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DEVELOPMENT OF SPACE STABLE THERMAL CONTROL COATINGS FOR USE ON LARGE SPACE VEHICLES

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FOREWORD

This is Report No. IITRI-C6233-36 (Triannual Report) of IITRI Project C6233, Contract No. NAS8-26791, entitled "Development of Space Stable Thermal Control Coatings for Use on Large Space Vehicles." This report covers the period from September 1 through December 31, 1973.

Major contributions to the program during this period include: Mr. J.E. Gilligan, Project Leader; Mr. Y. Harada and Mr. W. Logan, pigment manufacturing studies; Mr. F.O. Rogers, paint preparation; Mr. Paul Mencinskas, Irradiation experiments and reflectance measurements; and Dr. Audrone M. Stake, general consultation and administrative management.

The work reported herein was performed under the technical direction of the Space Sciences Laboratory of the George C. Marshall Space Flight Center; Mr. Daniel W. Gates acted as the Project Manager.

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ABSTRACT

The effort toward the development of a large scale manufacturing method for the production of a stable zinc orthotitanate pigment by means of an oxalate co-precipitation method has been continuing. Pigments were prepared at various temperatures. Major emphasis has been placed on the determination of the important parameters of post-precipitation firing and treatment. A large-scale process for the modification of Owens Illinois 650 Glass Resin was developed and paints were formulated in the resulting OI-650G vehicles.

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DEVELOPMENT OF SPACE STABLE THERMAL CONTROL COATINGS FOR USE ON LARGE SPACE VEHICLES

1. INTRODUCTION

The research effort in passive spacecraft temperature control has, historically, been concentrated on the development of the class of surfaces known as solar reflectors - that is, surfaces with high reflectance for solar radiation and with high emittance in the thermal (infrared) spectrum. Basically, these surfaces must be stable in the total environment that they will experience. This requirement means that, once an high level of intrinsic stability in these materials is attained in the laboratory, we must make certain that this stability is preserved in a scaled-up manufacturing process, protected throughout the entire pre-launch environment, and, finally, that this stability obtains in the space environment. In recent years the additional requirement for low outgassing paint surfaces has been imposed with increasing frequency and strictness. Contamination of optical surfaces by condensed species of thermal control surfaces has been recognized as a serious problem. Applications on large space vehicles, therefore, present new R&D problems - not simply traditional ones in greater dimensions.

The program consists of four major tasks: pigment manufacturing development, binder development, environmental effects evaluations, and general coatings investigations. The relative emphasis on each of these tasks varies according to the urgency of the problems elucidated in our investigations, and, of course, with the availability of time and funds. Our present efforts have been expended approximately equally on the development of a pigment manufacturing method and on the complementary environmental testing and evaluation activities, with modest efforts in the further development of OI-650G.

2. PIGMENT MANUFACTURING STUDIES

2.1 General Remarks

Zinc orthotitanate pigment samples were prepared for space simulation experiments, and studies were conducted to determine decomposition behavior vs temperature for the individual components of the coprecipitate as well as of the coprecipitate itself. Also additional batches of Zn_2TiO_4 were synthesized and subjected to irradiation testing; samples were also sent to Stanford Research Institute for their examination. The results of these studies are discussed in the following sections.

2.2 Irradiation Studies

A series of zinc orthotitanate powder samples were prepared and treated in various ways to determine in an IRIF irradiation test the effects of acid washing, of recalcination, and of encapsulation. A flow diagram of the preparatory history of these materials is shown in Figure 1. Descriptions of the sample designations appear in Table 1.

The samples for the irradiation test are those on the right hand side of the diagram in Figure 1. In addition to the basic heat treated samples, portions of each of these were encapsulated in lithium silicate and are designated with an "S" at the end, e.g., LH-102 (6-12-S). Paint formulations of these powders in OI-650G are now being subjected to ultraviolet irradiation in vacuum.

