

Interim Technical Report No. 5/February 1, 1971 to July 31, 1971

INDUCTION PLASMA CALCINING OF PIGMENT PARTICLES FOR THERMAL CONTROL COATINGS

By: E. P. FARLEY

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA 35812

CONTRACT NAS8-21270

CASE FILE
COPY



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



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

Interim Technical Report No. 5/February 1, 1971 to July 31, 1971

August 2, 1971

INDUCTION PLASMA CALCINING OF PIGMENT PARTICLES FOR THERMAL CONTROL COATINGS

By: E. P. FARLEY

Prepared for:

NATIONAL AERONAUTICS AND SPACE ADMINISTRATION
GEORGE C. MARSHALL SPACE FLIGHT CENTER
HUNTSVILLE, ALABAMA 35812

CONTRACT NAS8-21270
Funded Under Code No. 124-09-31-0000-33-1-004-680-2510

SRI Project PMU-7083

Approved by:

P. J. JORGENSEN, *Manager*
Ceramics Group

F. A. HALDEN, *Associate Director*
Physical Sciences (Materials)

Copy No. **22**

CONTENTS

	<u>Page</u>
I INTRODUCTION	1
II SUMMARY	2
III EXPERIMENTAL PROCEDURE	3
IV RESULTS AND DISCUSSION	5
A. Powder Feed Control	5
B. Plasma Calcining	5
C. X-Ray Diffraction Analysis	7
D. Electron Paramagnetic Resonance (EPR)	7
V FUTURE WORK	14
VI ACKNOWLEDGMENTS	14

ILLUSTRATIONS

		Page
Figure 1	Effect of Surface Treatment on Powder Feed Rate	6
Figure 2	X-Ray Diffraction Patterns	8
Figure 3	Scanning Electron Microscope Pictures of Calcined Powders	9
Figure 4	Electron Paramagnetic Resonance Spectra of Plasma- Calcined Pigments (K_2SiF_6 coated Zn_2TiO_4)	10
Figure 5	Electron Paramagnetic Resonance Spectra of Plasma- Calcined Pigments ($K_4Si_4W_{12}O_{40}$ coated Zn_2TiO_4)	11

TABLE

Table I	Effect of Surface Treatment on Characteristic EPR Peaks for Plasma-Calcined Zinc Orthotitanate Pigments	12
---------	---	----

I 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° 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 primarily concerned with plasma treating two additional surface-treated zinc orthotitanate powders at $1670^{\circ}C$, which has been found to be an optimum temperature for plasma calcining zinc orthotitanate. A secondary objective was to investigate the effect of increasing the amount of Zn_2TiO_4 powder produced to a rate of 5 lb per 8-hr shift.

II SUMMARY

Work performed during previous report periods indicated that the plasma calcining process significantly improves the stability of thermal control pigments. In the last report period a plasma-calcined silicate and phosphate-coated zinc orthotitanate powder exhibited the highest stability of any material known to date. During this research period it has been established from the data on hand that a material throughput level is possible in the present plasma system capable of producing 5 lb in an 8-hr shift (4.7 g/min). With structural modifications to the transport and recovery system the present reaction chamber could produce three times this level.

In summarizing the effect of plasma calcining to date and from previous reports the following points have been established:

1. Plasma calcining of ball milled silicated zinc oxide pigment increases its vacuum uv stability ($\Delta\alpha_s = 0.002 @ 1000 \text{ ESH}$).¹
2. Plasma calcining of ball milled 1:1 stoichiometric zinc orthotitanate pigment increases its vacuum uv stability.
3. Plasma calcining of ball milled 1:1 zinc orthotitanate pigment with excess ZnO increases the vacuum uv stability.
4. Plasma-calcined 1:1 zinc orthotitanate pigment with excess ZnO and treated with a silicate and phosphate coating exhibits the highest vacuum uv stability to date ($\Delta\alpha_s = 0 @ 2500 \text{ ESH}$).²
5. The optimum calcining temperature for zinc orthotitanate is at a ΔT of 1670°C .
6. Processing capacity up to 5 lb/8-hr shift is possible in the present system.

