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Interim Technical Report No. 3/August 1, 1969 to March 31, 1970

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
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CONTRACT NAS8-21270

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I INTRODUCTION

Zinc oxide (ZnO) and zinc orthotitanate (Zn_2TiO_4) are currently used as pigments for thermal control coatings on space vehicles. Both of these materials lose reflectance during space flight or space flight simulations because of ultraviolet radiation in vacuum.[1] To decrease susceptibility to damage from ultraviolet radiation, zinc oxide is coated with an alkali silicate, then heat treated at low temperature, and zinc orthotitanate is heated at temperatures between 900° and 1100°C.

Unfortunately, these heat treatments cause sintering and particle agglomeration, and a subsequent comminution processing step must be employed. The comminution apparently damages the zinc orthotitanate in one case, and results in zinc oxide particles that are not completely coated with alkali silicate 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 was 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.

The work during this report period has been primarily concerned with zinc orthotitanate.

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[1] G. A. Zerlaut et al., "Development of Space-Stable Thermal-Control Coatings," IITRI Report No. IITRI-06002-55, September 1967.

II SUMMARY

The crystal structure of the zinc orthotitanate pigment powders appears to be unaltered by plasma calcining. The particle morphology is altered to the extent that protuberances and sharp edges are removed, producing a rounding effect. Most of the particles are not appreciably altered in size, but the production of a new phase of very small particles shifts the average particle size at high plasma treatment temperatures.

The chemical impurities present in the zinc orthotitanate are from the DuPont anatase starting material and, apparently, from the ceramic vessels used during synthesis. Plasma calcining does not appreciably affect the impurity content.

Four electron paramagnetic resonances have been detected in the zinc orthotitanate. The changes in the value of these resonance lines indicate changes in susceptibility to UV radiation damage. Significant differences have been observed as a result of the synthesis procedure and the plasma treatment.

During the next research period emphasis will be placed on optimizing the calcination process, and on correlating electron paramagnetic resonance with solar simulation.

III EXPERIMENTAL PROCEDURE

The experimental zinc orthotitanate pigments were produced at IIT Research Institute under NASA contract NAS8-5379. Samples of the Zn_2TiO_4 pigments along with samples of their two synthesis components ZnO (SP500, New Jersey Zinc) and TiO_2 (FF anatase, DuPont) were received for plasma calcining and characterization. The pigments were processed through the RF plasma facility. The starting materials and calcined products were then analyzed by X-ray diffraction, scanning electron microscopy (SEM), emission spectrography, electron paramagnetic resonance (EPR), and spectroreflectometry.

The preparation of the pigments was described in Interim Technical Reports No. 1[2] and No. 2.[3] To facilitate comparing test data, the ball-milled zinc orthotitanate pigments have been given letter designations based on their synthesis and preparation (Table I).

The plasma apparatus used in this study was described in detail in Interim Technical Report No. 1, and the present operating conditions were described in Interim Technical Report No. 2. All runs were conducted at pressures between 633 and 710 torr. 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, input electrical energy, and the heat capacity of the argon plasma gas, and is given by equation (1).

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

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

[3] E. 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).

where J is the total gas flow rate in liters/min at S.T.P., E is plate voltage, and I is plate amperage. The plasma consisted entirely of argon, while 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.

Table I

PIGMENT DESCRIPTION AND DESIGNATION

Pigment Type	Description	SRI Sample No.	SRI Sample No.
A-0	Fired to 925°C for 18 hr. Extracted with 10% $HC_2H_3O_2$ Dry ground for 24 hr.	4	3
A-1	Calcined @ ΔT = 1950°C	4-7	3*
A-2	Calcined @ ΔT = 2950°C	4-8	3**
B-0	Fired to 925°C for 18 hr. Extracted with 10% $HC_2H_3O_2$ Re-fired to 1050°C for 5 hr. Dry ground for 24 hr.	6	4
B-1	Calcined @ ΔT = 1950°C	6-9	4*
B-2	Calcined @ ΔT = 2900°C	6-10	4**
C-0	Fired to 1050°C for 18 hr. Extracted with 10% $HC_2H_3O_2$ Dry ground for 24 hr.	3	6
C-1	Calcined @ ΔT = 1750°C	3-2	6*
C-2	Calcined @ ΔT = 2900°C	3-6	6**
D-0	Fired to 925°C for 18 hr. (with excess ZnO) No $HC_2H_3O_2$ extraction Dry ground for about 12 hr.	9	B229
D-1	Calcined @ ΔT = 2000°C	9-20	--

All X-ray diffraction studies were performed on a Norelco 2.5 KW generator equipped with a vertical goniometer using CuK_α radiation with a nickel filter. Scanning speed for general indexing was 2°/min. For lattice parameter and reflection contour determinations, the samples were scanned 1/8°/min. Samples were prepared by lightly pressing the pigment powders into a flat 1-mm thick layer.

All of the scanning electron microscope pictures in this report were made with a Japan Electron Optics Laboratory Co. JSM-2 unit. The pigment particles were dispersed in alcohol and placed on a 1-cm-dia. brass sample holder. They were dried and then given a thin ($\approx$ 50 Å) gold coating from two different angles to prevent charge accumulation. Original photographs were taken at 3,000, 10,000, and 30,000 magnification.

The electron paramagnetic resonance measurements were made with a Varian V-4502 X-band spectrometer equipped with a 12-inch magnet, a field dial, and a dual cavity (TE_{104}) operated from the microwave bridge in a low-power mode. The pigment sample was inserted in one of the cavities employing 10^5 Hz modulation at 2.50 Oe and containing a temperature-controlled dewar. Either a sample of 0.1% pitch in KCl for measuring cavity sensitivity (Ip) or a MgO:Mn sample for measuring g values was inserted in the other cavity employing 400 Hz modulation.

The pigment samples were prepared in the following manner: approximately 1 gram of the powder was placed in a 3-mm-ID quartz tube making a column about 1.5 cm high. The tube was then sealed to a vacuum system and evacuated to about 10^{-5} torr. The samples were heated under vacuum to 150°C for 30 min. The pigment samples were irradiated at a distance of 50 cm with unfiltered light from a 200-watt mercury-xenon lamp (PEK 210) that is in a housing equipped with quartz optics and a front surface mirror (system f-number, f/0.55). The quartz tube was rotated at about 1 rpm to provide uniform irradiation on all sides of the sample.

The reflectance measurements (spectroreflectometer) were made in the IITRI space-solar-simulation facility.

IV RESULTS AND DISCUSSION

The effect of calcining on pigment powders was determined by characterizing the particles before and after the RF plasma heat treatment. The component materials used in the synthesis of the zinc orthotitanate pigments, the beginning pigment powders, and the RF plasma calcined zinc orthotitanate powders were analyzed for crystal structure, chemical phases, particle morphology, particle size distribution, and chemical impurities. Susceptibility of these powders to vacuum UV irradiation damage was measured by EPR and spectroreflectance.