Samples which had been tested in IRIF-I-67 (ref. 1) were examined by x-ray techniques to determine any relationship between crystallographic size and processing history and/or stability to UV-vacuum. The results of these studies are shown in Table 2. The lattice constants (a_o) of pigments calcined at 1100°, 1200° and 1300°C were similar, while the 1400°C material revealed

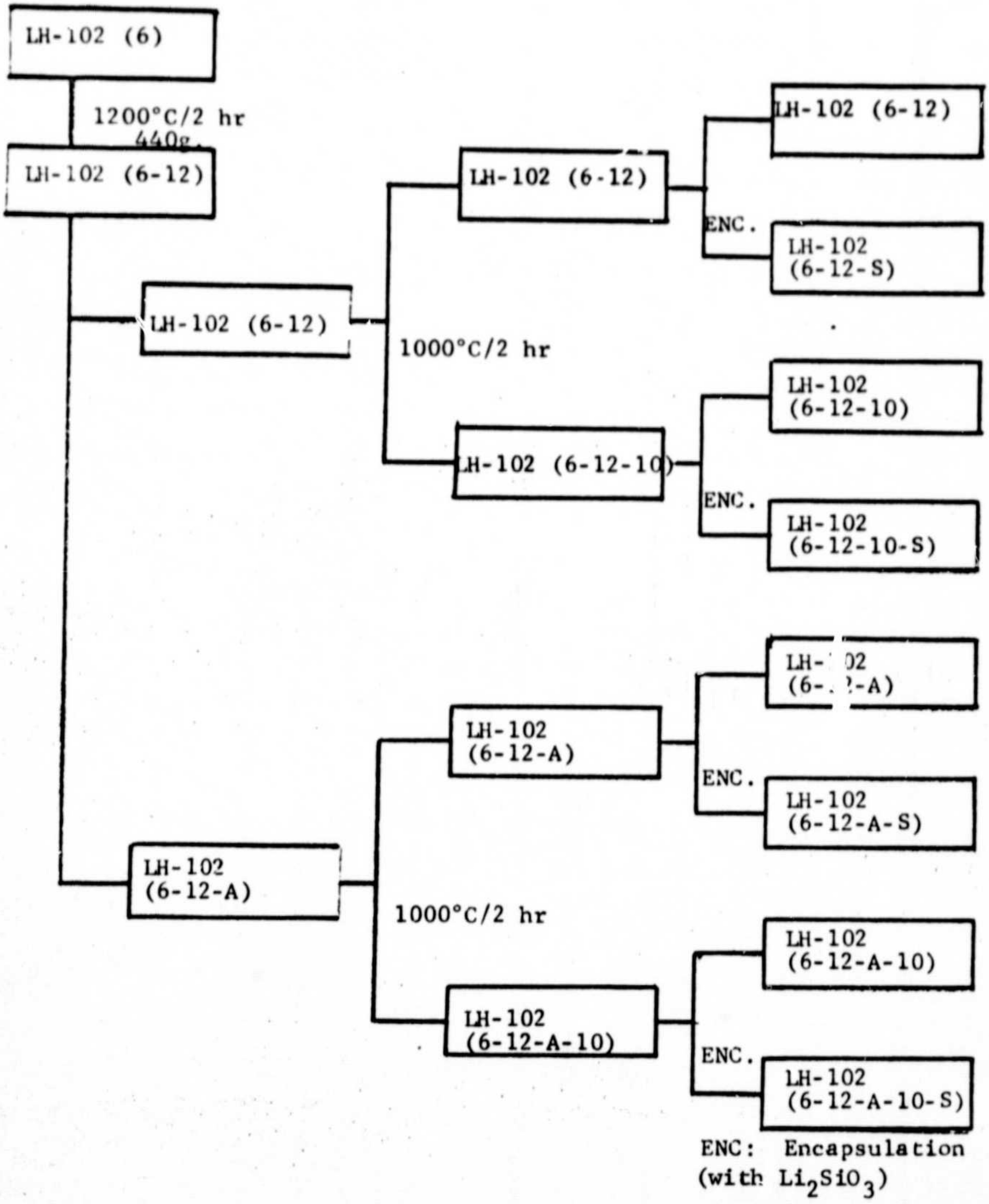

Figure 1. FLOW DIAGRAM FOR Zn_2TiO_4 PIGMENT PREPARATION

Table 1

Zn_2TiO_4 Sample Designations and Treatments

SAMPLE NO.	SAMPLE DESIGNATION	PROCESSING HISTORY	AMOUNT PROCESSED
1	LH-102 (6)	600°C/2 hr.	960 grams
2	LH-102 (6-12)	Same as #1 plus 1200°C/2 hr (f.C.)*	440 grams
3	LH-102 (6-12-A)	Same as #2 plus acetic acid leach and drying of thoroughly washed (pH=7) powder at 80°C/16 hr.	150 grams
4	LH-102 (6-12-A-10)	Same as #3 plus 1000°C/2 hr.	70 grams
5	LH-102 (6-12-10)	Same as #2 plus 1000°C/2 hr.	