¹N. A. Ashford and G. A. Zerlaut, "Development of Space-Stable Thermal-Control Coatings," IITRI Report No. IITRI-U6002-77 (Triannual Report) July 11, 1969)

²G. A. Zerlaut, J. E. Gilligan, and N. A. Ashford, "Space Radiation Environment Effects in Reactively Encapsulated Zinc Orthotitanates and their Paints," AIAA 6th Thermophysics Conference, Tullahoma, Tennessee (April 26-28, 1971)

III EXPERIMENTAL PROCEDURE

The experimental zinc orthotitanate (Zn_2TiO_4) pigments used in this investigation were produced at IIT Research Institute under NASA Contract No. NAS 8-26791. The preparation of the Zn_2TiO_4 pigments has been described in earlier reports.^{3,4,5} During this research period two new surface-treated zinc orthotitanate powders were supplied by IITRI. Presumably the starting zinc orthotitanate powder was the same as that used in producing SRI Sample No. 10 (IITRI Sample No. B296) from our last research period. The first new powder, designated as SRI Sample No. 12 (IITRI Lot No. C-077; Mfg 3/17/71), had received a K_2SiF_6 surface-treatment. The second new powder, designated as SRI Sample No. 14 (IITRI Lot No. C-149; Mfg 5/25/71), had received a $K_4Si_4W_{12}O_{40}$ surface-treatment.

The plasma apparatus used in this study was described in detail in Interim Technical Report No. 1,³ and the present operating conditions were described in Interim Technical Report No. 2.⁴ The pigments were injected downstream from the plasma. 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 (ΔT) 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)

$$\Delta T = 25 E_p I_p / J \quad (1)$$

where J is the total gas flow rate in liters/min at S.T.P., E_p is plate

³R. W. Bartlett, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 1, PMU-7083, (August 15, 1968)

⁴E. P. Farley and P. J. Jorgensen, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 2, PMU-7083 (July 30, 1969)

⁵G. A. Zerlaut and N. A. Ashford, "Development of Space-Stable Thermal Control Coatings," IITRI Triannual Report No. IITRI-46002-85 (February 20, 1970).

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 paramagnetic resonance (EPR). The materials were then submitted to IITRI for solar simulation and spectroreflectometry.

The EPR tests were run in the system described in Interim Technical Report No. 3⁴ with a modification in the sample holder that prevents oxygen contamination as described in Interim Technical Report No. 4.⁵ The EPR measurements were made before and after a vacuum uv irradiation time of one hour and at two temperatures, 300^o and 77^o K.

⁴E. P. Farley, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 3, PMU-7083 (May 8, 1970)

⁵E. P. Farley, "Induction Plasma Calcining of Pigment Particles for Thermal Control Coatings," SRI Interim Technical Report No. 4, PMU-7083 (February 5, 1971).

