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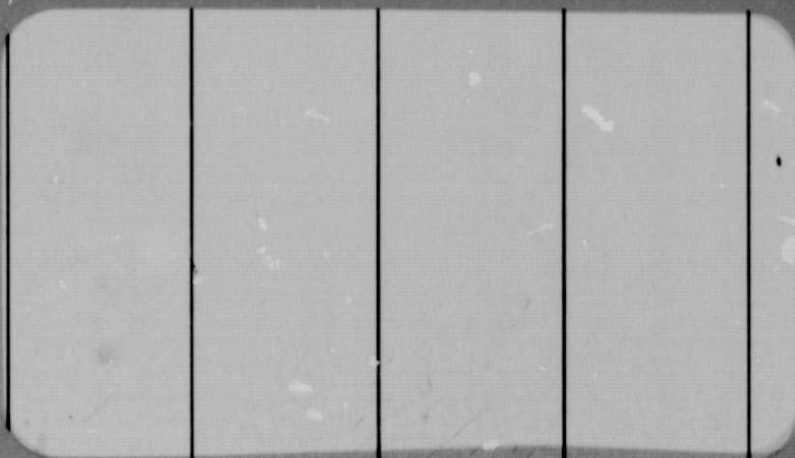
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SPACE STABLE THERMAL CONTROL COATINGS
National Aeronautics and
Space Administration
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IIT RESEARCH INSTITUTE

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SPACE STABLE THERMAL CONTROL COATINGS

1.0 INTRODUCTION AND SUMMARY

The potential that zinc orthotitanate possesses as a pigment for spacecraft thermal control applications has been thoroughly demonstrated in past studies at IITRI (Reference 1-3). The practical realization of this potential hinges most importantly on pigment stoichiometry and also on the production process and optimized preparative conditions associated with it. The "MOX" method, i.e., the use of zinc and titanium oxalate precursors, has the distinct advantages of simple and rapid processing, and of controlled pigment particle size. Thus, the primary goals of this program for obtaining a specification quality zinc orthotitanate are:

- 1) Determination of the chemical identity of $TiOX$ ("titanium oxalate");
- 1) Effect of Zn/Ti ratio on the reflectance spectra and stability to ultraviolet irradiation in vacuum for Zn_2TiO_4 ; and
- 3) Optimized processing parameters for reproducibly obtaining a pigment of the most desirable optical properties and behavior.

In order to achieve an engineering paint/coating, the binder studies are concerned with the well-characterized RTV 602 and the relatively new (but potentially more stable) RTV 615. The OI-650G resin has been developed in IITRI studies (Reference 1) into the most stable silicone binder available. However, the outgassing behavior of the resin in a vacuum environment seriously reduces its practical potential as a space stable binder.

The goal of obtaining a specification thermal control coating appears well within achievable reality. The studies discussed in this report are designed to yield a Zn_2TiO_4 -silicone engineering material for use on future spacecraft.

During the initial portion of this program, studies have been concerned with: 1) binder evaluation; 2) "TiOX" characterization; 3) mixing of precursor powders; and 4) stoichiometry effects. The most significant developments from our studies can be summarized as follows:

1. Preconditioning of "TiOX" by heating at 80°C, followed by storage in a dessicator over CaSO_4 , yields a more reproducible precursor of predictable weight loss. This is an important consideration in stoichiometry design of zinc to titanium ratios.
2. The use of polymeric as opposed to ceramic media in the ball milling tends to eliminate sticking of the powder mixture to the balls and mill walls. This offers the advantage of complete recovery of the milled powder and retention of precise stoichiometry.

2.0 BINDER STUDIES

2.1 Background

Binder studies at IITRI have included evaluation of PS7 potassium silicate (e.g., in Z93), RTV 602 methyl silicone (S-13G), and RTV602 stripped (S13G/LO). The most recent work has been concerned with Owens-Illinois 650 "Glass Resin". This binder would appear to be the most stable polymer to ultraviolet irradiation in vacuum.

The attempts to modify Owens-Illinois 650 "Glass Resin" were successful from the standpoint of eliminating "coasting". The modification process, however, apparently increases the outgassing potential of the modified (OI-650G) resin, seriously reducing its practical potential as a space stable binder. It should be used only in applications tolerant of contamination. The likelihood of developing an alternative process is extremely small. De-gassing the modified resin in the B-stage in vacuo holds some promise but could be very expensive. Further complicating an objective appraisal of its merits are the facts that the modified resin must be thermally cured; that, like the unmodified resin, it too has a tendency to predispose the pigment to extensive S-band degradation; and that the ratio of trimethylchlorosilane/OI-650 must be carefully controlled within a very narrow range.

Based on these shortcomings of OI-650, it appears desirable to investigate RTV602 stripped which has been shown to exhibit acceptable outgassing behavior. This is a proven material and would ease the path toward achieving an engineering material. A second binder candidate would be RTV 615 methyl silicone. Experiments conducted by Mr. Wayne Slemper at NASA-Langley Research Center have shown the RTV 615 to be significantly more stable than RTV 602 to ultraviolet irradiation in vacuum. As was the case with RTV 602, modification of 615 to obtain low outgassing characteristics should be an achievable goal. The merits of

RTV 615 as a paint binder, however, must be determined. Engineering studies which would evaluate its potential in this regard must be made to assure that it can meet the reasonable and applicable requirements such as those of NASA-MSFC Spec. No. 10 M01835 (for S-13G).