*f.c. - Flash calcine

Table 2

SUMMARY OF X-RAY DIFFRACTION STUDIES OF Zn_2TiO_4

Material	Calcination Temp., °C	Lattice Constant Å	ZnO	$\Delta\alpha_s$ 2054 ESH
LH-53(6-11)	1100	8.4468	Yes	.051
LH-53(6-11-A-10)*	1100	8.4639	No	.071
LH-53(6-12)	1200	8.4673	Yes	.064
LH-53(6-12-A-10)*	1200	8.4641	No	.075
LH-53(6-13)	1300	8.4668	Yes	.109
LH-53(6-13-A-10)*	1300	8.4638	No	.051
LH-53(6-14)	1400	8.4643	Yes	.129
LH-52(6-14-A-10)*	1400	8.4628	**	.055

* Acid washed, followed by heating at 1000°C/2 hrs.

** Very minor ZnO peak - peak weight would indicate less than 1%.

a cell size more closely approaching the reported value for fused Zn_2TiO_4 of 8.456 Å(ref. 2). Thus, there was no clear trend, at least in the 1100° to 1300°C temperature range, toward the ideal crystal size with increasing temperature. A trend of increasing stability with increasing calcination temperature, though far from definite, appears to be developing.

A difference in lattice constants does appear to exist between as-calcined pigments and those of the acid washed materials. The latter materials clearly exhibit smaller constants than the non-acid washed samples. Since acid washing removes the ZnO from the Zn_2TiO_4, this decrease in a_o may indicate a limited solubility of ZnO in the Zn_2TiO_4. In other words, removal of the ZnO permits a closer approach of the Zn_2TiO_4 crystal size to the ideal.

The X-ray diffraction scans also indicated the efficacy of acid treatment; ZnO was detected in the as-calcined and not in the acid-treated samples. No trace of TiO_2 was observed in any of the samples.

Examination of the lattice constant versus $\Delta\alpha_s$ data failed to reveal any correlation. For example, samples LH-53 (6-11) and LH-53 (6-13) which showed identical lattice sizes exhibited $\Delta\alpha_s$ values of .051 and .109. From this study it would appear that the lattice constant does not inherently relate to stability or to a lack thereof.

2.3 Decomposition Studies

The decomposition behavior of the coprecipitated mixture of and of the individual, zinc and titanium oxalates was sought to obtain a better understanding of the process for converting the oxalates to the respective oxides and of the relationships of conversion (of coprecipitated materials) to initial materials' parameters.

Materials which were examined included the individual oxalates as well as the coprecipitated mixture. Samples were heated at temperatures from 120° to 700°C for two hours each. Each sample was treated using direct insertion into and removal from the furnace at temperature in order to minimize the effects of heat-up and cool-down.

The results of the gravimetric analyses are tabulated in Table 3 and illustrated in Figure 2. They show that the titanium oxalate phase apparently decomposes at a lower temperature than does that of the zinc oxalate. The weight loss curve for the coprecipated mixture (referring to Figure 2) lies between the curves for the individual components, reflecting the different rates of decomposition.

The appearance of the powders after heat treatment and the results of analyses of X-ray powder patterns are presented in Table 4. After the 400° and 500°C calcinations, the zinc oxalate material was gray and lumpy. The weight loss data show that this is the range where rapid decomposition occurs. Interestingly, the converted zinc oxalate samples which had been calcined at 400° to 700°C all displayed some coloration. The converted titanium oxalate materials showed a lesser departure from white and were all free-flowing.

The mixed oxalate samples calcined at the various temperatures were also quite fine and did not display the aggregation shown by zinc oxalate samples. Samples calcined at 600° and 700°C were white, although the lower temperature samples showed some coloration.

