AFRL-ML-WP-TP-2004-411

DEVELOPMENT OF IMPROVED THERMAL CONTROL COATINGS FOR SPACE ASSETS

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November 2004

STINFO FINAL REPORT

**MATERIALS AND MANUFACTURING DIRECTORATE
AIR FORCE RESEARCH LABORATORY
AIR FORCE MATERIEL COMMAND
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750**

NOTICE

This technical report has been reviewed and is approved for publication.

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Pamela M. Schaefer
Principal Materials Engineer
Technical & Strategic Planning Office
Materials and Manufacturing Directorate

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE ***(DD-MM-YY)*** November 2004	**2. REPORT TYPE** Journal article preprint	**3. DATES COVERED** ***(From - To)***

4. TITLE AND SUBTITLE
DEVELOPMENT OF IMPROVED THERMAL CONTROL COATINGS FOR SPACE ASSETS

5a. CONTRACT NUMBER
IN-HOUSE

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER
N/A

6. AUTHOR(S)
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5d. PROJECT NUMBER
M06R

5e. TASK NUMBER
20

5f. WORK UNIT NUMBER
00

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

Nonstructural Materials Branch (MLBT)
Nonmetallic Materials Division
Materials and Manufacturing Directorate
Air Force Research Laboratory, Air Force Materiel Command
Wright-Patterson Air Force Base, OH 45433-7750

University of Dayton
Research Institute

Southwestern Ohio Council
for Higher Education

Alion Science and
Technology Corporation

8. PERFORMING ORGANIZATION REPORT NUMBER
AFRL-ML-WP-TP-2004-411

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Materials and Manufacturing Directorate
Air Force Research Laboratory
Air Force Materiel Command
Wright-Patterson Air Force Base, OH 45433-7750

10. SPONSORING/MONITORING AGENCY ACRONYM(S)
AFRL/MLBT

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S)
AFRL-ML-WP-TP-2004-411

12. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

13. SUPPLEMENTARY NOTES

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ABSTRACT ***(Maximum 200 Words***

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15. SUBJECT TERMS
Thermal Management, Pigments/Colorants, Space Environment

16. SECURITY CLASSIFICATION OF:			**17. LIMITATION OF ABSTRACT:**	**18. NUMBER OF PAGES**	**19a. NAME OF RESPONSIBLE PERSON** (Monitor)
a. REPORT Unclassified	**b. ABSTRACT** Unclassified	**c. THIS PAGE** Unclassified	SAR	16	Michael J. Shepard **19b. TELEPHONE NUMBER** *(Include Area Code)* (937) 255-4651

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

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ABSTRACT

Thermal control coatings play a critical role in the thermal management of space assets through reflection of incident solar energy and emittance of infrared heat. An investigation into the potential minimization of required film thickness through optimization of zinc oxide pigment particle size was performed. The utilization of a 1.5 micron average particle size pigment in the coating formulation resulted in a slightly improved solar absorptance/emittance value of 0.132 in comparison with the currently used 5.0 micron average particle size pigment. Furthermore, this improved value was obtained at a dry film thickness 18% thinner (4.9 mils) than the current state of the art, which translates to weight savings without a sacrifice in thermal management properties. Use of the smaller particle size pigment also resulted in an improvement in the measured emittance (0.94), likely due to a more uniform surface roughness and fewer large pores present in the film.

KEYWORDS: Thermal Management, Pigments/Colorants, Space Environment

1. INTRODUCTION

Space assets such as satellites, stations, and rovers have very complex thermal management requirements due to their unique operational environments. The incident solar radiation in space is primarily composed of ultraviolet (UV), visible (VIS), and near-infrared (NIR) wavelengths containing a significantly greater amount of energy than observed on earth (1,2). Absorption of this radiation generally results in conversion to thermal energy and can lead to dramatic increases in temperature. Furthermore, internal heat generated by onboard electronics adds to this overheating problem. The performance of thermally sensitive components designed to operate within specific temperature windows may be jeopardized without adequate thermal control. Therefore, suitable methods must be employed to reduce and maintain temperatures at acceptable levels. Unfortunately, since convection heat transfer is unavailable in a vacuous environment to dissipate thermal energy, asset cooling is limited to radiative heat transfer (i.e., emission of infrared light). Various methods are employed to transfer heat from within an asset to radiator surfaces, which can then dissipate the heat as infrared (IR) radiation back into the space environment (3).