2.2 Paint Preparation

Binder studies for this program are concerned with RTV 602 and RTV 615, along with stripped modifications of these silicones. The RTV 615 material has been reported to be more stable than RTV 602 in an ultraviolet vacuum environment. In order to obtain an assessment of this reported behavior, specimens were prepared for UV-vacuum and outgassing testing. The initial group of samples prepared and submitted to NASA-MSFC were as follows:

- Binder Films: 1) RTV615
- 2) RTV602
- 3) RTV602-LO
- Paints: 1) RTV615 + LH-111(6-12) zinc orthotitanate
- 2) RTV602 + ZnO (S-13G)
- 3) RTV602-LO + ZnO (S-13G/LO)

A second set of paint samples were prepared and submitted to NASA-MSFC for additional evaluation. The data for these samples are listed in Table I.

The results of outgassing studies and of ultraviolet irradiation in vacuum are not available as of the date of this report preparation. This information is being generated now and should be available in the near future.

2.3 Working Characteristics of RTV615

Experimentation with RTV 615 has revealed certain characteristics of this binder material which can be summarized as follows:

Table I

PAINT SAMPLES SUBMITTED TO NASA-MSFC

	Number		
	E-208	E-209	E-210
Binder	RTV 602	RTV 602-LO	RTV 615
Pigment	LH-111(6-12)	LH-111(6-12)	LH-111(6-12)
Pigment/Binder, by weight	2.55/1	2.82/1	2.67/1
Cure	RT	RT	100°C/16 hours
Thickness, mils	8-10	8-10	8-10

1. Catalysis -RTV 615 does not cure with SRC-05 or with tetramethyl guanidene (used with RTV 602). A G.E. furnished catalyst termed RTV 615B effects a cure.
2. Curing - an elevated temperature (100°C/16 hr.) has been found to be desirable for obtaining a tack-free film or paint.
3. Solubility - the best single solvent appears to be toluene. Isopropyl alcohol is an assisting solvent but will not dissolve the polymer by itself. A previously used solvent (thinner) designated X-99 has been found to be an effective component. Its composition is: toluene-40%; isopropanol-20%; xylene-20%; butane-15%; and butyl acetate-5%.

3.0 PIGMENT STUDIES

3.1 Synthesis of Zinc Orthotitanate: Background

The synthesis of Zn_2TiO_4 can be accomplished by various methods, all of which involve calcination of zinc and titanium precursors. The three processes which have been studied in past programs at IITRI are discussed in the following sections.

3.1.1 Solid State Reaction

The initial method studied at IITRI for producing Zn_2TiO_4 consisted of reacting zinc oxide with titanium dioxide. A series of grinding and mixing operations are carried out at low temperature to assure good particle-to-particle contact, and hence, reactivity, of the two oxides. Formation of the Zn_2TiO_4 pigment is accomplished by firing at 925°C for 18 hours, additional grinding, followed by reactive encapsulation and/or induction plasma calcining (Reference 3) to obtain a stable product. A total of four hours of wet grinding and 1/2 hour of dry grinding is conducted prior to firing and this is followed by an additional 12-24 hours of grinding for comminution of the Zn_2TiO_4 product.

The multitude of grinding steps in this process has the disadvantages of long processing times and the dangers of introducing degradable contaminants. Although plasma calcining appear to be favorable for achieving a stable pigment, it involves a rather sophisticated apparatus, and the yield is somewhat low. Another disadvantage of the solid state reaction process is the relatively limited control of the pigment particle size. In view of the aforementioned limitations, studies of the use of salt precursors for Zn and Ti were conducted in an effort to gain a superior product.

3.1.2 Coprecipitation (COP)

The purpose of the coprecipitation method (COP) is to obtain an intimate mixture of zinc and titanium compounds. This excellent mixing along with the highly reactive nature of the

oxides derived upon decomposition of these compounds, permits conversion to Zn_2TiO_4 under moderate conditions of $600^\circ\text{C}/2$ hours. Other investigators (References 4 and 5) have shown that higher temperatures and/or longer times are necessary using less reactive zinc and titanium precursors.

The coprecipitation method involves the simultaneous addition of a mixed solution of zinc and titanium chlorides to a solution of oxalic acid. The resulting solution is then heated to, and held at a specified temperature, during which time it is continuously stirred while the precipitate is formed.

Calcination and firing are performed in standard atmospheric Globar furnaces. Powders are contained in fused silica boats for firings up to 1300°C and in platinum crucibles at 1400°C .

A definite advantage of this method is that no grinding is necessary for obtaining pigment particles amenable to incorporation into a paint. Laboratory scale-up studies showed that batches of about 1.5 pounds could be produced; further scale-up should be easily attainable with larger reaction vessels.