A. Pigment Analysis

1. Crystalline Structure

Zinc orthotitanate is reported to have an inverse spinel structure.[4] The crystallographic description is given as H_o^7-Fd3m; 32 oxygen atoms in approximately cubic closest packing, 8 Zn^{2+} ions in A sites with tetrahedral coordination, and 8 Zn^{2+} + 8 Ti^{4+} ions distributed randomly in B sites with octahedral coordination. The ASTM file card 13-536 based on reference 4 lists 17 observed reflections (Table II) for Zn_2TiO_4. Also listed in Table II are 8 additional reflections that we have observed and indexed in the back reflection region. Agreement in position and intensity of the 17 reference reflections is quite good. The ASTM material was 2 ZnO:1 TiO_2 mixture fired at 1200°C for 3 hours. Our experimental material C-0 was fired to 1050°C for 18 hours.

Bartram and Slepetys observed a shrinkage in the lattice parameter for Zn_2TiO_4 as it was fired to higher temperatures ($\approx$ 0.020 Å shrinkage from 900° to 1400°C). This agrees with an observed tendency for the pigments fired at lower temperatures (925°C) to exhibit a slightly higher lattice parameter (by $\approx$ 0.005 Å) than that of pigment C-0. Pigment B-0

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[4] Bartram and Slepetys, "Compound Formation and Crystal Structure in the System ZnO-TiO_2," J. Am. Ceram. Soc., 44:10, p. 493-499 (1961).

is anomalous in two respects: first, the lattice parameter is smaller (by ≈ 0.010 Å) than those of A-0 and C-0; second the 844 back reflection is distorted into a characteristic skew (Fig. 1) which appears to be unaffected by plasma heat treatment.

Table II

OBSERVED X-RAY REFLECTIONS AND INTENSITIES FOR Zn_2TiO_4

	ASTM 13-536		Experimental	
hkl	I/I_1	d	I/I_1	d
111	6	4.92	8	4.90
220	45	3.00	48	3.00
311	100	2.557	100	2.557
222	8	2.449	9	2.445
400	16	2.121	22	2.115
422	16	1.730	15	1.729
511, 333	40	1.630	38	1.629
440	45	1.496	42	1.497
620	4	1.338	5	1.339
533	10	1.293	11	1.291
622	4	1.276	4	1.277
444	2	1.223	2	1.222
642	6	1.130	4	1.131
731,553	14	1.101	11	1.102
800	4	1.058	(4)	1.058
822, 660	2	0.997	(3)	0.997
751, 555	10	0.977	(6)	0.978
662			(2)	0.971
840			(2)	0.947
664			(1)	0.902
931			(5)	0.887
844			(8)	0.864
862			(2)	0.830
951, 773			(6)	0.818
666			(2)	0.815

( ) Intensities for back reflection region were normalized to agree with ASTM 1° slit intensity for 800 reflection.

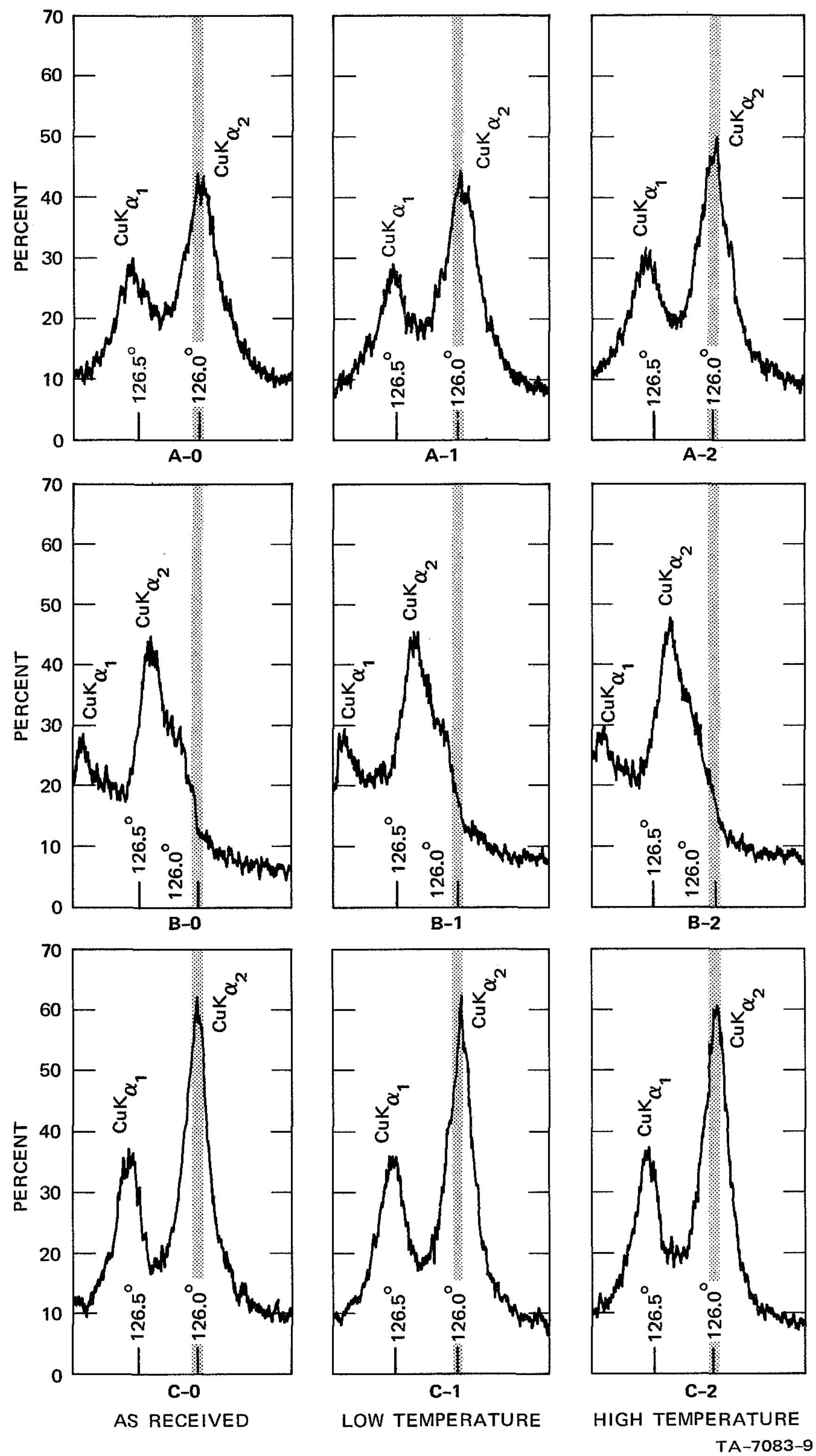

FIGURE 1 BACK REFLECTION PEAKS FROM 844 CRYSTALLOGRAPHIC PLANES IN ZINC ORTHOTITANATE

All pigments are in a particle size range that should be large enough to eliminate line broadening. Therefore the 30% stronger reflections in sample C-0 over sample A-0 are an indication of better crystallinity. Reflections of D-0 (obtained subsequently), which were prepared in the same manner as A-0, are 30% higher than those of C-0. The only differences between the pigments are an excess of ZnO in the formulation of D-0 and the fact that $HC_2H_3O_2$ extraction was not employed. Also the final grinding time was somewhat less (approximately 18 hours compared with 24 hours) for D-0.