IV RESULTS AND DISCUSSION

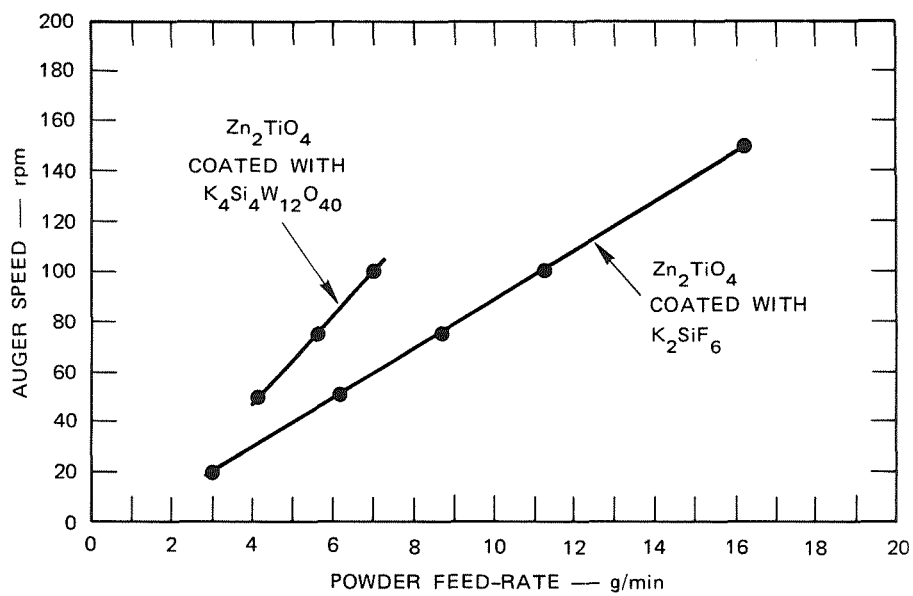
A. Powder Feed Control

In the past the auger-vibratory feeder described and illustrated in Interim Technical Report No. 1 has given reliable and reproducible feed rate control. The two new pigments submitted for calcining during this research period exhibited a marked difference in flow characteristics and required recalibration of the powder feed parameters. The calibration curve for each pigment is shown in Figure 1. Not enough material was on hand to produce a curve for any other specific pigment used earlier in the program. A general comparison can be made in that at a given setting the new pigments flow at a rate 3 to 5 times that of the earlier pigments. The difference is due to a change in the flow characteristics of powder particles as they compact and fill in around the auger.

B. Plasma Calcining

The two pigments were both calcined at the optimum ΔT value of 1670°C . To investigate the effect of powder feed rate the potassium hexafluoro-silicate (K_2SiF_6) treated pigment (SRI No. 12) was processed at three different rates: 1.3, 5.6, and 15.7 g/min. This range of feeding rates encompasses the contract goal of 4.7 g/min (5 lb per 8-hr shift).

All test results to date indicate that feeding rates up to 15.7 g/min do not affect the visual nature of the calcined products. The most evident effect of calcining these new pigments was a loss in total reflectance or graying of the powders. The degree of graying was equal regardless of feed rate for the No. 12 pigment. The second new pigment (SRI No. 14) treated with potassium silicotungstate ($\text{K}_4\text{Si}_4\text{W}_{12}\text{O}_{40}$) exhibited the greatest loss in reflectance. Samples collected in the small condenser bank from each run were sent to IITRI for solar simulation and spectroreflectometry. These tests should establish the reflectance loss quantitatively.