Thermal control coatings (TCCs) are used to coat radiators as well as many other surfaces that are often in direct solar exposure. They play a critical role by providing a surface that reflects most of the incident solar energy, while providing a high emittance surface to efficiently liberate IR heat. Space asset temperature is determined by the balance between heat lost through emittance of thermal IR radiation (q_R) and heat gained through absorption of solar radiation (q_A) at an equilibrium state, where $q_R = \sigma \varepsilon A_R T^4$ and $q_A = S \alpha_S A_S$. T is absolute temperature in Kelvin (K), α_S is the solar absorbance of the exterior surface, ε is the emissivity at temperature T, σ is the Stefan-Boltzmann constant ($5.57\mathrm{E}^{-12}$ $\mathrm{W{\cdot}cm^{-2}{\cdot}K^{-4}}$), A_R is the area in cm^2 capable of IR emittance, S is the solar constant ($0.135\ \mathrm{w/cm^2}$), and A_S is the area in cm^2 exposed to incident radiation. Given the many constants in this relationship, it is evident that the inherent temperature performance of TCCs is governed by the ratio of surface solar absorption (α_S) to emissivity (ε) as shown in Equation 1.

$$T = \sqrt[4]{\frac{S \cdot \alpha_s \cdot A_s}{\sigma \cdot \varepsilon \cdot A_R}} \quad \propto \quad \frac{\alpha_s}{\varepsilon} \qquad [1]$$

The current state of the art thermal control coating was originally developed in the 1960's and consists of zinc oxide (ZnO) pigment dispersed within an aqueous potassium silicate binder solution (e.g., Alion Science & Technology's Z-93P coating). After application onto the substrate, the resultant dry film is aesthetically bright white in appearance due to its low solar absorptance properties (i.e., high reflectance). The choice of materials to be used in formulating a TCC is rather limited because both the pigment and binder must be stable in the very harsh space environment. Despite poor mechanical properties, binder selection is often limited to silicates because polymeric binders are readily degraded by the intense UV radiation. This results in the formation of absorptive species that increase α_S values. Pigment selection is limited to "white" pigments; materials with no inherent absorption of visible or near-infrared wavelengths, that have high refractive indices to promote light scattering, and are stable in the efficiency is extremely dependent upon the particle size distribution of the pigment. It is well known from Mie scattering theory that as the pigment particle diameter approaches approximately one-half that of the incident radiation wavelength, scattering is increased dramatically. The Air Force Research Laboratory (AFRL) Materials and Manufacturing Directorate has previously modeled the theoretical scattering coefficient of ZnO as a function of particle diameter in a silicate binder matrix (6). The results of this work indicated that an optimum particle size distribution would be between 0.25 and 0.45 microns, and particles greater than 1.5 microns provide very little Mie scattering contributions. The currently used ZnO pigment (SP-500C, Zinc Corp. of America) has an effective size distribution greater than 1.5 μm diameter. Scattering efficiency in dry films is also a function of pigment volume concentration (PVC). Therefore, AFRL has begun its initial examination of alternative ZnO pigments for thermal control coatings with identical PVC's to elucidate the effects of particle size on scattering efficiency.

AFRL obtained a smaller diameter ZnO pigment (Zinvisible™ Nano-Fine Zinc Oxide, Zinc Corp. of America) to experimentally investigate its effects on scattering efficiency. The literature particle size of this material is 0.15 μm, slightly below the optimal size range, however aggregates and agglomerates are present as larger particle clusters. Identical PVC coating formulations were prepared using the standard SP-500C and alternative Zinvisible™ pigments by Alion Science and Technology. Comparative performance analysis of the films included experimental determination of the α_s/ε values, minimum film thickness requirements, and scanning electron microscopy (SEM).

2. EXPERIMENTAL

Zinc Corporation of America SP-500C and Zinvisible™ grades of ZnO were calcined at 600°F for three hours prior to use in all experiments to promote further purification and ensure stability of any interstitial crystal lattice defects. The optical purities of both materials were analyzed by measuring the diffuse hemispherical reflectance (DHR) spectra of their respective powders using a Perkin-Elmer Lamda 9 spectrophotometer. The particle size of each ZnO grade was determined by first dispersing the dry powder for 30 minutes in de-ionized water using a sterile ball mill. Size analysis of the dispersion in water was performed using a Coulter LS-230 Fraunhoffer diffraction laser light scattering instrument. This technique ensured that the "effective" particle size of the pigment as used in subsequent coating formulations was measured rather than the "ideal" primary particle size. Due to the omission of any chemical dispersants or aggressive dispersion techniques used in this class of coating, a complete dispersion into primary particles is not expected, thus, particle *agglomerate* size is of greater importance.