Table 3

WEIGHT LOSSES FOR ZINC OXALATE, TITANIUM OXALATE, AND COPRECIPITATED OXALATES AS A FUNCTION OF TEMPERATURE

	Temperature, °C, % Wt. Loss		
Temperature, °C	Zinc Oxalate	Titanium Oxalate	Coprecipitated Oxalates
120	14.5		4.8
150		8.1	
200	18.4	30.7	15.8
230		42.2	
300	19.0	45.7	28.0
340		44.5	
400	36.7	46.0	53.4
500	57.2	45.5	53.5
600	57.3		
700	57.4	46.4	54.0

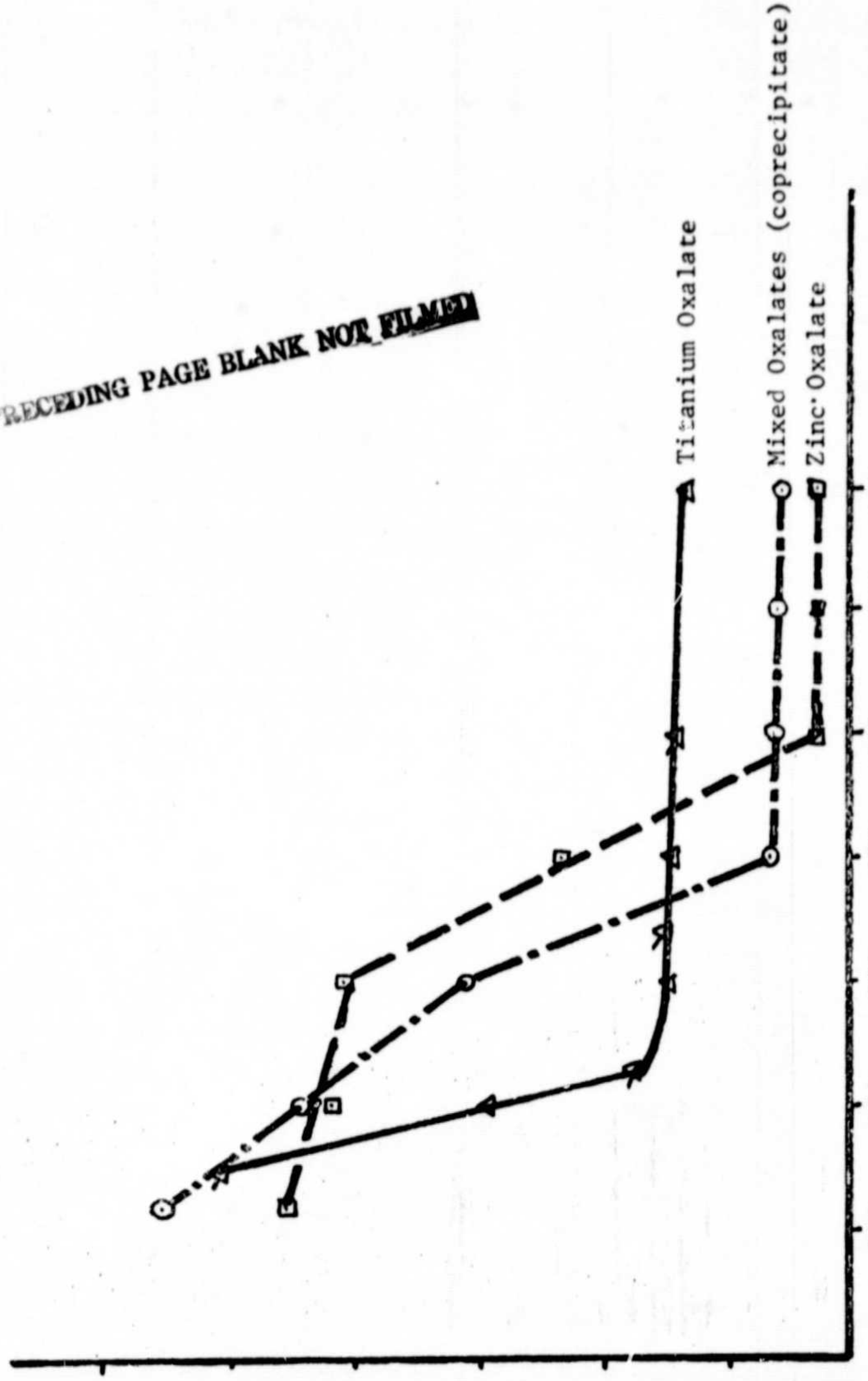

Fig 2 Weight loss % (of Initial Weight) vs Temperature-Zinc and Titanium Oxalates

