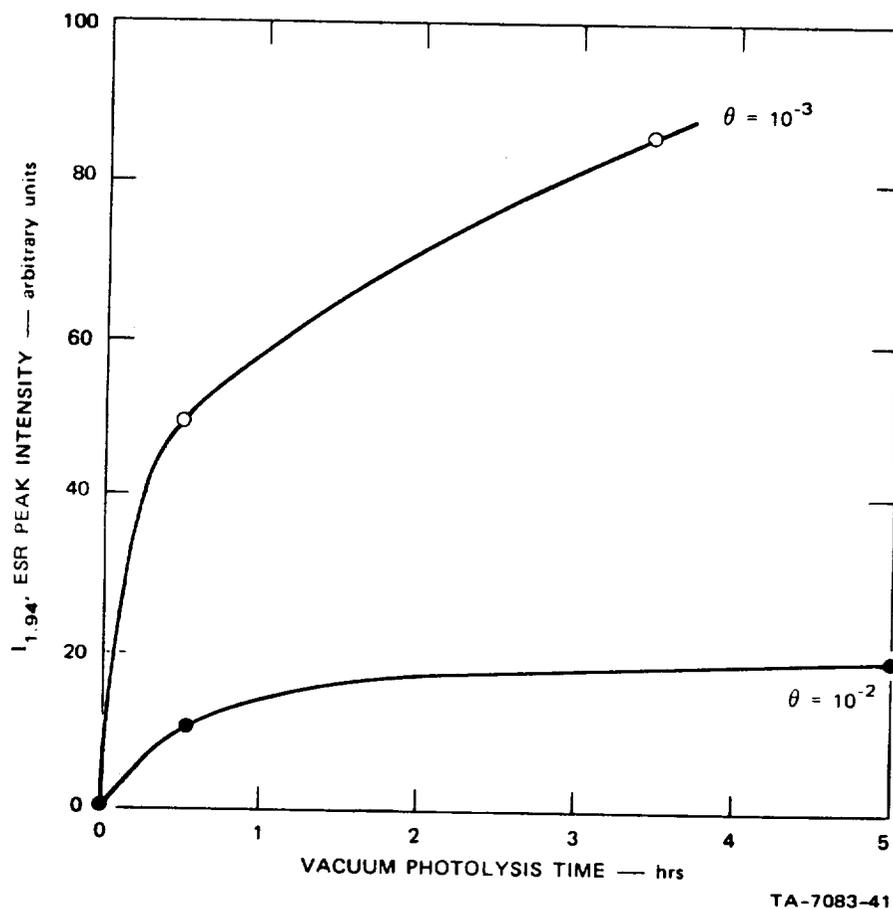


FIGURE 2 EFFECT OF SURFACE COVERAGE  $\theta$  OF  $\text{Fe}(\text{CN})_6^{-4}/\text{Fe}(\text{CN})_6^{-3}$  ADDITIVES ON THE ESR OF  $\text{Zn}_2\text{TiO}_4$  DURING VACUUM PHOTOLYSIS