No measurable changes in the crystal structure of any of the powders studied were observed as a result of plasma treatment.

2. Chemical Phases

Zinc orthotitanate was the only phase apparent in pigments A-0 and C-0, while B-0 contained approximately 1% free ZnO. Pigment D-0, formulated with 0.5% excess ZnO, exhibited a free ZnO content of approximately 5%, which probably resulted from the omission of the acid washing step after firing. All powders treated in the plasma at a ΔT greater than 2900°C showed the presence of excess ZnO. These quantitative analyses are based on comparing the X-ray diffraction patterns of the pigments with patterns of synthetic mechanical mixtures of C-0 and SP500 ZnO formulated to give 1, 2, 5, 10, and 20% by weight of free ZnO. The resulting diffraction patterns are shown in Fig. 2.

3. Particle Morphology and Size

Figure 3 contains scanning electron micrographs and X-ray diffraction spectra of the two components that enter into the formation of zinc orthotitanate and the same data for the final product A-0. The zinc oxide and anatase were physically mixed and held (18 hours) at a temperature (925°C) sufficient to form the orthotitanate structure. It has been suggested that the ZnO diffuses into the TiO_2.[5] The SP500 ZnO has an average size

[5] Kubo, Ternichiro, et al., "Solid State Reaction of the TiO_2-ZnO System," J. of the Chem. Soc. of Japan, Industrial Chem. Sec. 66:4, pp. 403-407 (1963).