Two thermal control coatings were formulated at identical pigment volume concentrations of 65.1%. The first formulation contained SP-500C pigment and was used as a standard reference to the currently implemented coating used on many space assets. The second formulation contained the smaller size grade as a direct substitution for the standard pigment. Both formulations contained the same ratio of potassium silicate binder solution to pigment. However, additional water was required with the Zinvisible™ formulation to achieve a suitable spray rheology because the higher surface area of smaller particles increases viscosity. The additional water does not effect the composition of the final film. The details of each formulation are provided in Table 1.

TABLE 1. THERMAL CONTROL COATING FORMULATIONS

Component	Supplier	SP-500C Formula	Zinvisible™ Formula
Kasil 2130	PQ Corp.	231.58 g	231.58 g
SP-500C	ZCA Corp.	300.00 g	-
Zinvisible™	ZCA Corp.	-	300.00 g
DI Water	n/a	191.00 g	421.00 g
Pigment Volume Conc. =		65.1%	65.1%
Non-Volatile Volume =		18.9%	12.4%

Both of the formulations were prepared by charging a ceramic ball mill with all of the material components, followed by rolling for 30 minutes to assist in the dispersion of ZnO pigment agglomerates. Upon completion, the formulation was filtered using cheesecloth to strain out the dispersion media. An optically absorbing substrate was desired to exclude any substrate reflection when analyzing non-opaque film thicknesses, therefore, 0.25 inch Graylite 14 black glass plates (PPG, Inc.) with the back surface painted flat black (Krylon 1602) were used. Each formulation was applied using a high volume low pressure (HVLP) spray gun onto these substrates under ambient temperature and 50% relative humidity conditions. Several passes were used to build up the film thickness with intervals of approximately one hour between each application. Samples were taken from each spray pass to evaluate reflectance properties as a function of film thickness.

The coated black glass plates were allowed to dry under ambient conditions for one week. The reflectance spectra from 200 to 2500 nm wavelengths were measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. Each sample, along with a representative uncoated substrate, was measured with the specular reflection component included. The reflectance data was then used to calculate the solar absorptance (α_s) based upon ASTM space solar irradiance data (1). The exact location on the substrate that the reflectance data was taken was also marked to ensure that the subsequent measured film thickness was representative of the actual reflectance measurement area. Film thickness measurements for each sample were performed by scraping off a portion of the coating in the proper location to expose the glass substrate followed by measuring the step height from the coating to glass with a KLA-Tencor P-10 stylus profilometer. The total normal emittance (ε) of each dry film sample was measured using a Gier-Dunkle DB-100 infrared reflectometer.

3. RESULTS AND DISCUSSION

Results of prior Mie theory modeling work to determine the ZnO particle size had suggested that improvements could be made over the existing material. However, one of the limitations to selection of an alternate pigment grade was the material's inherent optical purity. Any absorptive contaminates present in the pigment would decrease the total attainable reflectance. The Zinvisible™ material was selected as the best option after surveying many commercially available alternative size ZnO pigments and comparing purity. The optical purity, as measured space environment. The conventional white pigment used in common terrestrial coatings, titanium dioxide, is not used in TCCs due to degradation by intense space UV exposure. Furthermore, TCCs must be composed of materials that are resistant to both the proton and electron flux possible from solar winds.

The scattering of incident radiation by the ZnO pigment is a critical element for desired performance. Thermal control coatings, as well as all white paints, rely upon the refractive index difference between the pigment and binder to promote scattering of incident radiation as is passes through the film. The total scattering is a combination of surface reflections, refraction through particles, and diffractive Mie scattering. Given appropriate film thickness and number of scattering events, the overall resultant effect is diffuse reflection of nearly all the incident radiation back out the front surface. Reviews on the material property requirements of white pigments are available in the literature (4,5). While an ideal TCC would reflect all incident radiation, the use of high refractive index pigments that have an affiliated strong UV absorption results in some absorptive heating. This is offset by the emittance of the film surface and fortunately most non-metallic materials have high emissivity properties. A simplified schematic of a typical TCC is provided in Figure 1.