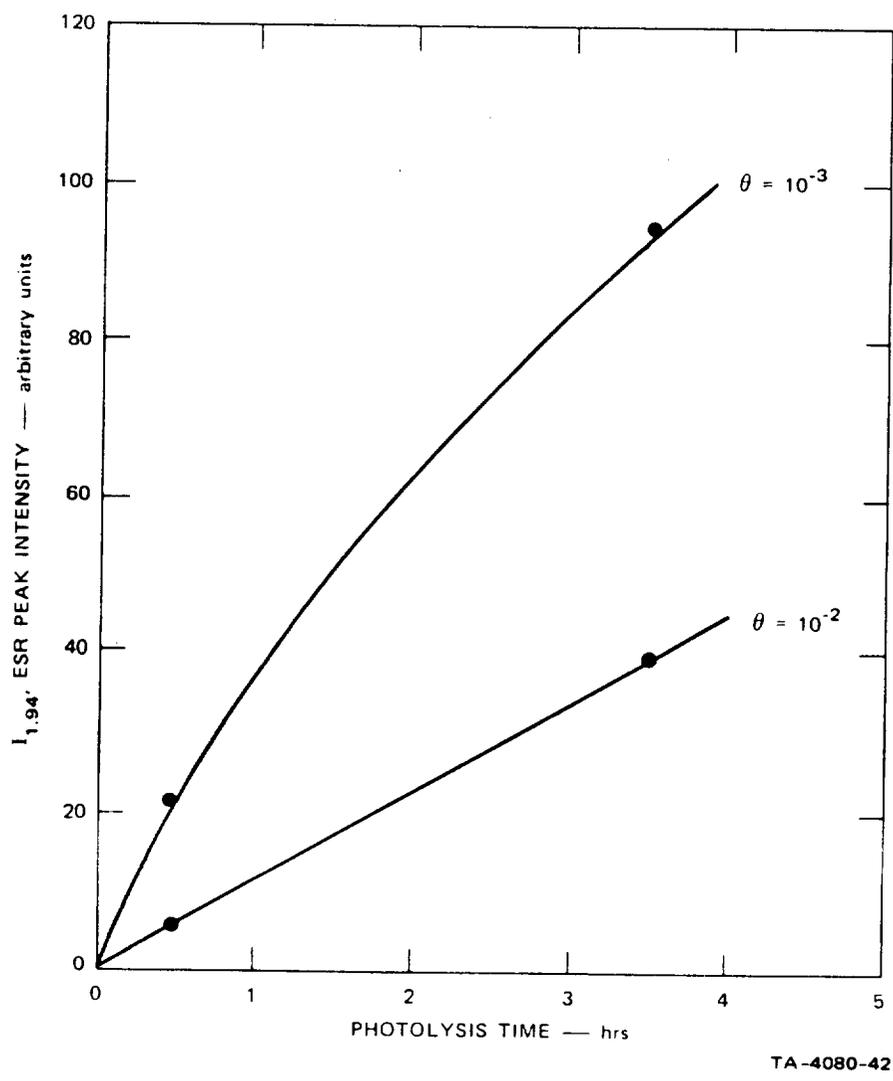


FIGURE 3 EFFECT OF SURFACE COVERAGE  $\theta$  OF  $\text{IrCl}_6^{-3}/\text{IrCl}_6^{-2}$  ADDITIVES ON THE ESR OF  $\text{Zn}_2\text{TiO}_4$  DURING VACUUM PHOTOLYSIS

The comparative photoprotection afforded by these two redox couple additives as a function of fractional monolayer surface coverage of the additives is shown in Figure 4. For each additive, the peak intensities are shown for both the 1.97- and 1.94-lines. Several general observations can be made: (1) less photodamage occurs at higher surface concentrations of the additives; (2) photoprotection becomes evident at about  $10^{-5}$  monolayers; (3) the iridium chloride couple provides slightly more protection than the iron cyanide couple; (4) over the range of surface coverage ( $10^{-6}$  to  $10^{-2}$ ), it appears that the percent change of the intensity of the 1.94-line is greater than that of the 1.97-line. Hence, the additive appears to be more effective in inhibiting the photodamage process giving rise to the 1.94-line, i.e., the  $Zn_1$  center. This latter point is further supported in Figure 5, which is a replot of the data of Figure 4. In Figure 5 the ratio of the ESR intensities,  $I_{1.97}/I_{1.94}$ , is shown as a function of additive coverage. The results indicate that higher surface concentrations of the iron cyanide couple cause the intensity of the 1.94-line to decrease faster than that of the 1.97-line. The iridium chloride additive shows relatively small effect.

The data in Figures 4 and 5 show some scatter, not only in the intensities of the ESR lines, but also in the ratios of the two lines. The effect is quite pronounced for the iron cyanide additive at  $\theta = 10^{-3}$ . The blank values were also unaccountably low. These observations show that uncontrolled factors are altering the photostability of the pigment. Hence, further work to eliminate this uncertainty is indicated.