TA-7083-35

FIGURE 1 EFFECT OF SURFACE TREATMENT ON POWDER FEED RATE

C. X-Ray Diffraction Analysis

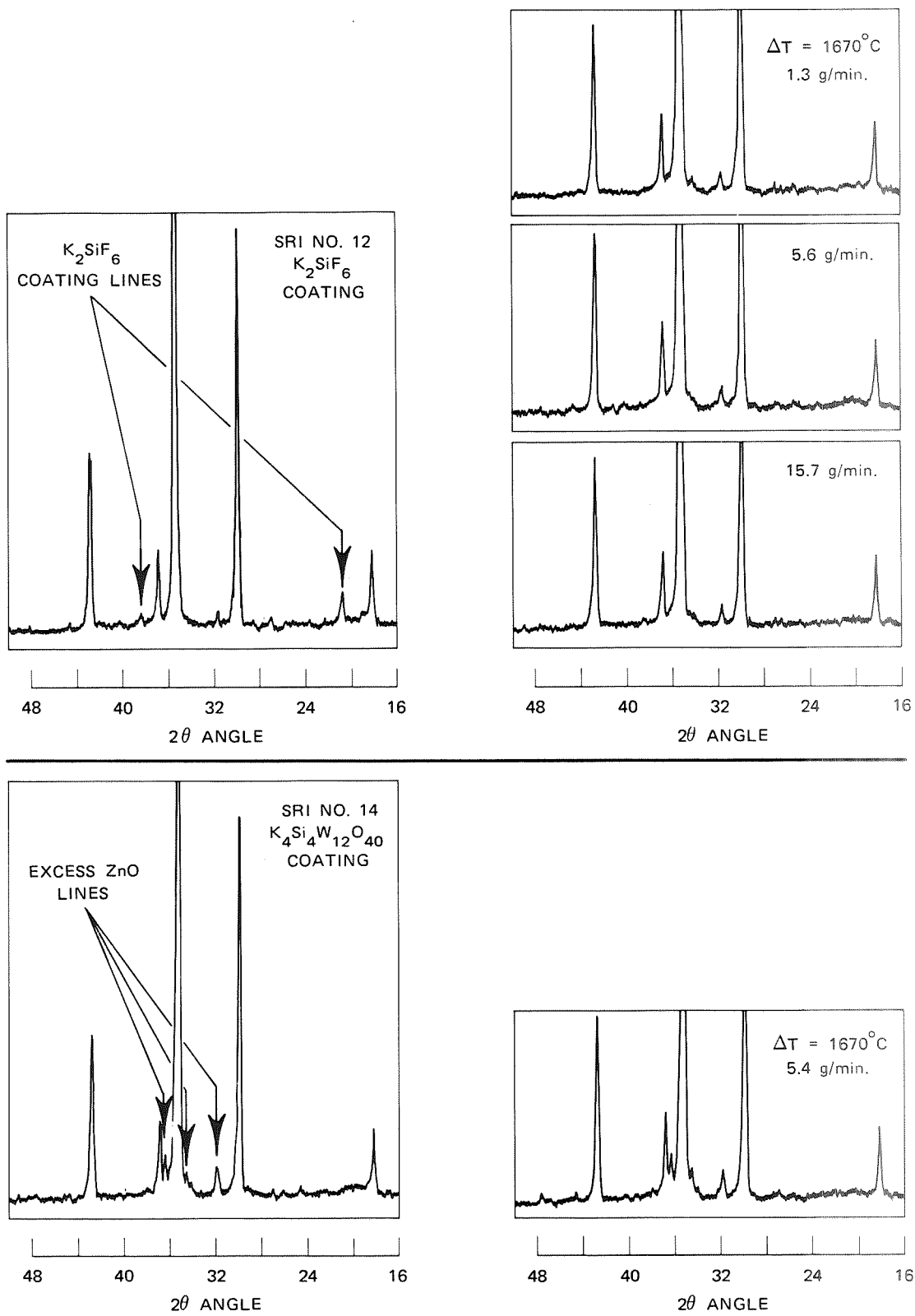
The distribution of crystalline phases both in the starting materials and the calcined products is evident in the diffraction patterns shown in Figure 2. Excess ZnO as a separate phase was not observed in the potassium hexafluorosilicate treated pigment. The major ZnO lines are present in silicotungstate treated pigment and show that the calcining produces no apparent change. The minor phase due to the hexafluorosilicate treatment disappears in each of the calcined products. Scanning electron microscope (SEM) pictures (Figure 3) show the presence of a small particulate phase on the surface of the larger calcined particles, but the quantity is much too small to be detected by x-ray diffraction.

D. Electron Paramagnetic Resonance (EPR)

EPR spectra were recorded in order to establish quality control in future processing for each pigment and calcined product (Figures 4 and 5). Due to the limited funds available for this research period no extensive attempt was made to draw correlations from these data.

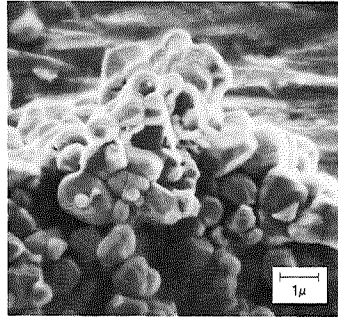
The effect of surface treatment on EPR line intensities of plasma-calcined zinc orthotitanate pigments is illustrated in Table I. Each of the samples was treated under the same ΔT value (1670°C). Samples 6, 9, and 10 are from earlier research periods and are shown for comparison. Samples 6 and 9 have not been surface treated.

Three principal EPR lines are evident at g values of 2.003, 1.98, and 1.96. At 300°K the 2.003 line exhibits the greatest intensity in the fluorosilicate treated powder and tends to decrease in intensity on plasma calcining (Figure 4); the line is of unknown origin but arises from an essentially free electron.

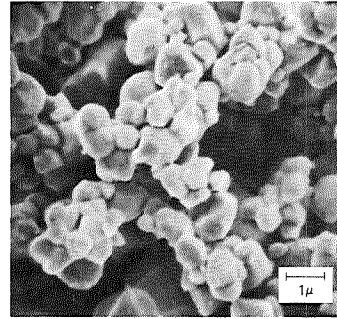


TA-7083-36

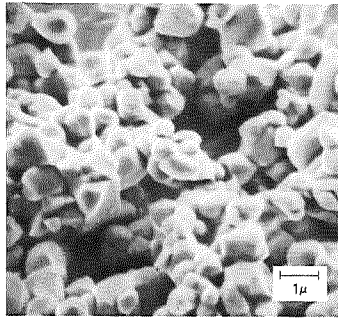
FIGURE 2 X-RAY DIFFRACTION PATTERNS (left figures are as-received powders, right figures are plasma calcined products)