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Table 4

APPEARANCE AND PHASES PRESENT FOR ZINC OXALATE, TITANIUM OXALATE, AND COPRECIPITATED OXALATES AS A FUNCTION OF CALCINATION TEMPERATURE

	APPEARANCE*			PHASES PRESENT***		
Temp., °C	Zinc Oxalate	Titanium Oxalate	Mixed (Coprec'd) Oxalates	Zinc Oxalate	Titanium Oxalate	Coprec. Oxalates
120	white		white		TiOx	
200	white	light yellow	white** (blue)		TiOx	ZnOx + TiOx + "X"
300	white	light yellow	light yellow	ZnOx + "X"	TiO_2	"X"
400	gray, lumpy	light yellow	yellow	ZnO + "X"	TiO_2	ZnO
500	light gray, lumpy	light yellow	yellow	ZnO	TiO_2	ZnO + TiO_2
600	tan	white	white	ZnO	TiO_2	Zn_2TiO_4 + ZnO
700	yellow	white	white	ZnO	TiO_2	Zn_2TiO_4 + ZnO

* All powders free flowing unless otherwise indicated.

** This sample turned blue (a surface effect) when exposed to fluorescent lighting,

*** ZnOx - Zinc oxalate; TiOx - titanium oxalate; "X" - apparently an intermediate phase in the decomposition of zinc oxalate.

X-ray analyses revealed the existence of an intermediate phase in the decomposition of zinc oxalate. The principal lines for this phase, termed the "X" phase (see table 4) are 3.70, 2.36 and 4.10 A. "X" is also found in the lower temperature coprecipitated oxalate samples (200° and 300°C). These studies also show that a minimum temperature of 600°C is necessary for the formation of zinc orthotitanate.

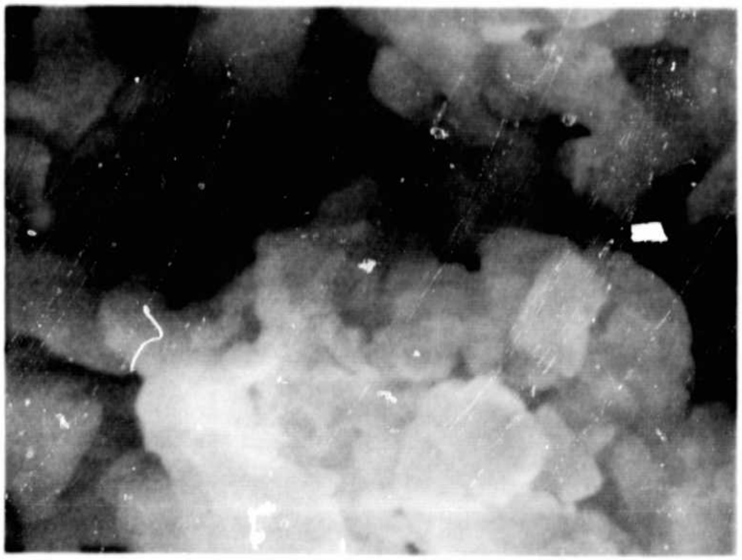
The various fired (conversion) products of the three precursors (mixed and individual oxalates) in this study have also been examined using the scanning electron microscope (SEM). Although this study is not yet complete, some preliminary observations may be made:

1. Zinc oxalate - the products at 400°C and higher (or those undergoing or having undergone decomposition) exhibit an extremely fine particle morphology. This can be seen by comparing the 300° and 400°C materials in Figure 3. This fine particle size persists also in the 500° and 700°C products, as shown in Figure 4.