#### Cerium-Acid Additives

When zinc orthotitanate was treated with a cerium redox couple additive (from  $10^{-2}$  N perchloric acid solutions of the cerium salts) at surface concentrations in the range of  $10^{-6}$  to  $10^{-2}$  monolayers, no

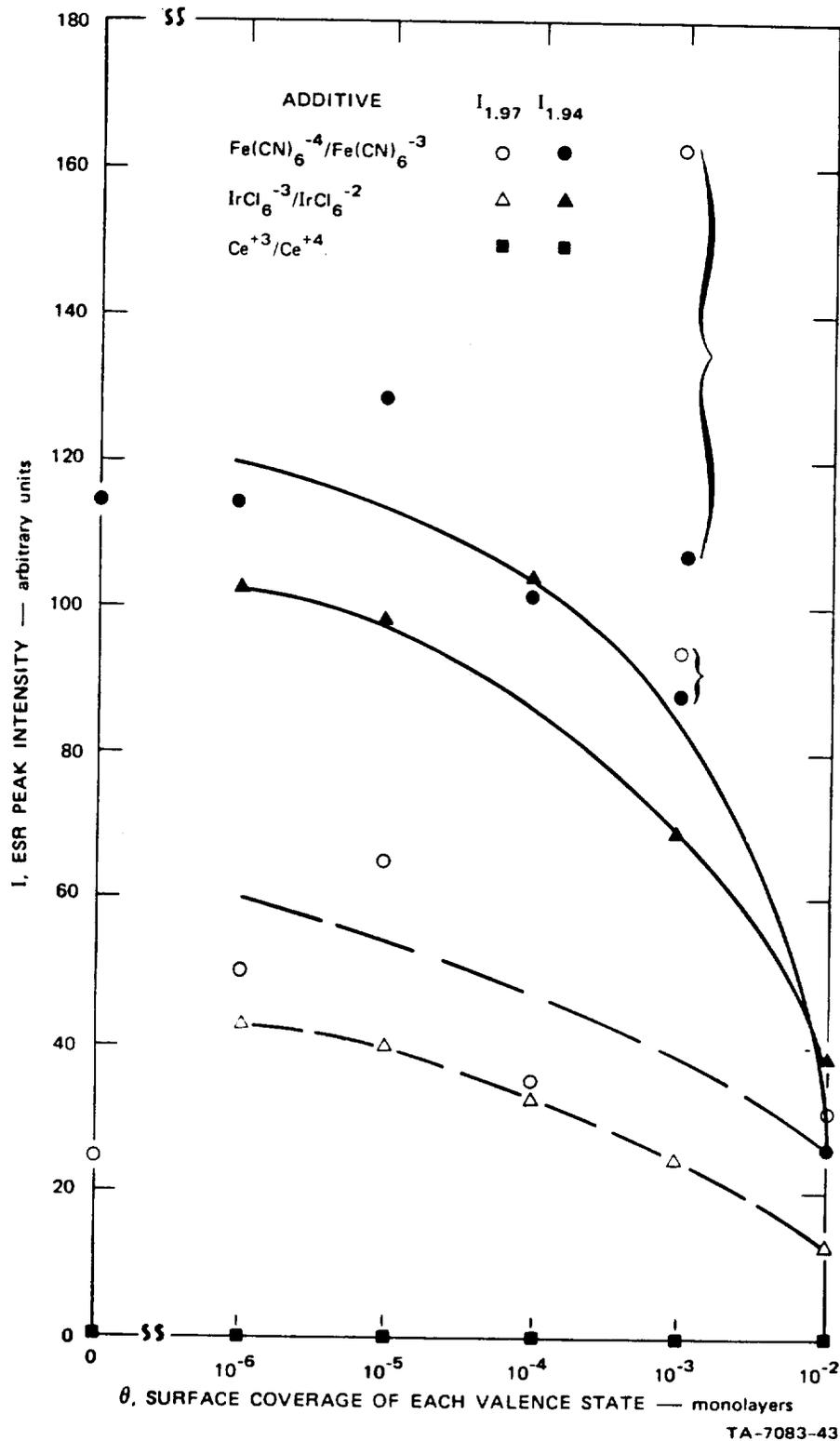


FIGURE 4 EFFECT OF SURFACE COVERAGE  $\theta$  OF ADDITIVES ON THE ESR (1.97- AND 1.94-LINES) OF  $\text{Zn}_2\text{TiO}_4$  PHOTOLYZED IN VACUUM FOR 3.5 HOURS  
 The two brackets represent duplicate runs.