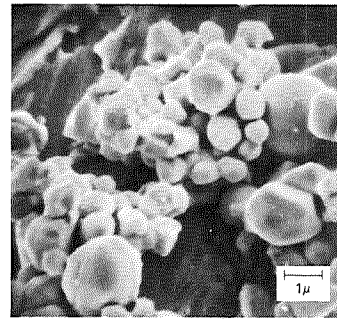
SRI NO. 12
 K_2SiF_6 COATING
(as received) 5000X



12-31.3
 $\Delta T = 1670^\circ C$ 5000X



SRI NO. 14
 $K_4Si_4W_{12}O_{40}$ COATING
(as received) 5000X



14-32.3
 $\Delta T = 1670^\circ C$ 5000X

TA-7083-37

FIGURE 3 SCANNING ELECTRON MICROSCOPE PICTURES OF CALCINED POWDERS

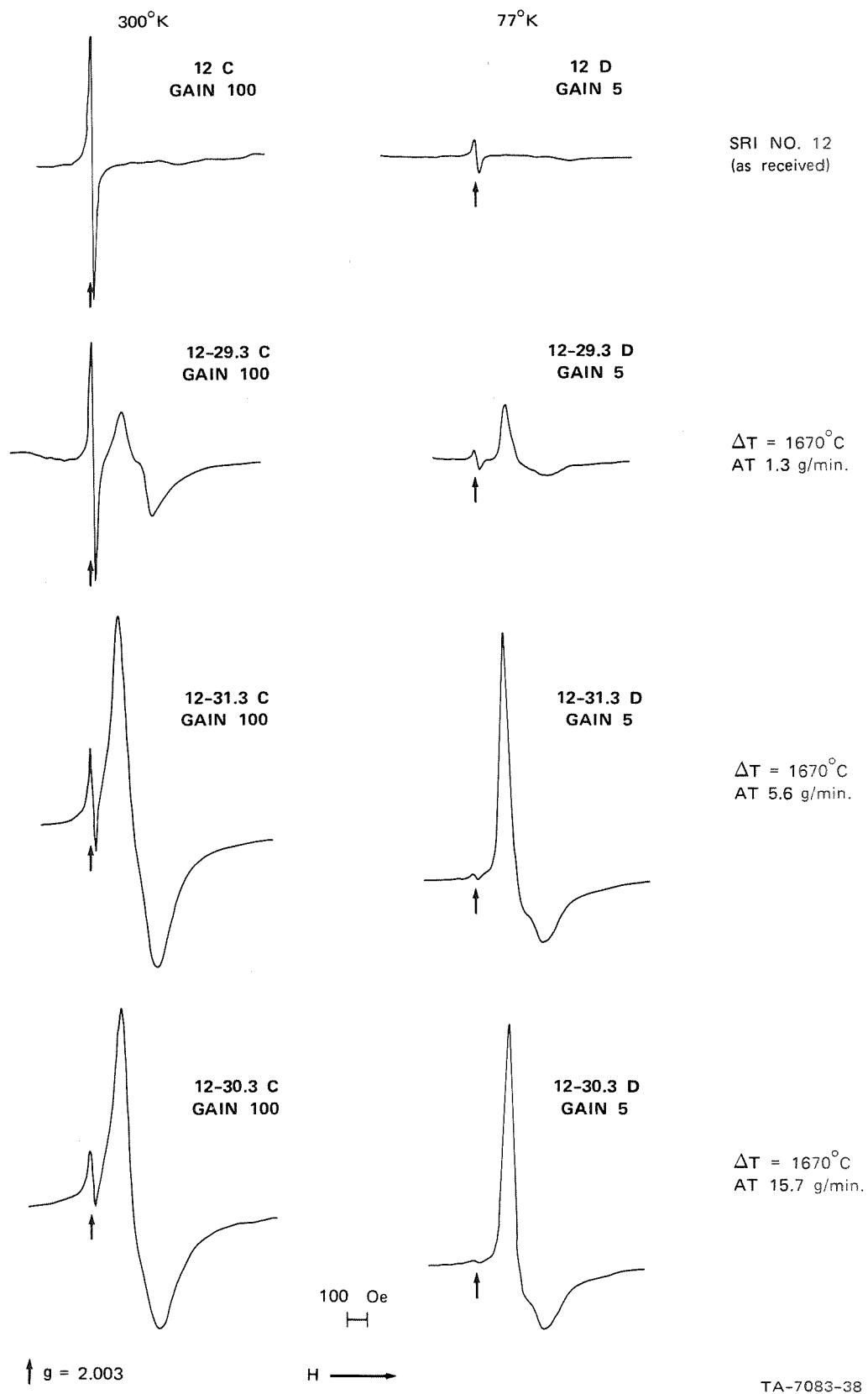
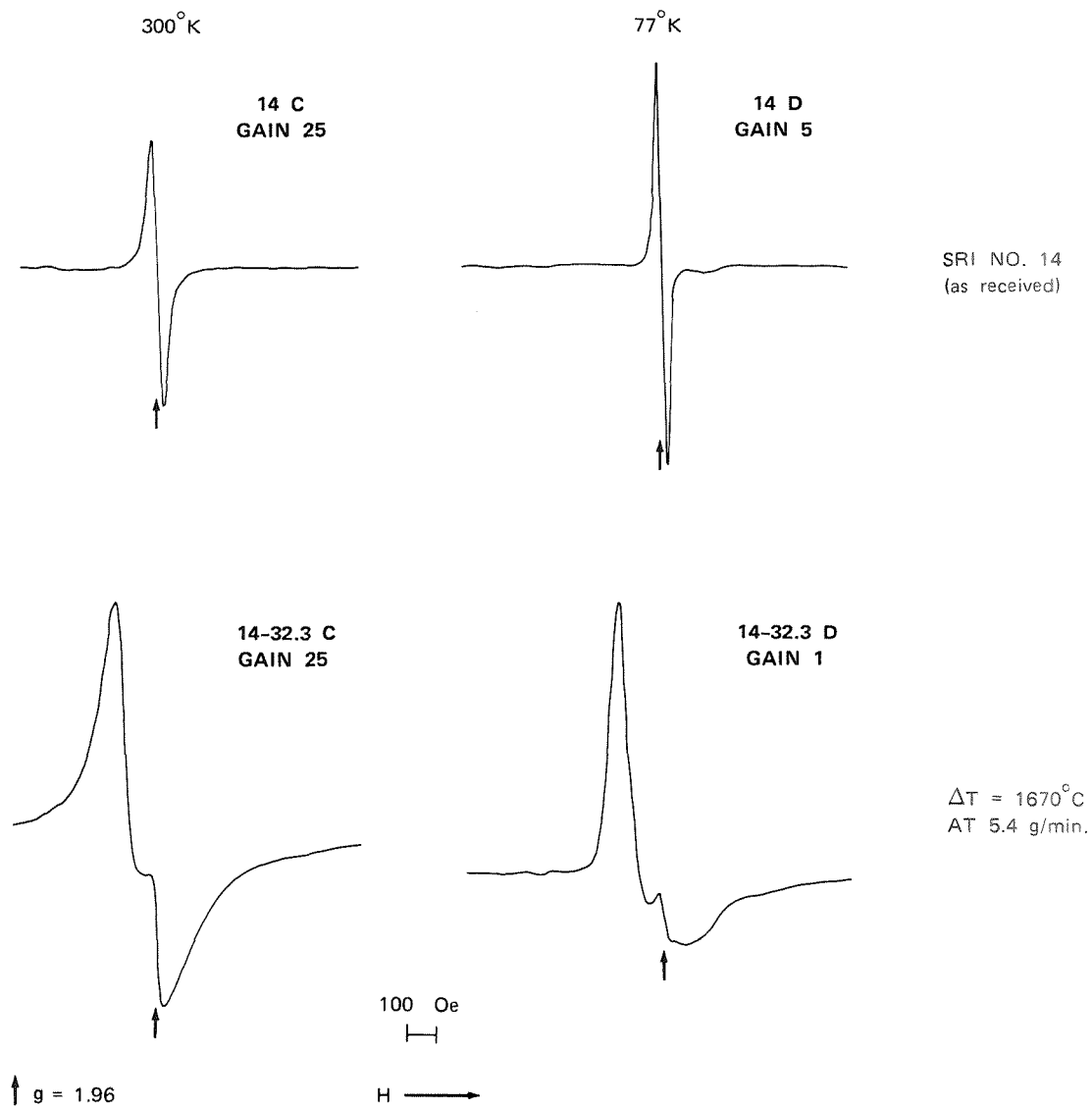