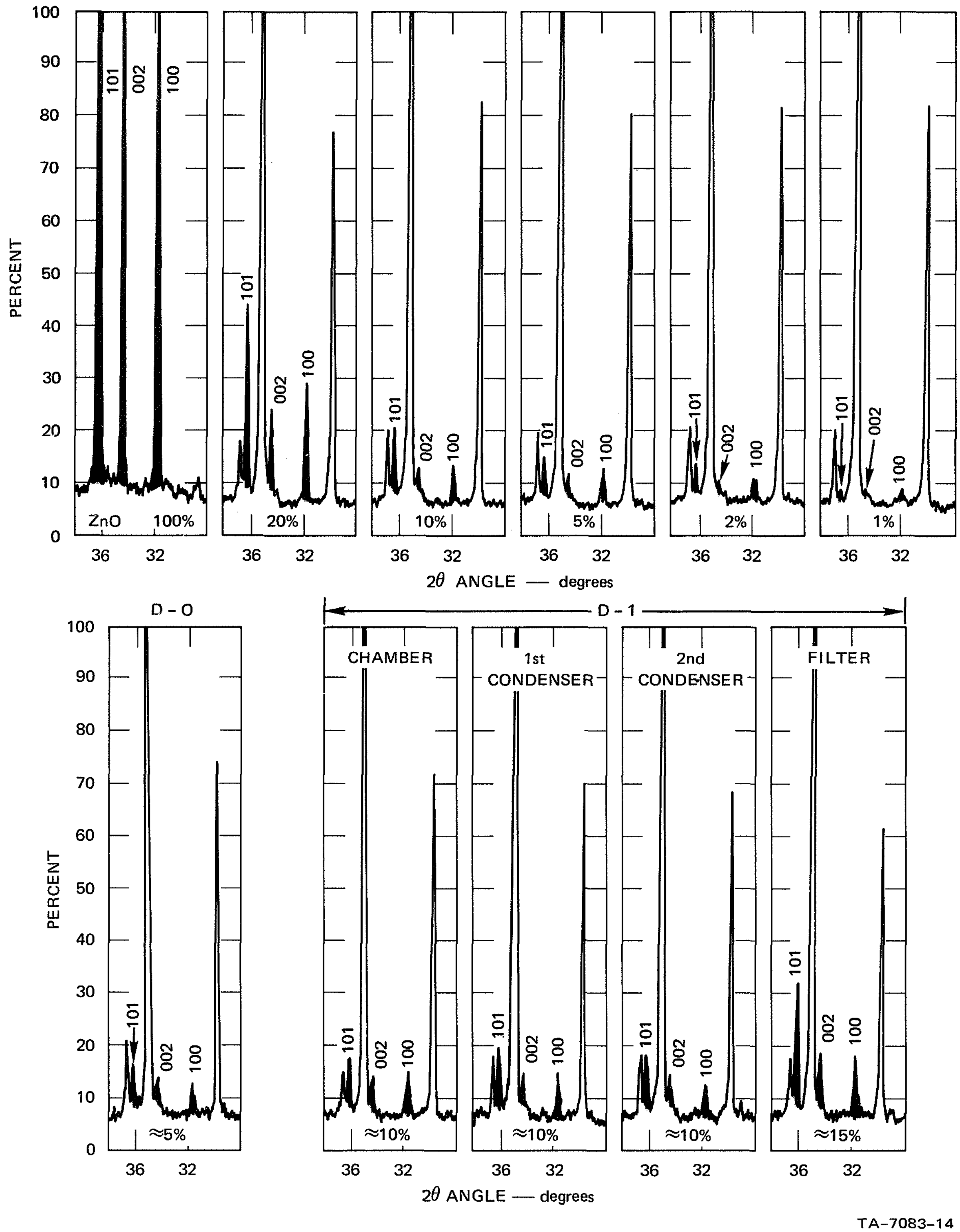

FIGURE 2 QUANTITATIVE DETERMINATIONS OF FREE ZnO MIXED WITH Zn_2TiO_4

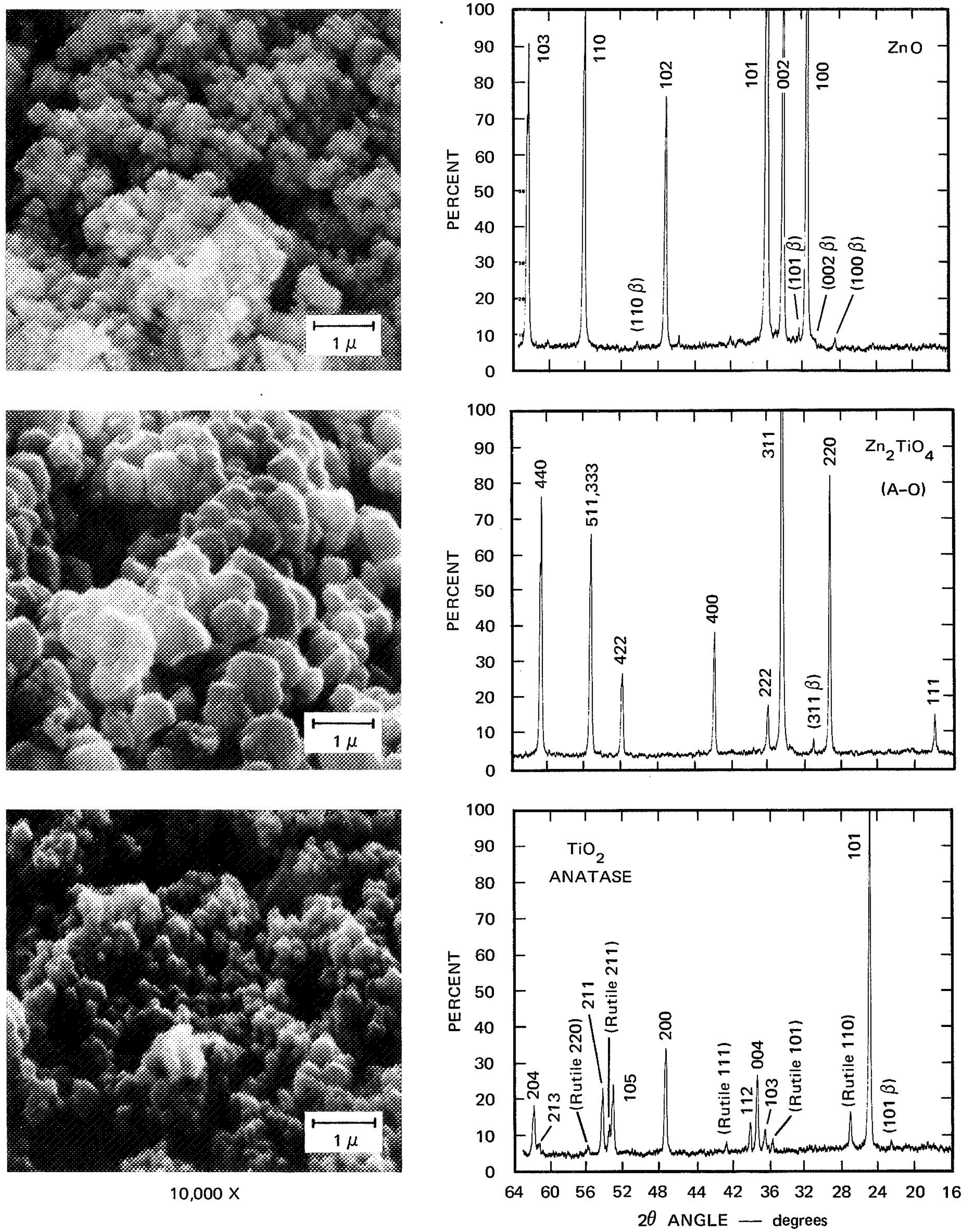

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FIGURE 3 SYNTHESIS OF ZINC ORTHOTITANATE of about 0.3 micron and the DuPont FF anatase has an average of about 0.2 micron. The largest particle observed in ZnO was 0.5 micron and in TiO_2 was 0.4 micron. Using the average figures for starting diameters the calculated diameter at completion of the reaction should be 0.4 micron. The observed values measured from the SEM photographs are given in Table III.

Table III

PIGMENT GRAIN DIAMETERS (MICRONS)

Sample	Minimum	Average	Maximum
A-0	0.4	0.7	1.4
B-0	0.5	1.1	1.7
C-0	0.7	1.2	2.0
D-0	0.5	0.8	1.4

These values indicate a grain growth of 100% at 925°C (18 hours) and 300% at 1050°C (18 hours). As might be expected, B-0 with its two firings lies between the others. Figure 4 illustrates the particle size distribution for A-0 and B-0 measured by the MSA technique. The presence of size fractions above the observed maximum grain sizes are the result of sintered agglomerates.

All pigment particles are generally angular in morphology, except for B-0 which exhibits a tendency toward rounding. A-0 and C-0 show small surface features about 0.1 micron in diameter. These are believed to be related to the $HC_2H_3O_2$ leach given these two pigments before grinding. B-0 was fired again just before grinding and D-0 was not subjected to leaching. These surface features may be related to the presence of free ZnO. The reflectivity curves show a ZnO shoulder at 0.350 nm for A-0 and C-0. D-0, which was formulated to contain excess ZnO, shows a very large 0.350 nm shoulder. This shoulder was not detected on B-0. Figure 5 illustrates typical scanning electron microscope (SEM) photos of the pigment grains before and after plasma treatment. All pigments showed little effect of plasma heating on the observed average particle size. The earlier reported measurements of particle size by the Fisher technique indicated a size reduction at ΔT temperatures in the 2900°C range. The