In a previous program (Reference 1), a number of COP materials designated the LH-series were evaluated. Optimization of these materials in terms of optical properties and stability was achieved through studies of precipitation parameters, calcination conditions, acid leaching for excess ZnO , and encapsulation. The LH pigments can thus be considered a viable backup pigment to the MOX materials which are discussed in the next section.

3.1.3 Mixed Oxalate Process (MOX)

The mixed oxalate studies were conducted to determine if the particle size of the precursor oxalates and the Zn_2TiO_4 obtained from their calcination could be controlled. This investigation was prompted by the observation that COP materials had a tendency toward agglomeration; it was felt that this might be avoided through mixing of the individually precipitated zinc and titanium oxalates.

The "MOX" method, distinguished from the COP method, employs two independent and separate steps in the production of the zinc and titanium oxalates. Unlike those in the COP process, the conditions and parameters in the "MOX" method may be separately established and controlled to produce an optimum precipitated product.

Studies (Reference 1) have shown that the precipitation conditions for producing an optimum ZnOx product differ markedly from those for "TiOX". In the COP method, the need for a 90°C precipitation condition for "TiOX" requires that the zinc oxalate also be precipitated at this temperature. However, it has been shown in our recent studies that zinc oxalate of finer particle size can be obtained at temperature as low as 10°C . A finer particle size zinc oxalate is desirable from two standpoints: First, to obtain precursors of finer particle size and thus, also of the fired product, and second, to obtain improved mixing of zinc oxalate with "TiOX". A closer match of the particle sizes of the zinc oxalate and "TiOX" should improve mixing and enhance the reactivity as well as the uniformity in the reacted binary oxide.

Experimental results showed that a finer particle size zinc orthotitanate was achieved using the very fine precursors. The MOX process consequently holds a distinct advantage in that conditions for optimum products and yields of zinc oxalate and "TiOX" can be established for each independently. Zn_2TiO_4 obtained by calcination of the mixed "TiOX" and ZnOx precipitates can be

utilized as a pigment with no grinding. Ultraviolet stability tests, of course, must be accomplished to determine whether Zn_2TiO_4 prepared from "MOX" precursors is stable under simulated space conditions and also to determine the calcination conditions which promote environmental stability.

3.2 Materials Preparation

The initial work with pigments was involved with the acquisition of chemicals and preparation of "TiOX" and zinc oxalate. These were needed for the "TiOX" characterization studies and for the MOX studies for preparing zinc orthotitanate powders.

The precipitation conditions for "TiOX" preparation are $90^\circ\text{C}/1$ hour in an aqueous medium. Zinc oxalate is being precipitated at room temperature (also in water) in order to obtain the finer particle size achieved at lower temperatures.

The preparation of both "TiOX" and zinc oxalate will be a continuing part of this program. X-ray and gravimetric checks show good reproducibility in these precipitates from batch to batch, each weighing about 550 grams.

3.3 "TiOX" Characterization

3.3.1 Gravimetric Analysis

It has been established in previous studies that calcination of "TiOX" at temperatures of 400°C or higher results in the formation of TiO_2 with a weight loss of about 54%. This weight loss, however, could vary as much as $\pm 1\%$, thus making the design of exact stoichiometry difficult. The molecular weight assigned to "TiOX" in earlier work was calculated as:

$$\frac{79.90}{x} = 0.54$$

where 79.90 = molecular weight of TiO_2

54.0 = fractional amount of TiO_2 residue

x = molecular weight of "TiOX" = 147.96

If the fractional residue were 0.53 or 0.55, the apparent molecular weight of the "TiOX" precursor would be 150.75 or 145.27, respectively.

During the present studies, the "TiOX" was preconditioned by heating at 80°C for 16 hours, followed by storage in a dessicator over CaSO_4 . This material was then carefully weighed, converted to TiO_2 at 850°C, and reweighed to determine the fractional residue. The data showed a reproducible value of 143.2 ± 0.1 as the molecular weight of the "TiOX".

These experiments indicate the value of preconditioning in that a more constant (reproducible) precursor of predictable weight loss, and thus, TiO_2 product, is obtained. This is accomplished through removal of moisture which adsorbs on the high surface area "TiOX". Variability in this adsorbed water can occur due to temperature and humidity conditions as well as the amount of activity of the available surfaces of the "TiOX" particles. Therefore, such preconditioning has been incorporated into the processing procedure for preparing "TiOX"-zinc oxalate mixtures and ultimately, Zn_2TiO_4 .

In contrast, zinc oxalate has been found to be much more stable in storage, exhibiting calcination weight losses of 57.02 to 57.10% or very close to the theoretical value of 57.04%. Therefore, no preconditioning is used for zinc oxalate.