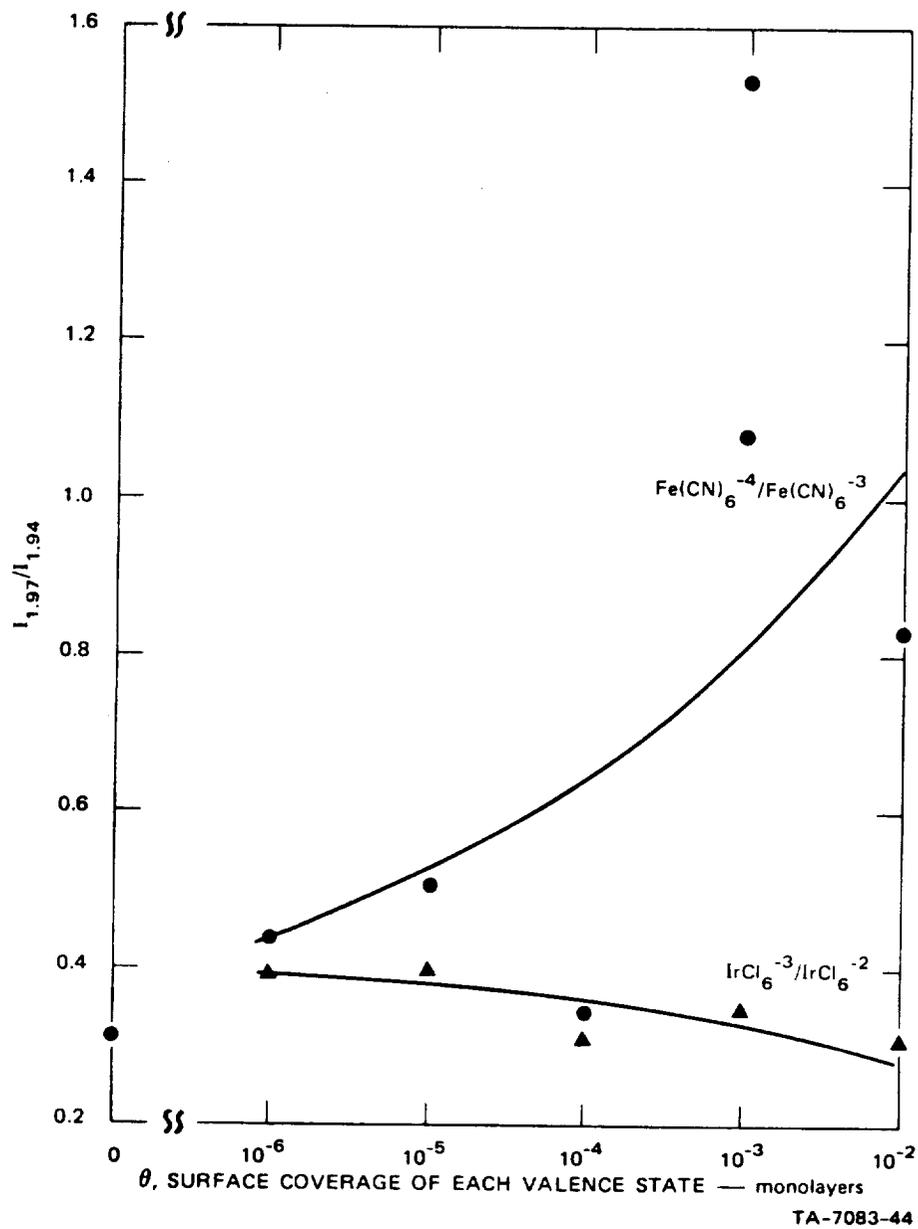


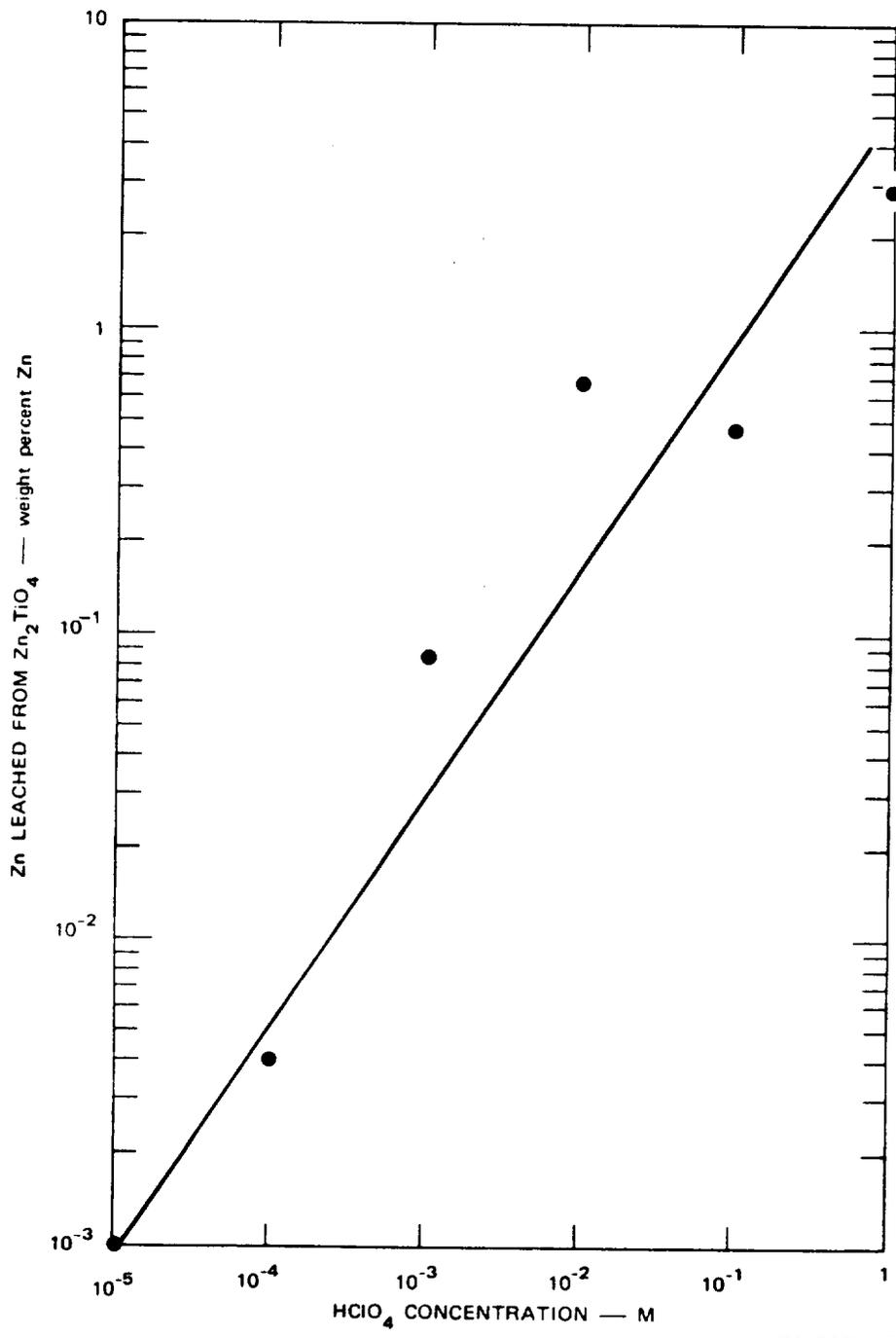
FIGURE 5 EFFECT OF SURFACE COVERAGE OF ADDITIVES ON THE RATIO OF INTENSITIES OF THE 1.97- AND 1.94-LINES OF  $Zn_2TiO_4$  PHOTOLYZED IN VACUUM 3.5 HOURS

detectable ESR lines were observed as a result of photoirradiation. Similar behavior was observed when the pigment was treated only with the  $10^{-2}$  N perchloric acid. It thus appears that excellent photoprotection of the pigment can be achieved by using an acid wash. From the quinoline photolysis work to be discussed later, it will be shown that the cerium redox additive itself provides some protection.