FIGURE 4 ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF PLASMA-CALCINED PIGMENTS (K_2SiF_6 COATED Zn_2TiO_4)



TA-7083-39

FIGURE 5 ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF PLASMA-CALCINED PIGMENTS ($\text{K}_4\text{Si}_4\text{W}_{12}\text{O}_{40}$ COATED Zn_2TiO_4)

Table I

EFFECT OF SURFACE TREATMENT ON CHARACTERISTIC EPR LINES
FOR PLASMA-CALCINED* ZINC ORTHOTITANATE PIGMENTS

Surface Treatment Description	Sample Number	EPR Line Intensity (mm) [†]							
		g = 2.056		g = 2.003		g = 1.98 ^{††}		g = 1.96	
		300°K	77°K	300°K	77°K	300°K	77°K	300°K	77°K
Untreated (1:1)	6-26.3	--	25	4	10	5	200	16	50
Untreated (1:1 excess ZnO)	9-25.3	--	280	35	55	--	15	420	3,000
Silicate & phosphate	10-22.3	--	90	18	30	4	65	110	720
K ₂ SiF ₆	12-31.3	--	--	160	200	330	7,700	--	--
K ₄ Si ₄ W ₁₂ O ₄₀	14-32.3	--	--	10	130	870	25,000	530	4,500

* $\Delta T = 1670^{\circ}\text{C}$

[†] Line intensities normalized to a gain of 250

^{††} Intensity measured at $g = 1.98$.

The line at about $g = 1.98$, which has been ascribed to a Ti^{+3} center, exhibited an intensity and shape that depended on the sample and pretreatment. This line was absent in the as-received samples, but was more intense for the calcined product than it was in the products of previous plasma runs. The silicotungstate product (14-32.3) showed the greatest intensity. Excluding the 1.96 line, the shape of the 1.98 line suggests the presence of two different, and perhaps related, paramagnetic centers. This effect is more evident at room temperature.

The intensity of the 1.98 line increases with increasing loss of reflectance except in the case of hexafluorosilicate coated powder processed at 1.3 g/min. In this case the loss of reflectance is equal to that at the other two feed rates but the 1.98 line is weaker.

The 1.96 line, which is ascribed to donors in ZnO, appears in the calcined material as a satellite signal on the 1.98 line and only for the silicotungstate treated sample. The 1.96 line is most evident in the as-received sample and tends to decrease after plasma calcining (Figure 5). Although the K_2SiF_6 treated sample (SRI No. 12) originally contained excess zinc oxide (0.5%), both the x-ray and the EPR results show no evidence of this phase. However, excess ZnO in the original sample of the silicotungstate treated sample is evident by both techniques.

The interpretation of the behavior of the EPR lines is difficult from the experimental data available at present. However, some tentative suggestions can be made subject to further experimental testing. In the case of the K_2SiF_6 treated sample, if the 1.98 line is due to the Ti^{+3} center, it is possible that F^- ions serve as electron donors if they enter substitutionally for $O^{=}$ ions in the lattice of the Zn_2TiO_4 . The case of the silicotungstate treated sample is more difficult to interpret because there is no obvious mechanism to account for increasing the concentration of donors that could lead to the very large increase of the 1.98 line.

V FUTURE WORK

During the next research period the following areas should be considered for investigation:

1. The effect of residence time. This should be examined by multiple passes or through modifications to the reaction chamber transport and mixing characteristics.
2. Optimum recovery or processing yield. This should be investigated through design modifications to the collection system.
3. Reactive plasma environments. This is to provide improved stability in uncoated pigment particles.

Suggestions 1 and 2 would require a large quantity (2 to 3 lb) of one pigment powder to act as a control standard to measure the effect of modifications in calcining parameters and equipment.

VI ACKNOWLEDGMENTS

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