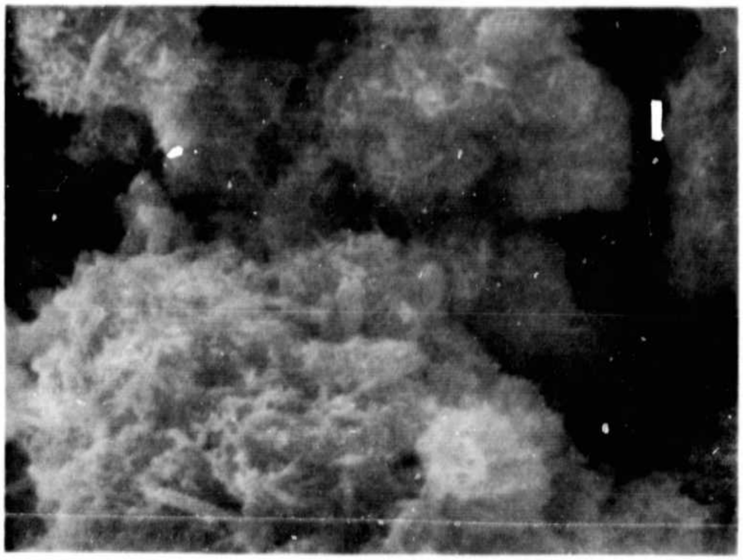
2. Titanium oxalate - Preliminary SEM studies of titanium oxalate materials show that the TiO_2 products at 500° and 700°C are uniformly fine with a particle size (see Fig. 5) slightly larger than that of the zinc oxalate materials.

3. Coprecipitated oxalates - These materials appear more heterogeneous (see Fig. 6) than might be expected from the appearance of the individual oxalate products. There also exists some comparatively large particles. This may be due to interrupted or enhanced grain growth due to the intimacy of the two phases in the coprecipitated material.

These studies do suggest some directions for obtaining a more uniform and finer particle size in zinc orthotitanate.