Using a Fisher Model 260P Differential Thermal Analyzer programmed for a temperature rise of 10°C per minute, 100 mg samples of "TiOX" and of zinc oxalate were run against 100 mg of fused silica. In the case of "TiOX" the test revealed a single large endotherm starting at approximately 160°C and peaking at 260°C, and no further marked thermal activity to 750°C (Figure 1). The existence of only one

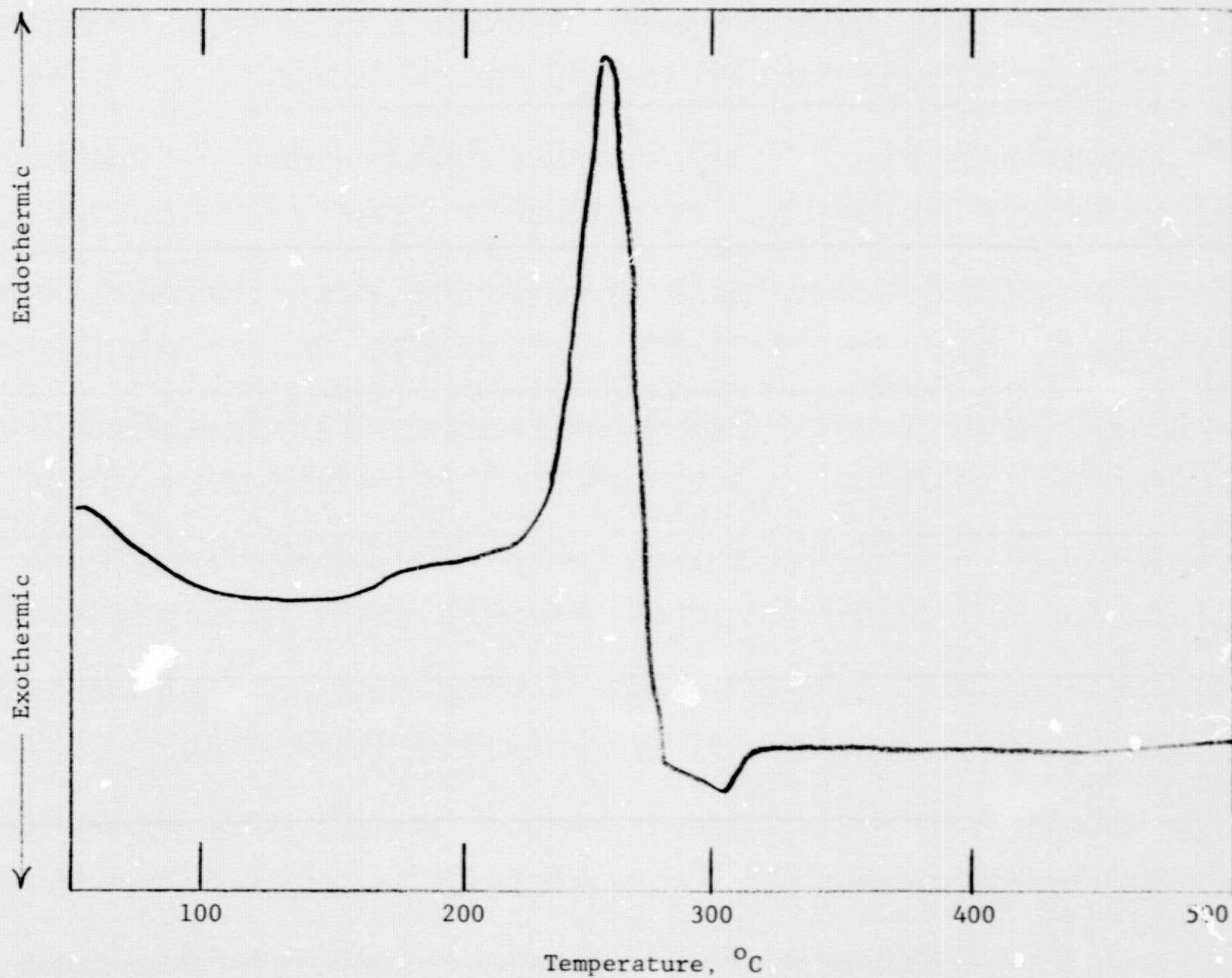


Figure 1. DTA Study of "TiOX" Decomposition

relatively sharp endotherm indicates that "TiOX" is not a hydrate. However, water of hydration may be hidden by the large endotherm. The zinc oxalate showed two endothermic peaks typical of hydrate, one beginning at approximately 107°C and peaking at 165°C, followed by a second peak beginning slightly above 310°C and peaking at 408°C, and showed no further thermal activity to 750°C (Figure 2).

3.3.2 SEM and X-ray Analysis

Examination of four batches of "TiOX" ("TiOX-2" through "TiOX-5") show the material to consist of sphere-like aggregates of particles which are less than one micron in size (Figures 3 and 4). Good uniformity from batch to batch was evident, and this morphology is similar to that determined on a previous program.

The "TiOX" materials have also been examined using X-ray analysis. Debye-Scherrer powder patterns show that the current materials are identical in crystalline structure to that produced in previous programs. This shows that the present preconditioned "TiOX" with a molecular weight of about 143 (as compared to the "old" material of about 147) has had only adsorbed surface water removed; loss of chemically combined water would generally result in a change in crystal structure or size.