It was suspected that the acid wash achieved the photostability by removal of excess zinc from the pigment. To test this hypothesis the pigment, which had previously been washed with 10% acetic acid, was slurried with various concentrations of perchloric acid for 10 minutes, and the supernatant liquid was separated by centrifugation. The acid solutions were then analyzed by atomic absorption spectroscopy for dissolved zinc. The results shown in Figure 6 indicate that greater amounts of zinc are removed from the pigment by higher concentrations of acid. The  $10^{-2}$  N perchloric acid solution removed an appreciable 0.6 wt% zinc. It is not certain whether the perchloric acid dissolved zinc which originated from excess ZnO in the pigment or from the zinc orthotitanate pigment itself. Incidentally, 2.6 wt% zinc was removed by the 10% acetic acid.

It does seem significant that the acid removal of zinc inhibited photodamage to both damage centers. Hence, it appears that there is an energy transfer mechanism whereby excess zinc promotes photodamage leading to  $Ti^{+3}$  damage centers.

It should be noted that the zinc orthotitanate pigment prior to treatment by 10% acetic acid exhibited a very intense resonance at  $g = 1.94$ . Upon ultraviolet irradiation under vacuum for 3.5 hours, the intensity of this line increased by a factor of about 2, at which time its intensity was about 300 times greater than that for the pigment treated with 10% acetic acid and photoirradiated for 3.5 hours.



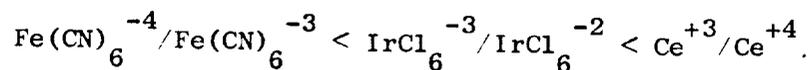
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FIGURE 6 ACID REMOVAL OF ZINC FROM Zn<sub>2</sub>TiO<sub>4</sub> (B-229) AFTER TREATMENT WITH 10% ACETIC ACID

### Quinoline Photolysis

The results of the quinoline photolysis study are summarized for three redox couple additives in Figure 7. The value of  $I_{2.003}$ , the peak intensity of the ESR line at  $g = 2.003$  was measured after 10 minutes of ultraviolet irradiation with a gas mixture of 0.4% oxygen in helium passing over the pigment. The pigments are the same as were studied by vacuum photolysis.