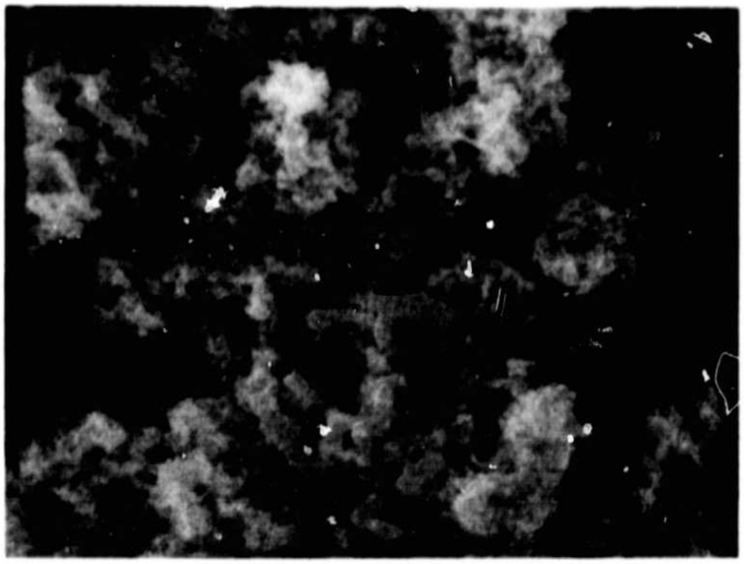


#0293 300°C 3000x



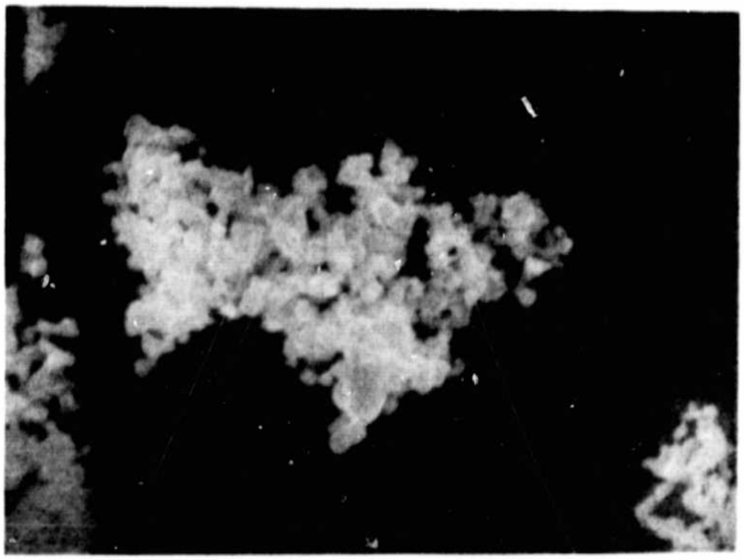
#0292 400°C 3000X

Figure 3. ZINC OXALATE DECOMPOSITION PRODUCTS AT 300° AND 400°C



#0290 3000X

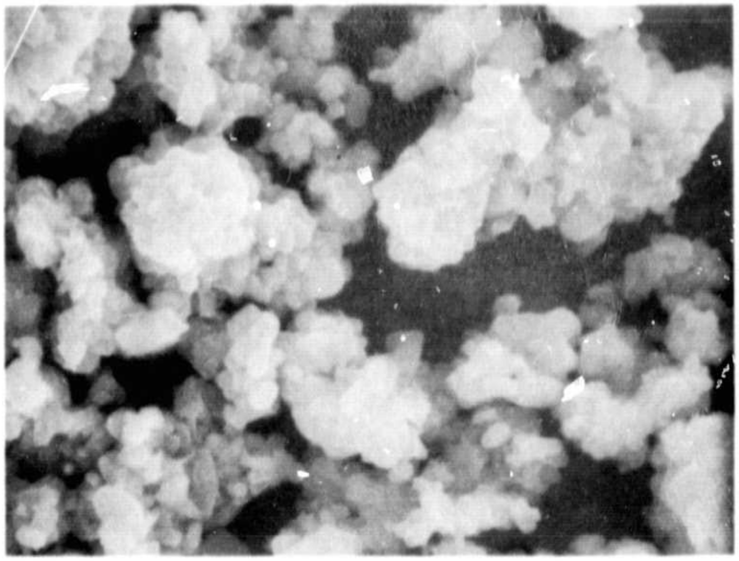
500°C



#0289 3000X

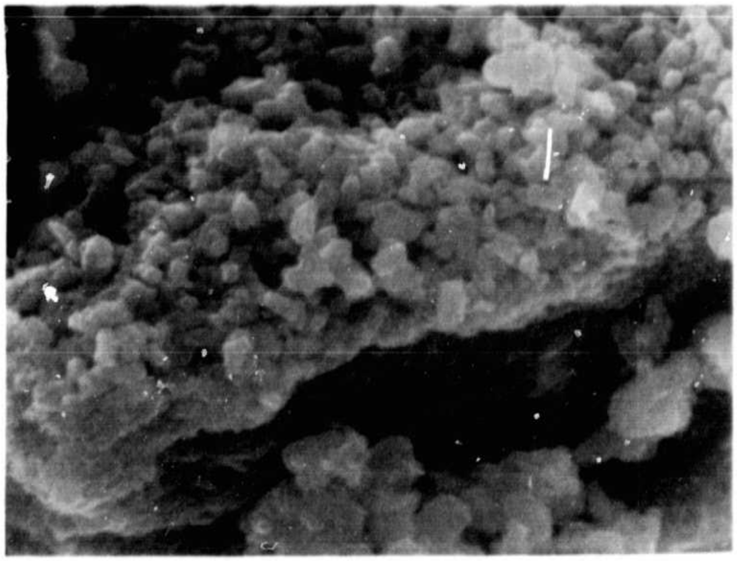
700°C

Figure 4. ZINC OXALATE DECOMPOSITION PRODUCTS AT 500° AND 700°C



#0201 3000X

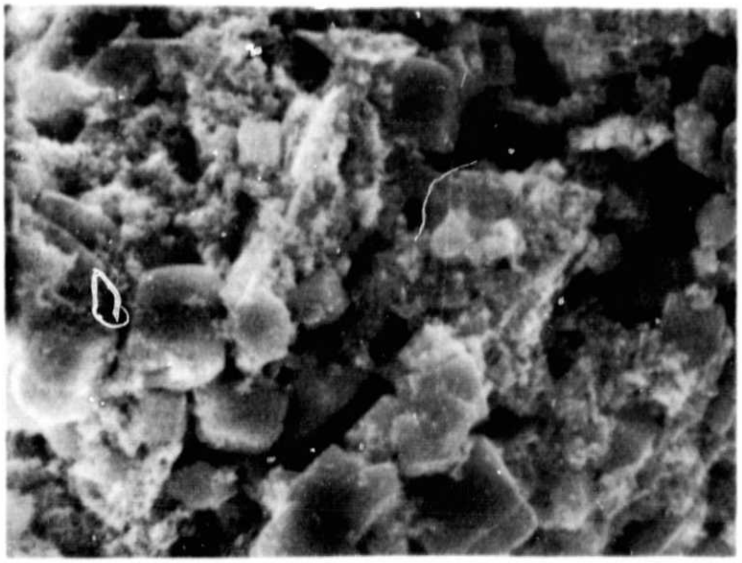
500°C



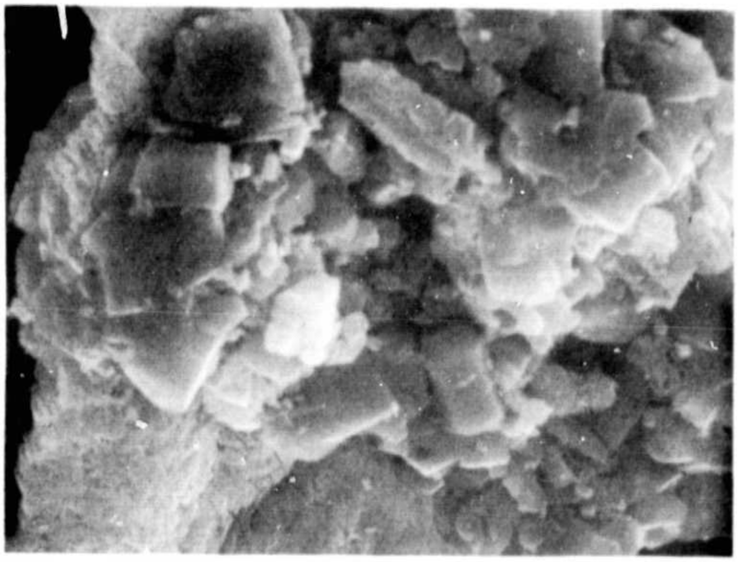
#0204 3000X

700°C

Figure 5. TITANIUM OXALATE DECOMPOSITION PRODUCTS AT 500° AND 700°C


#0240 3000X

500°C


#0241 3000X

700°C

Figure 6. COPRECIPITATED OXALATES DECOMPOSITION PRODUCTS AT 500° AND 700°C

It is evident, for example, that a rapid calcination at 600°C will yield zinc orthotitanate and provide a somewhat finer and more uniform particle size than the hitherto used method of heating to 600°C in about two hours.

3. BINDER DEVELOPMENT

3.1 Owens Illinois 650 Glass Resin Modification

The work on modified OI-650 has been primarily devoted to scale-up studies for the synthesis of this resin. A batch of 300g of modified resin has been successfully prepared. Preparation of modified OI-650 resin in a 300g quantity required a change in the procedure previously employed. It was found that, for the same trimethylchlorosilane/O.I.650 ratio, increasing the batch size leads to increased silanol condensation with subsequent gel formation and insolubilization of the product. Since the HCl by-product of the end-blocking reaction catalyzes the silanol group condensation, end-blocking and condensation are competitive reactions. The rate of condensation (and subsequent insolubilization) increases