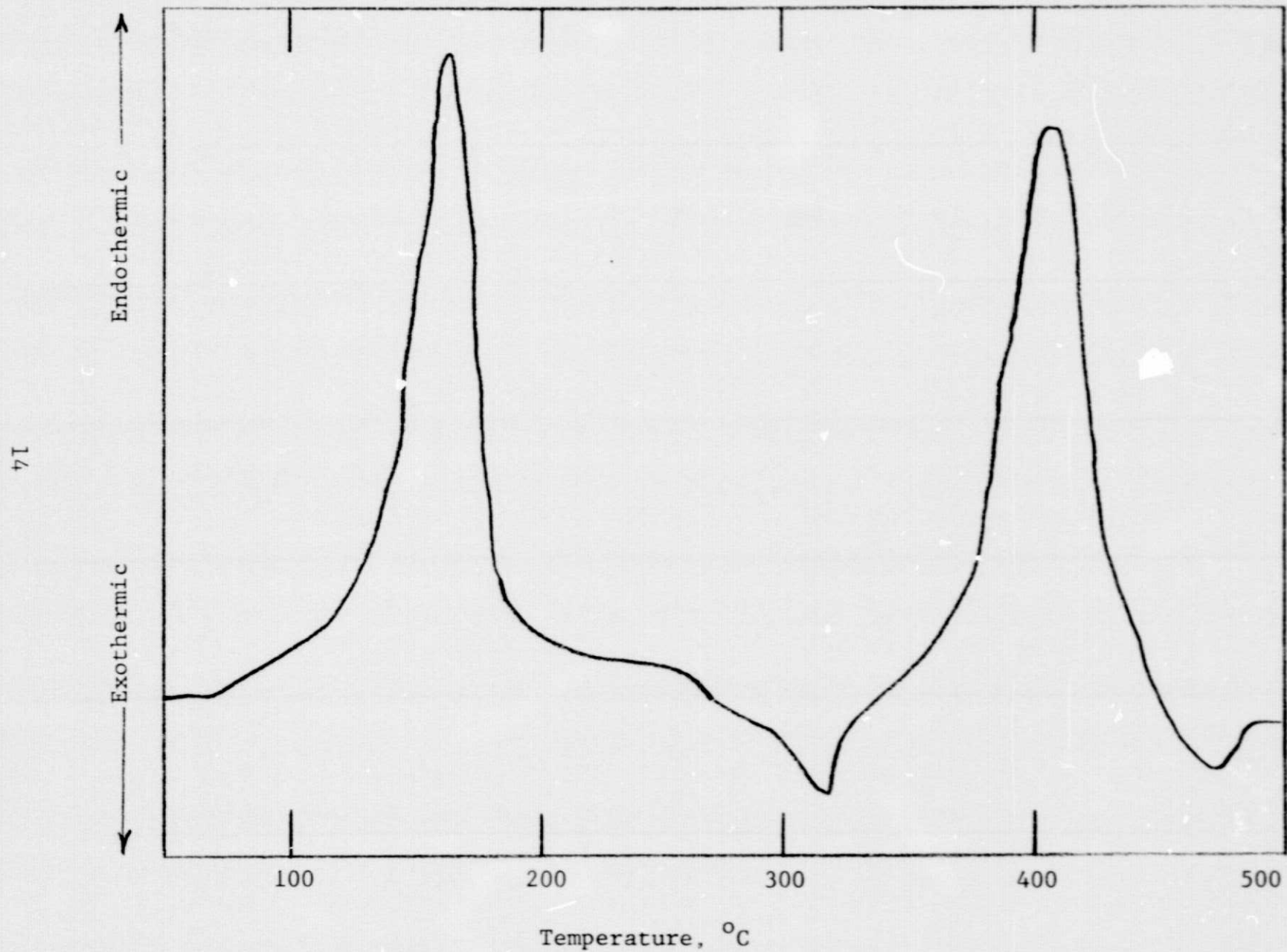
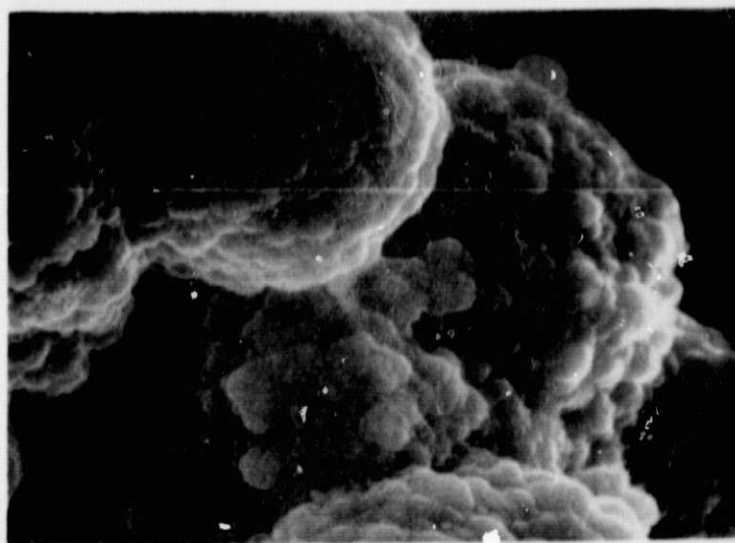