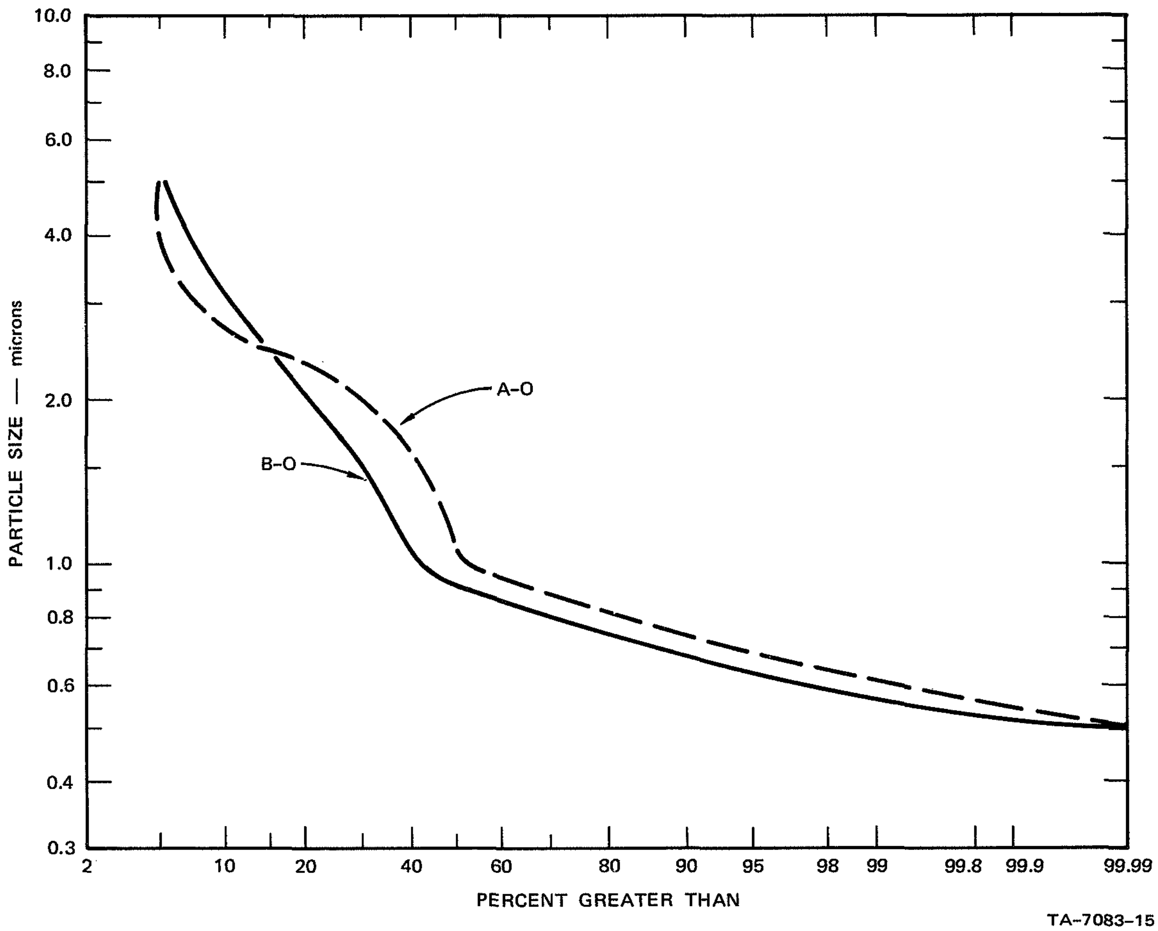
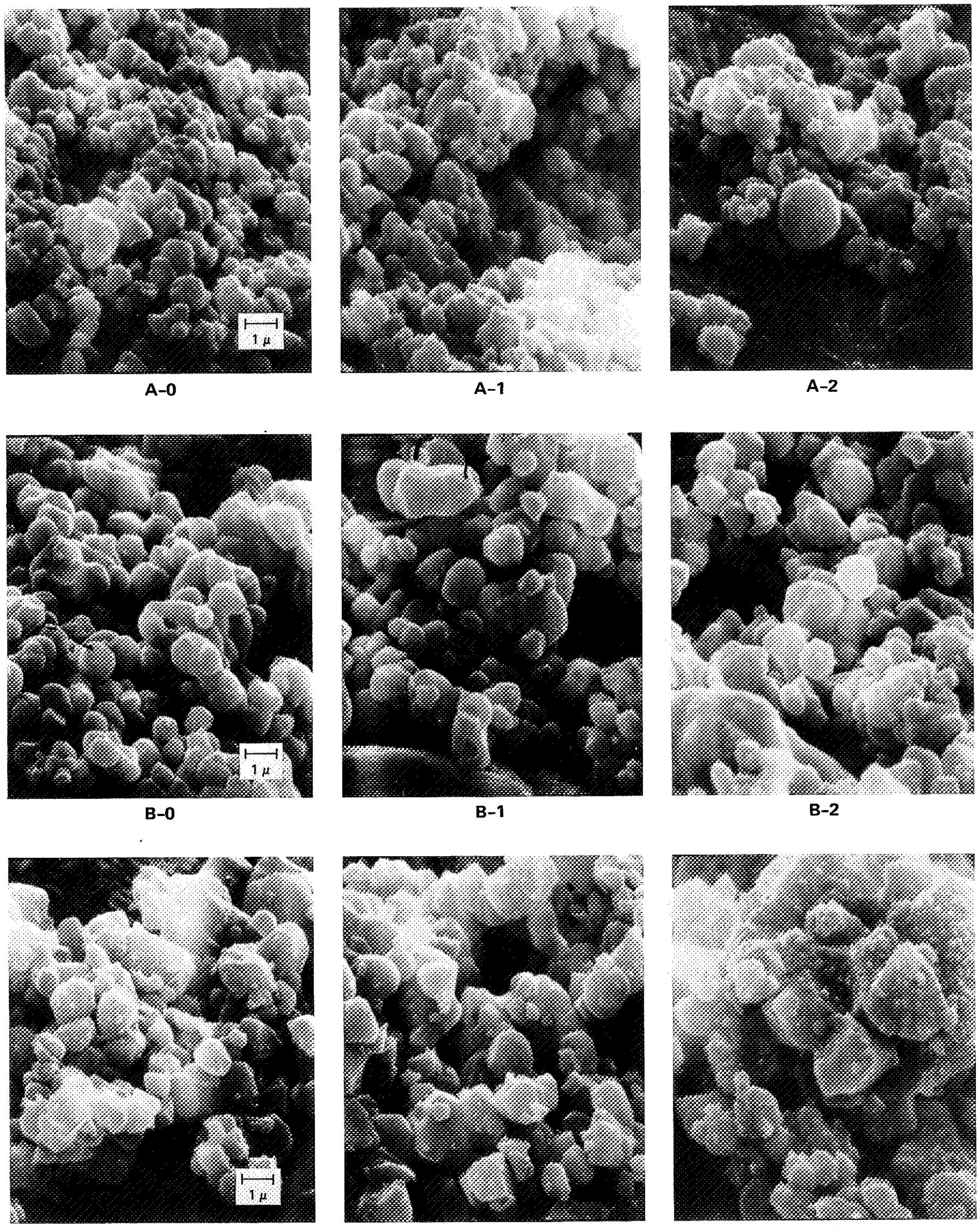


FIGURE 4 MSA PARTICLE SIZE DISTRIBUTION



A-0 A-1 A-2

B-0 B-1 B-2

C-0 C-1 C-2

BEFORE LOW TEMPERATURE HIGH TEMPERATURE

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FIGURE 5 PLASMA TREATED PIGMENT PARTICLES

SEM pictures reveal that the low average particle size values are due to the appearance of new or second-phase particles similar in size to the original surface features observed on pigments A-0 and C-0. After the high temperature plasma treatment, these very small particles (0.1 to 0.2 micron) amount to about 4% in A-2, based on a calculation of a shift in average Fisher size value. The distribution varies between the three pigments in the following ratio: A-2 > C-2 > B-2.

4. <u>Chemical Impurities</u>

In previous studies on other materials, plasma heat treating has been observed to boil out impurities and actually upgrade a given powder. To follow any possible effect on impurities in these pigments, samples were submitted for semi-quantitative emission spectrographic analysis. The results (Table IV) show that the impurities originate from the anatase and during the synthesis of Zn_2TiO_4, and not affected during the plasma calcining treatment.

Table IV

SEMI-QUANTITATIVE SPECTROGRAPHIC ANALYSIS
(Quantities are reported as oxides of elements listed)

	SP500 ZnO	FF Anatase	A-0	A-1	A-2	B-0	D-0
Zn	Princ.*	nd	Princ.	Princ.	Princ.	Princ.	Princ.
Ti	nd**	Princ.	Princ.	Princ.	Princ.	Princ.	Princ.
Mg	nd	0.015	0.02	0.02	0.03	0.03	0.025
Si	nd	0.15	0.5	1.	1.	1.2	0.1
Fe	nd	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Cu	nd	<0.001	<0.001	0.001	0.001	<0.001	0.002
Ca	nd	0.004	0.002	0.003	0.002	0.005	0.003
Al	nd	0.12	0.3	0.4	0.6	0.7	0.25
Nb	nd	0.15	0.05	0.05	0.05	0.05	0.05

* Princ. means principal constituents

** nd means not detected

B. Effect of Vacuum UV Irradiation

The ultimate test of a pigment powder is on the surface of a space vehicle in flight. The next best test is in a solar simulator. All pigment products from this program have been submitted to IIT Research Institute for testing in their IRIF simulation facility. At the same time, to help in identifying the nature of the UV damage, and to provide a faster analysis, the electron spin resonance technique was investigated. All test results have not yet been received from the solar simulator tests, and consequently these will be discussed in a future report.