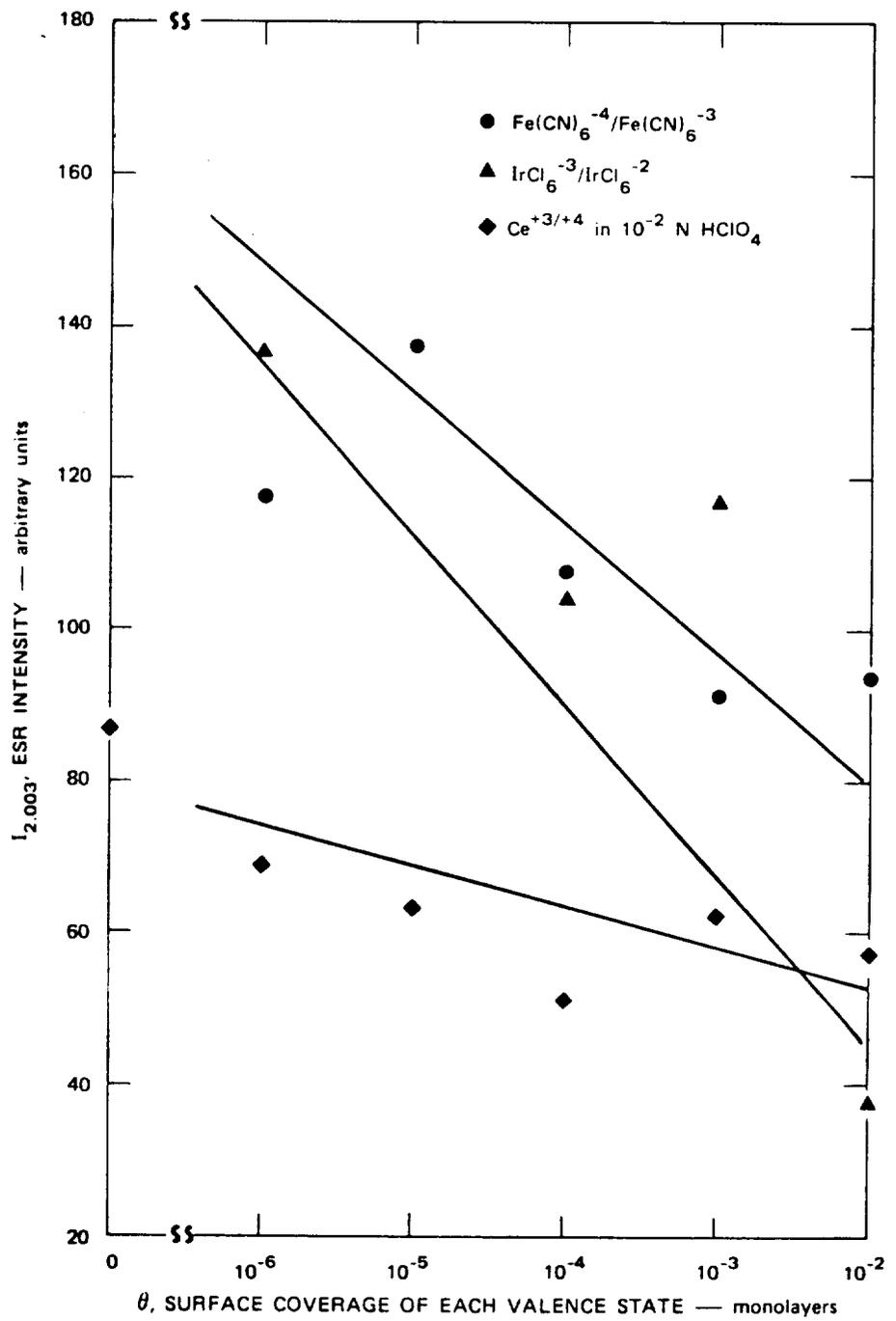
In general, the results show that: (1) greater passivation of the pigment (greater photoprotection of the quinoline) is achieved at higher surface concentrations of the additives, and (2) passivation of the pigment by the additives follows the same order of increased effectiveness of passivation as that for vacuum photolysis.



It is of interest to note that the  $10^{-2}$  N perchloric acid wash did not provide passivation of the pigment against quinoline photolysis.

### Valence State of the Redox Additive on the Pigment

Experiments were initiated by means of a potentiometric titration technique to determine the amount of each valence state of a redox couple additive on a pigment. It was the purpose of the measurement to ascertain whether changes occurred during the pretreatment of the additive on the pigment. Without knowledge of the relative percentage of each valence state, the interpretation of the behavior is much less quantitative. Titanium dioxide pigment was added to the solutions to simulate the zinc orthotitanate, which is in limited supply. The measurements were carried out in as dilute solution as possible in order to analyze for low concentrations of surface additives on a pigment. Present results suggest that it may be possible to make an analysis with as little as  $10^{-2}$  monolayers



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FIGURE 7 THE EFFECTS ON QUINOLINE PHOTOLYSIS OF COVERAGE OF THREE ADDITIVES ON  $\text{Zn}_2\text{TiO}_4$

Results after 10 min uv with gas flow of 0.4%  $\text{O}_2$  in helium.

of additive for 1 gram of pigment. However, tests have not yet been made to determine if the presence of excess zinc on the zinc orthotitanate pigment may cause interference. To increase the sensitivity of detection, it will be necessary to minimize the polarization effects of the electrodes and use various titration solutions.