Figure 2. DTA Study of Zinc Oxalate Decomposition

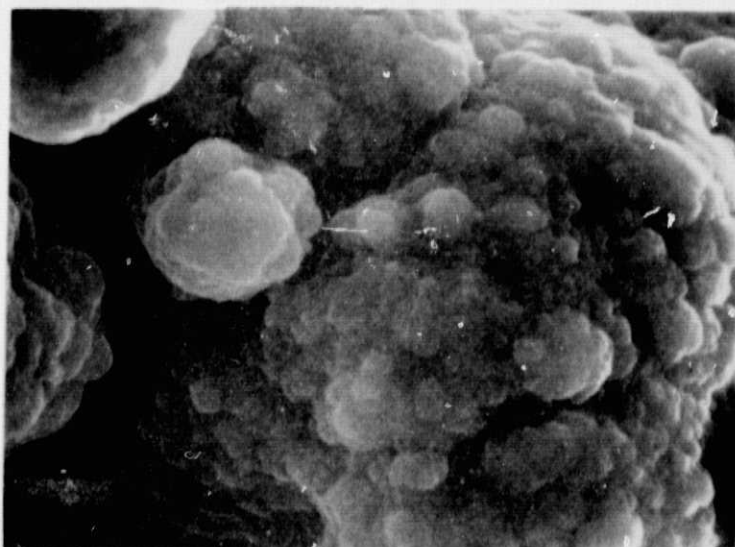
10 μ



958

"TiOX"-2

3KX



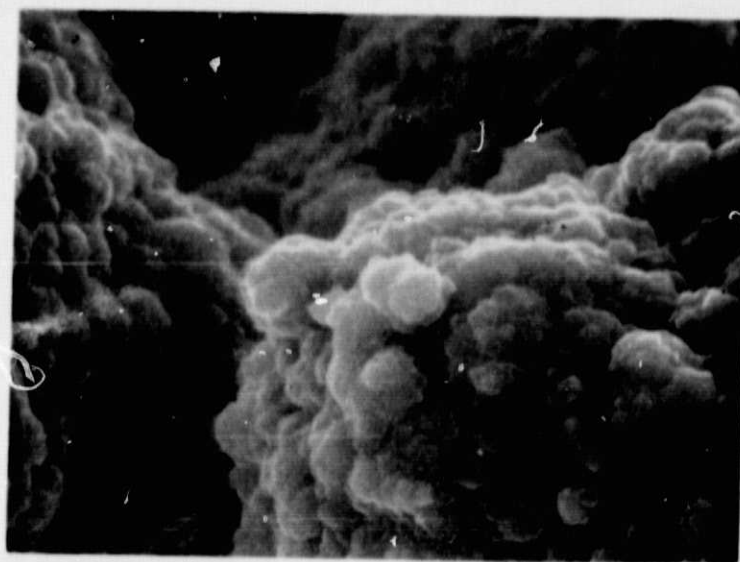
958

"TiOX"-3

3KX

Figure 3. SEM Views of "TiOX", Batches 2 and 3

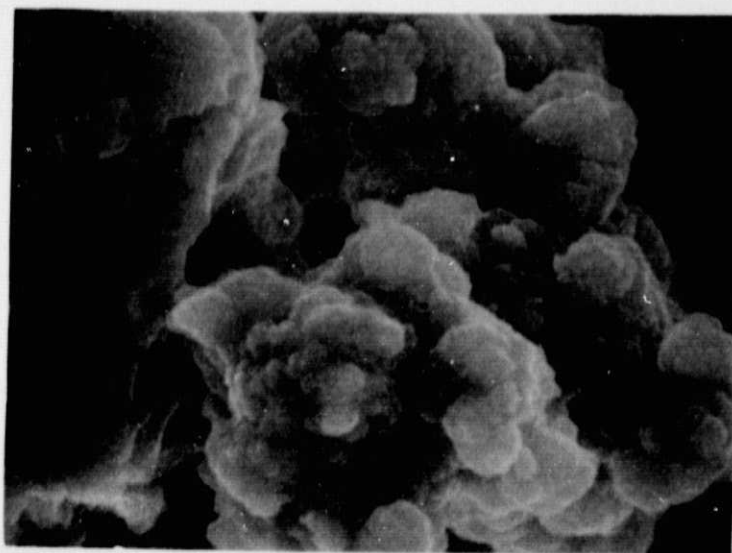
10 μ



962

"TiOX"-4

3KX



959

"TiOX"-5

3KX

Figure 4. SEM Views of "TiOX", Batches 4 and 5

3.3.3 Chemical Analysis

Characterization of "TiOX" has included chemical analysis and examination by scanning electron microscopy (SEM). The results of the analyses by two laboratories are as follows:

<u>Laboratory</u>	<u>Sample</u>	<u>% C</u>	<u>% H</u>
M	1	8.98	1.85
M	2	8.95	1.84
P	3	8.75	2.11
P	4	8.98	2.10

Based on a molecular weight of 143.2, the results from Lab "M" would correspond to 12.85 grams of carbon and 2.65 grams of hydrogen, which may be translated to one atom of carbon and three atoms of hydrogen. The Lab "P" data would be 12.66 grams C and 3.01 grams H, or one atom C and three atoms H. Based on these results along with an assumption that the balance is oxygen, the atomic makeup of "TiOX" may be written as TiCH_3O_5 . However, this still does not constitute a clear definition of the "TiOX" formula, despite the uniformity in weight loss on conversion to TiO_2 .