Electron paramagnetic resonance (EPR) is a form of spectroscopy adaptable to studying photodamage in materials that have electron paramagnetic centers. This technique has been used extensively in this laboratory in the study of ZnO pigments and their susceptibility to UV damage.[6,7] A preliminary examination was made during this research period to apply this technique to the zinc orthotitanate pigments.

The detection of paramagnetic electrons by the electron spin resonance technique is illustrated in Fig. 6. The sample to be examined is simultaneously irradiated by microwave radiation at a fixed frequency, ν, and exposed to a variable dc magnetic field, H. At $H = 0$, the magnetic moments of the electrons are randomly oriented, and the energies of all paramagnetic electrons are equal. Upon increasing the magnetic field, the magnetic moments of the electrons either orient with the magnetic field, $m_s = +1/2$, or against the field, $m_s = -1/2$. The greater the magnetic field, the greater the energy difference, ΔE, between these two states.

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[6] S. R. Morrison and K. M. Sancier, "Effect of Environment on Thermal Control Coatings," SRI Interim Report No. 2 (Dec. 3, 1968).

[7] S. R. Morrison and K. M. Sancier, "Effect of Environment on Thermal Control Coatings," SRI Final Report PAD-6146 (Oct. 15, 1969).

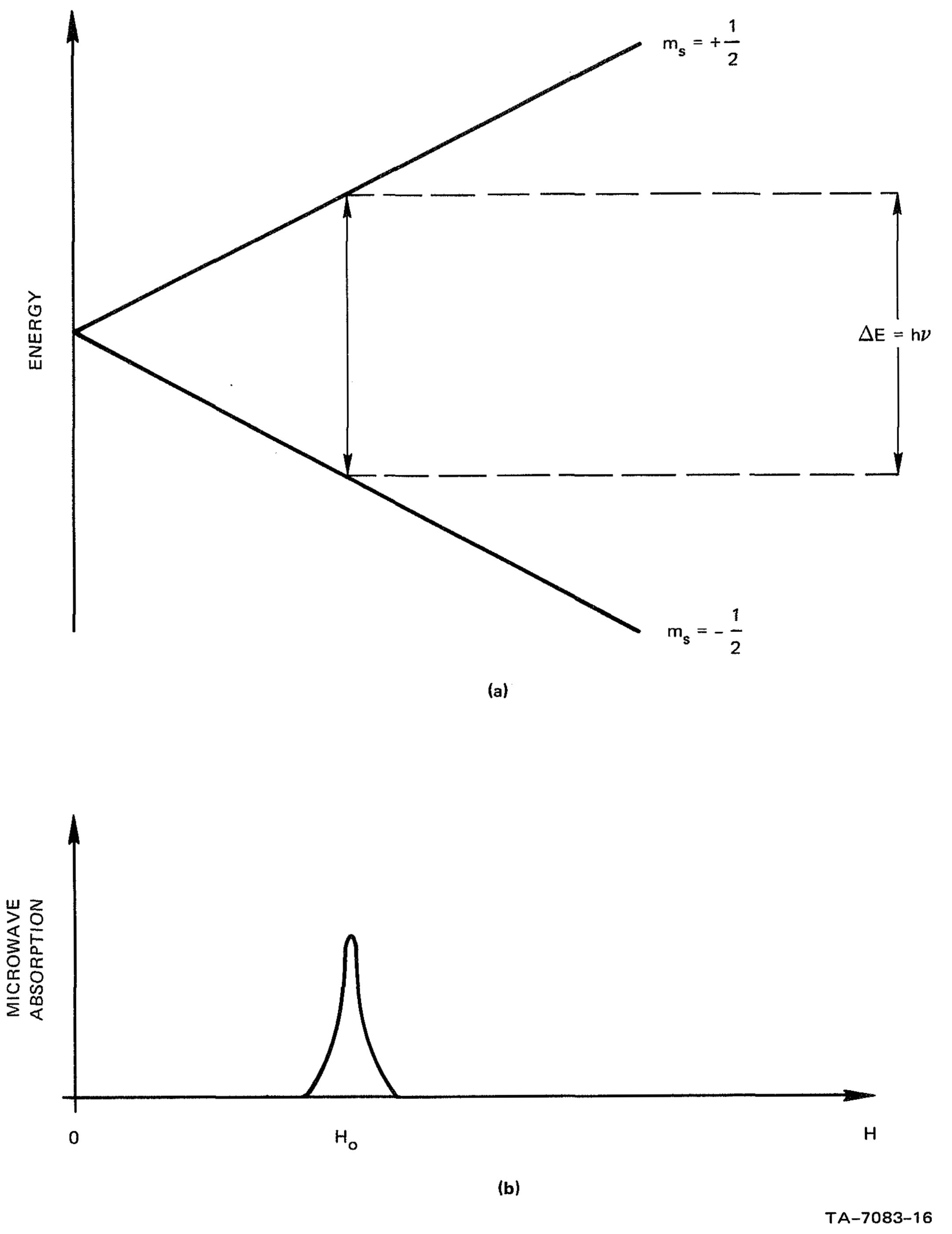


FIGURE 6 EPR THEORY

A resonance condition occurs at a magnetic field of H_o that provides an energy difference of spin states equal to the microwave energy, $h\nu$. This resonance condition is given by

$$h\nu = g\beta H_o \tag{2}$$

where g is the spectroscopic splitting constant, which is the desired quantity, h is Planck's constant, and β is the Bohr magneton.

At resonance, microwave energy is absorbed by the sample as shown in the lower figure. The amount of absorption is proportional to the number of paramagnetic electrons and depends on the difference in population of the upper n_+ and lower n_- states according to

$$n_+ = n_- \exp(-\frac{\Delta E}{kT}) \tag{3}$$

where k is the Boltzman constant, and T is the absolute temperature. Equation (3) indicates that the sensitivity for detection of paramagnetic electrons is greater at lower temperatures where the population is greater.

Several EPR parameters may be measured and used to characterize the paramagnetic electron and its environment:

1. The g value indicates if an electron is free or interacts with angular orbital moments (e.g., p- or d-orbitals).
2. A resonance line may be split when the resonance center has lower than spherical symmetry, and then we speak of anisotropic g values.
3. Hyperfine splitting results from the interaction between the magnetic moment of the electron and that of the nucleus of the atom.
4. The line width of the resonance indicates the relaxation processes by which the absorbed microwave energy is dissipated.
5. The microwave power saturation properties reflect the relaxation processes and often can be used to separate overlapping resonance lines with different relaxation properties.

Two major resonances were found to be associated with Zn_2TiO_4 at liquid nitrogen temperatures. The resonances are designated as follows: (x) g = 1.974 and (y) g = 1.960. The resonance (y) is identical to that observed in ZnO. The response to irradiation and subsequent oxygen bleaching suggests that the resonance corresponds to photodamage defects that cause optical absorption in the far infrared. The resonance (x) has been attributed by IITRI to correspond to photodamage in which Ti^{+4} is converted to Ti^{+3}. Based on the results of this investigation, no clear correlation can be seen between these defects and the optical absorption in the near infrared 800 to 900 nm region.