## SUMMARY

The surface additive approach for photoprotection of semiconductor oxides, which was successfully applied in theory and practice to zinc oxide, has been shown to apply to zinc orthotitanate. With the limited funds available on this program we have demonstrated feasibility, but we have not been able to investigate various problem areas in depth.

The evaluation of the additives by the vacuum photolysis studies is undoubtedly more significant, albeit very time-consuming. Vacuum photolysis studies show that ultraviolet irradiation produces two types of damage centers, whose formation is inhibited differently by the various additives. The increasing order of passivation of the pigment by the additive is: iron cyanide < iridium chloride < acid wash-cerium. The fact that under some circumstances, not entirely understood, the two damage centers (1.97- and 1.94-lines) are differently affected by the two additives (iron cyanide and iridium chloride) suggests that it may be beneficial to develop a surface additive consisting of two redox couples.

The most dramatic protection against development of the damage centers associated with the 1.94-line appears to be imparted by washing the zinc orthotitanate pigment with  $10^{-2}$  N perchloric acid, with or without a cerium redox couple additive in solution. The acid seems to provide protection by removing zinc from the pigment. These pigments had been treated previously with 10% acetic acid to remove excess zinc, but apparently more zinc can be leached out by stronger acids. If the  $10^{-2}$  N acid removes excess zinc, it is understandable that photodamage leading to  $Zn_i$  interstitial zinc (1.94-line) will not occur. Since the acid treatment also inhibits formation of the  $Ti^{+3}$  damage center (1.97-line),

it is supposed that a formation of this center depends upon energy transfer from the process leading to the  $Zn_i$  center.

The quinoline photolysis study qualitatively confirms the results of the vacuum photolysis study; the cerium redox couple does in fact passivate the pigment. The order of increasing passivation of the pigment by redox couple additives is the same as that for vacuum photolysis. The fact that the perchloric acid treatment did not passivate the pigment against photooxidation of quinoline indicates that a different mechanism is active in the presence of quinoline and oxygen than under vacuum. Therefore, to evaluate pigment-binder interactions for a thermal protection coating, it will be necessary to determine the extent of interaction under vacuum conditions between an additive-treated pigment and the binder of choice.

## CONCLUSIONS AND RECOMMENDATIONS

The photodegradation of zinc orthotitanate during ultraviolet irradiation under vacuum conditions can be essentially prevented by application of surface recombination centers, in particular by cerium. This conclusion has been tested by ESR measurements on the pigment as well as in the presence of a "substitute paint vehicle," quinoline.

It is our belief that there is a high probability that by combining the knowledge and technique developed in this program with empirical techniques presently known, an exceptionally stable coating could be formulated with a minimum of development tests. The formulations to be tested would combine: pigments treated with surface additives; hydrous oxide coatings on the additive-treated pigment to preclude additive vehicle interactions; and state-of-the-art paint vehicle formulations.

### Pigment-Additive Systems to be Tested

Results from the present program indicate that pigment composition, as altered by acid treatment, may be as important as surface additives to obtain pigment photostability. Thus, we recommend that future studies include a comparative investigation of the effects of surface additives on selected zinc orthotitanate pigments of various compositions. For this study, the three surface additives developed in the present program should be used at one or two surface concentrations. The pigments of various compositions and known stabilities should be selected from those prepared by IIT Research Institute and should include some plasma-annealed samples.

### Space-Simulated Tests

We recommend that the most photostable pigments identified in the above study be treated with redox surface additives according to the information developed in this program and then be evaluated in space-simulated tests.

These additive-treated pigments would be coated with a hydrous oxide to increase photostability in the presence of a paint binder and to aid in the dispersion of the pigment in the paint vehicle. We are presently applying such technology to additive-treated rutile pigments, which will be used to develop superior chalk-resistant paints.\* The procedures necessary to develop the formulations are available; for example, we would use the quinoline-photolysis technique to evaluate the extent of coverage of the pigment by the hydrous oxide coating.

Samples of these pigments prepared at SRI could be tested in a simulated space environment, for example, at IIT Research Institute.

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\* Industrial multiclient-sponsored program.

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