3.3.4 Summary

The "TiOX" characterization studies have shown how it can be rendered into a more reproducible material in terms of weight loss, i.e. by the preconditioning step. Although the chemical makeup of "TiOX" has not been precisely determined, the prime objective of this program, i.e., to obtain an engineering material, requires moving into other studies to achieve this goal.

3.4 Mixing Studies

Previous methods used to mix "TiOX" with zinc oxalate have involved the use of porcelain balls in glass ball mills. However, this resulted in sticking of the powder mixture to both the balls and the mill wall, leading, not only to loss of material, but also to the possibility of change in the Zn/Ti ratio of the mixture.

Experiments were conducted with polymeric materials, i.e., 1/2" nylon balls in polypropylene containers, in an effort to preclude such sticking. Mixtures of zinc oxalate with "TiOX" to yield a Zn/Ti ratio of 2 to 1 were ball milled dry and wet (isopropyl alcohol). After recovery of the materials from the polymeric mills, samples were calcined and evaluated gravimetrically and optically.

The data obtained are summarized in Table II. General observations are that after dry mixing, essentially complete recovery of powder was effected; this is reflected in the very small differences in weights before and after mixing. Recovery of powder after wet mixing is somewhat more involved in that the powder must be separated from the liquid (isopropanol) as well as the balls. The added handling necessary resulted in greater weight changes as compared to dry mixing. Mix No. 3 gained 0.75% while Mix No. 4 lost 1.86%.

The samples were subjected to a precalcine of 500°C/2 hours, followed by formation of Zn_2TiO_4 at 900°C/2 hours. The weight losses due to the decomposition-reaction process were all quite close to theoretical, as seen in the last column in Table II.

Reflectance curves of 900°C calcined materials prepared from dry milled and wet milled precursors are shown in Figure 5. Both show a "knee", indicative of excess zinc oxide. The wet milled-based material exhibits the "knee" at lower reflectance,

Table II

SUMMARY OF MIXING STUDIES						
MIX NR.	Medium	Material Weight, gms		% Weight Change	Weight % Residue*	
		Into Mill	Recovered From Mill		500°C/2 Hr.	900°C/2 Hr.
1	Dry	91.75	91.41	- 0.37	46.54	45.86
2	Dry	91.75	91.81	+ 0.06	46.70	46.20
3	Isopropanol	91.75	92.44	+ 0.75	47.13	46.51
4	Isopropanol	91.75	90.04	- 1.86	47.89	47.17