Table V summarizes the changes observed in the EPR traces illustrated in Fig. 7. Because the scale factors differ between the traces, an attempt has been made to normalize the peak intensities based on the size of the (x) resonance peak in UV treated pigment A-2 taken arbitrarily as a value of 100.

Table V

NORMALIZED EPR RESONANCE INTENSITIES

		Before UV		After UV	
		(x)	(y)	(x)	(y)
Sample A at 97°K	A-0	nd*	nd	60	nd
	A-1	10	nd	30	nd
	A-2	85	400	100	530
Sample B at 77°K	B-0	5	nd	60	nd
	B-1	75	nd	100	nd
	B-2	400	350	350	320

*nd means not detected.

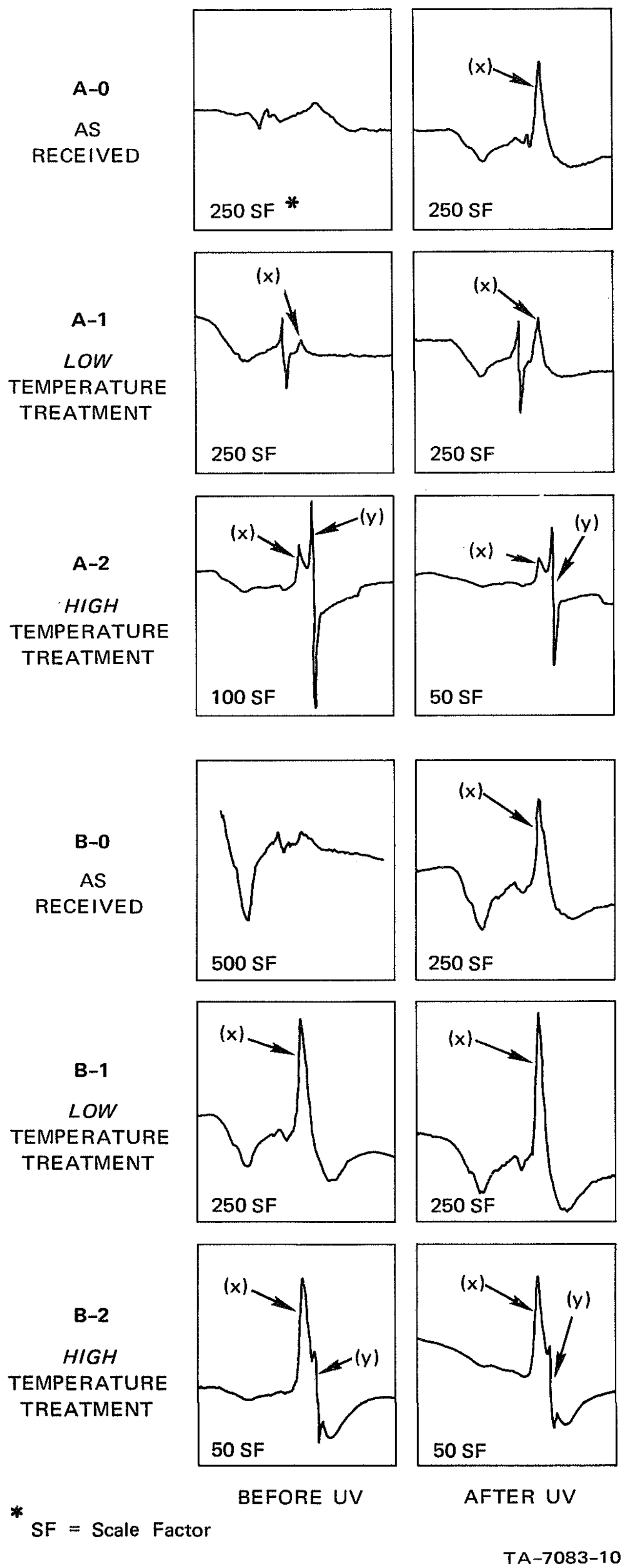
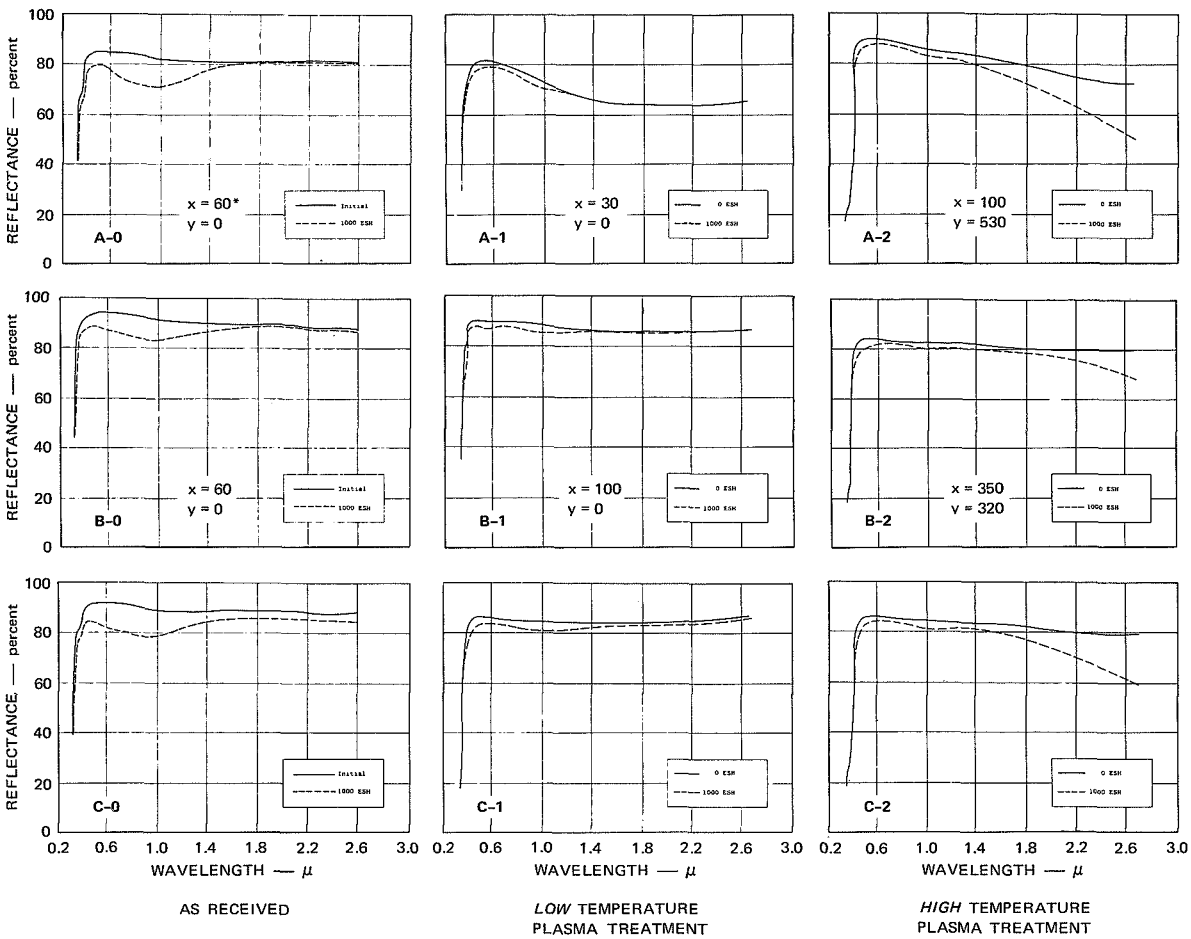