with increasing temperature of the system. By enlarging the batch size, the total heat of reaction becomes greater and gel formation occurs. Even when the rate ot trimethylchlorosilane addition was reduced to the extent required to keep the temperature of the system under 30°C, gel formation was evident. In order to prevent gelation of the resin, it is necessary to add trimethylchlorosilane at a relatively fast rate while cooling the solution with ice. By using this procedure, a 300g batch was successfully prepared.

A study of the outgassing of modified OI650 has been performed by using isothermal TGA in conjunction with a diffusion pump (10^{-5} mm Hg). This apparatus allows continuous recording of the weight of the sample. For the purpose of determining the effect of curing temperature on outgassing, two paint samples of A-429M have been tested, one cured at 325°F, the other at 400°F. A-429M designates the system: $ZnO:K_2SiO_3$/OI-650G. The samples were maintained under vacuum at ambient temperature, then heated at 125°C for 24 hr. As expected, the total weight loss due to outgassing decreases with increasing curing temperature. The weight loss from a sample cured at 325°F was 1.05% at room temperature (in vacuo) and 1.25% after subsequently heating it under vacuum at 125°C (total loss, 2.33%). The weight loss of the sample cured at 400°F averaged 0.59% at room temperature (in vacuo) and 0.39% after heating in vacuum at 125°C (total loss, 0.98%).

4. REFERENCES

1. J.E. Gilligan and Y. Harada, "Development of Space Stable Thermal Control Coatings for Use on Large Space Vehicles," IITRI Report No. C6233-32, Nov. 1973.

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