*Theoretical: 46.57%

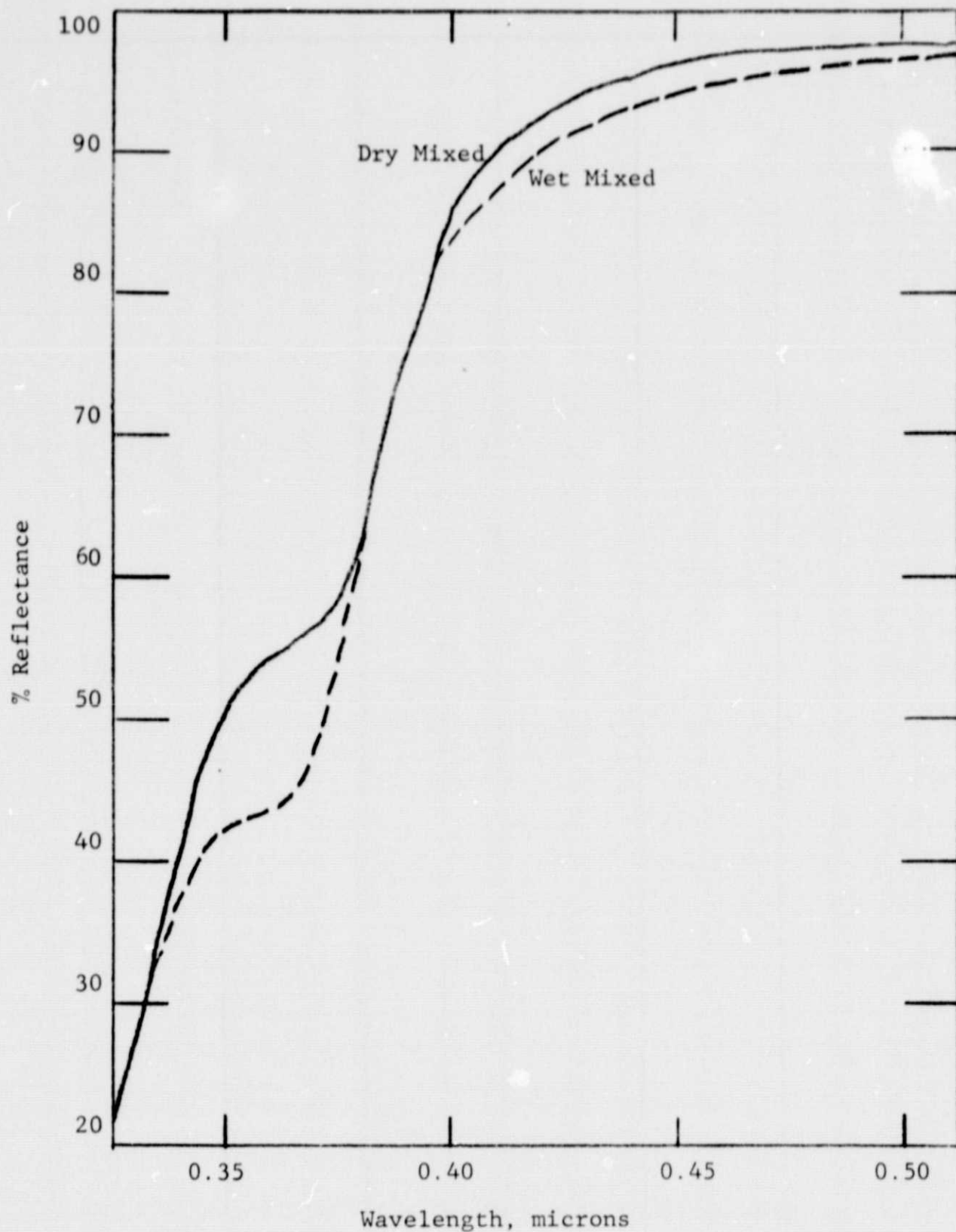


Figure 5. Reflectance of Zn_2TiO_4 Powders prepared from Dry Mixed and Wet Mixed Precursors

suggesting higher ZnO content. A full analysis of these curves will appear in a subsequent report.

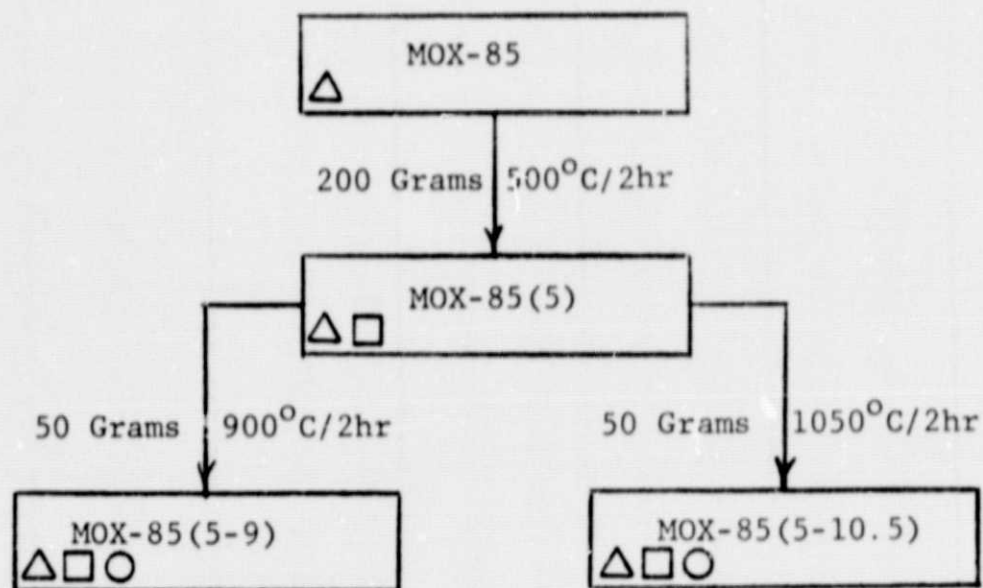
These results show that the use of polymeric media results in practically no sticking and loss of powder. This may be due to a "non-charged" nature of the plastics and/or the use of a preconditioned, dried "TiO₂". Thus, the new mixing techniques minimize loss of material in milling, and the potential change in mixture stoichiometry through such loss has been greatly reduced. This offers a positive step toward definition of engineering specifications for processing of MOX materials.

3.5 Stoichiometry Studies

Examination of the effect of varying Zn to Ti ratios on optical properties has been initiated with the processing of five compositions. These have been designated as follows:

<u>Designation</u>	<u>Zn/Ti Ratio</u>
MOX-85	1.85/1
MOX-90	1.90/1
MOX-95	1.95/1
MOX-00	2.00/1
MOX-05	2.05/1

A flow diagram showing the processing being received by these materials appears in Figure 6. Full evaluation by gravimetric, X-ray, and optical analysis is now being completed, and will appear in the next report.



Analyses:

- △ X-ray
- Gravimetric
- Optical

Figure 6. Flow Diagram for Zn_2TiO_4 Synthesis in Stoichiometry Studies

4.0 CONTRIBUTING PERSONNEL AND-LOGBOOK RECORDS

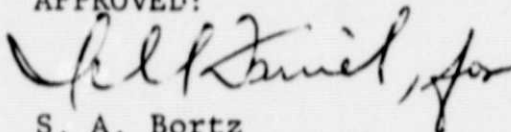
Personnel who have contributed to this work include
W. L. Stepp, F. O. Rogers, J. E. Gilligan, and Y. Harada.
Data are contained in IITRI Logbook Numbers C22620 and C22630.

Respectfully submitted,



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APPROVED:



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