FIGURE 7 EPR TRACES SHOWING EFFECT OF PLASMA CALCINING AND UV EXPOSURE ON TWO PIGMENTS

Changes observed in resonance (x) indicate an effectiveness of plasma heat-treating to cause changes in paramagnetic resonances but there are insufficient data at present to correlate the changes with reflectance data. For ease of correlation, the values presented in Table V are shown on the appropriate curves in Fig. 8. The relationship between the observed UV damage on the high temperature plasma products in the far infrared and the value of resonance (y) is quite apparent. It is also apparent that more work must be done in developing a correlation between resonance (x) and solar simulation testing.

The IITRI data in Fig. 9, γ-irradiated orthotitanate samples run at 77°K, are included to illustrate again the apparent structural difference between pigments A-0 and C-0 and pigment B-0.

Resonances (d) and (e) are apparently associated with the orthotitanate structure and not with the beginning materials. There is a reversal in intensities between these resonances, wherein Samples A and C (having one synthesis heat treatment period) show (e) as predominant and Sample B (with two heat treatment periods) shows (d) as predominant.



* *EPR normalized intensities.*

SOURCE: G. A. Zerlaut, "Development of Space-Stable Thermal Control Coatings," IITRI Letter Report No. IITRI-U6002-75 (March 4, 1969)

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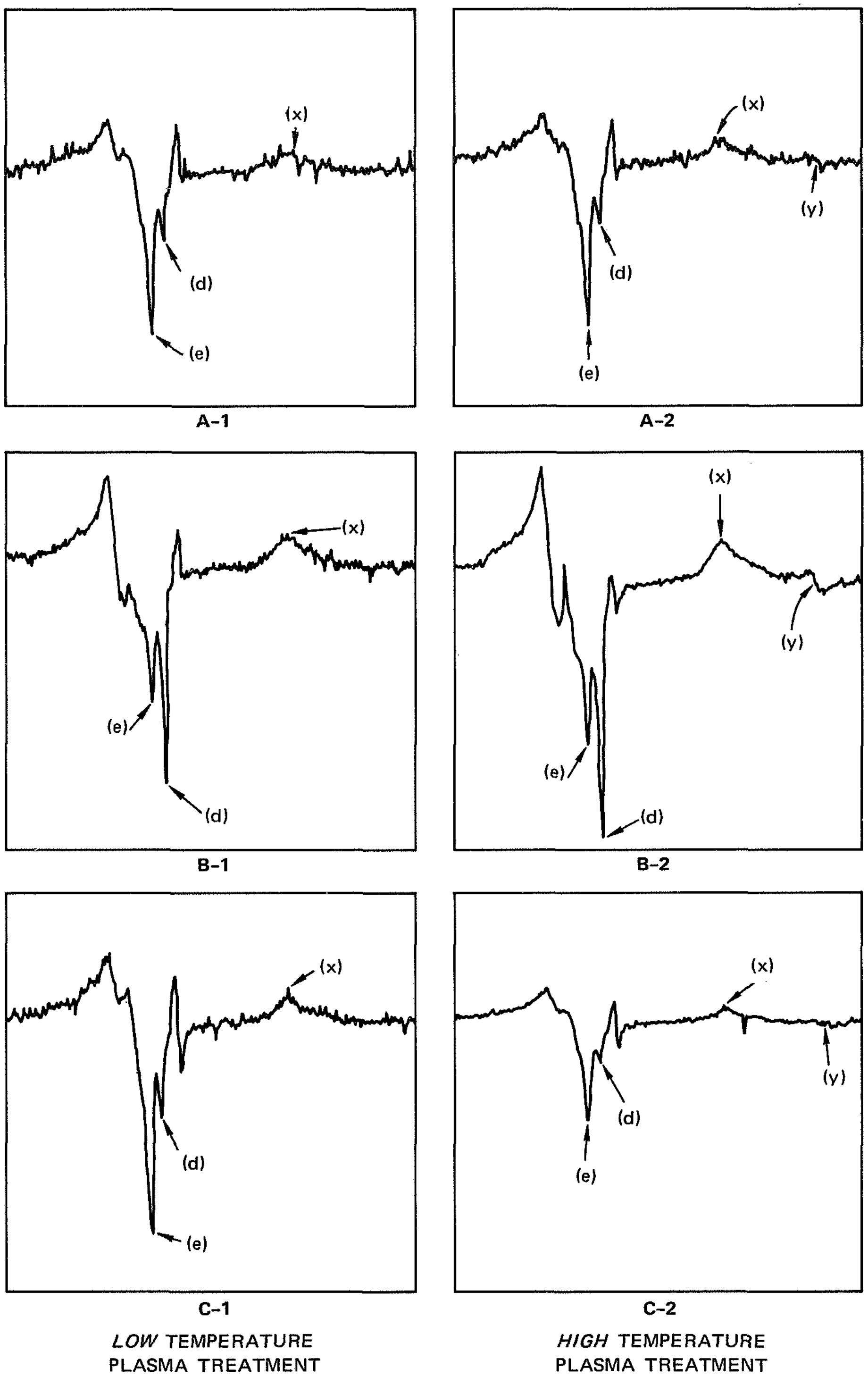
FIGURE 8 REFLECTANCE SPECTRA ON PLASMA TREATED PIGMENTS SUBJECTED TO UV IRRADIATION



SOURCE: N. A. Ashford and G. A. Zerlaut, "Development of Space-Stable Thermal Control Coatings," IITRI Triannual Report No. IITRI-U6002-77 (April 30, 1969)

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FIGURE 9 EPR TRACES OF GAMMA IRRADIATED PIGMENTS SUBJECTED TO TWO PLASMA TREATMENT TEMPERATURE RANGES

V FUTURE WORK

The possibility of altering particle physical features by multiple plasma treatment offers a new approach to pigment preparation. The effect of residence time must be ascertained. The EPR studies should be enlarged to correlate more with the reflectance data from solar simulation tests, and physical testing should include more plasma products from the new excess-ZnO orthotitanate formulations. Pigments should be subjected to different reactive plasma environments to attempt a correlation between the calcining atmosphere and the subsequent EPR characteristics. Once a correlation is established, the plasma parameters should be easily optimized for a given Zn_2TiO_4 pigment. The effect of plasma calcining on other pigments could then be undertaken.