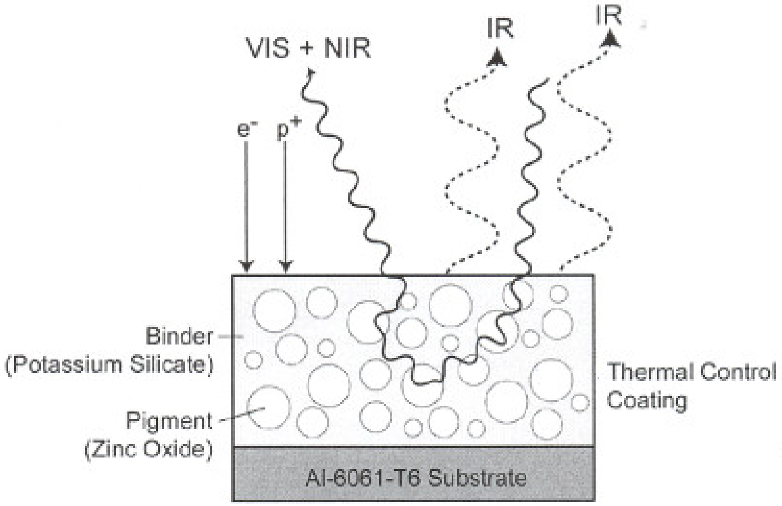

FIGURE 1. Cross-sectional schematic of a thermal control coating in which pigment reflects incident radiation through scattering and temperature is reduced through emittance of infrared heat. The coating must also be resistant to electron and proton flux from solar winds.

Provided the inherent limitations in availability of materials that meet both space stability and stringent optical property requirements, improvements to this heritage coating technology have been limited. However, reduction in coating weight is also an important factor to consider due to high launch costs and payload capacities. Weight reduction is expected to be possible through the use of thinner films and/or formulations that reduce the concentration of dense ZnO pigment (5.6 g/cm^3) while retaining all thermal performance characteristics. The amount of dry film thickness required is dependent upon the scattering efficiency of the coating system. This by the reflectance of the bulk powder, for both the standard SP-500C and Zinvisible™ pigments are shown in Figure 2. As can be seen, the purity of the smaller pigment is very close to that of the standard pigment, which suggests that no decrease in ultimate performance should be realized due to contaminates. The strong UV absorption band starting at approximately 380 nm is also evident, characteristic of ZnO.

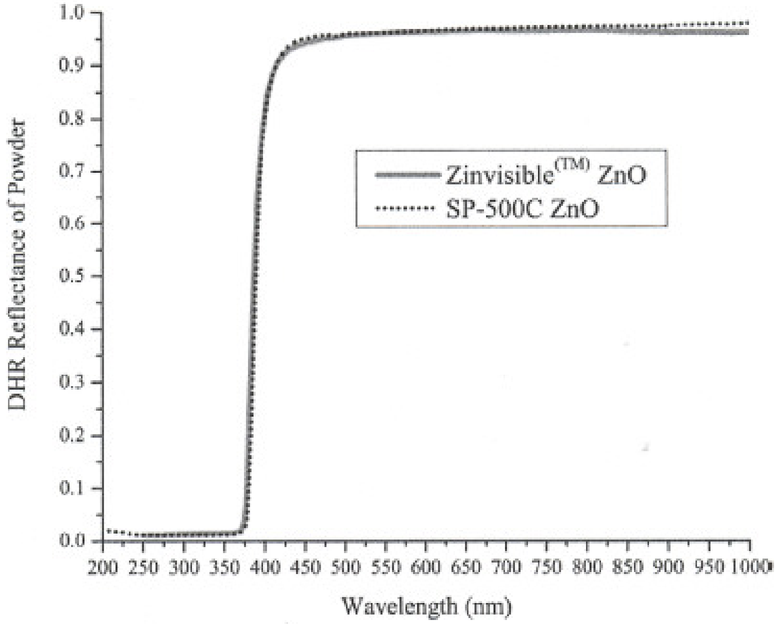

FIGURE 2. DHR reflectance spectra of ZnO pigment powders to determine inherent optical purity. Negligible difference was observed between the two grades of pigment.

The results of particle size analysis between the standard SP-500C and smaller size grade of ZnO displayed a significant difference between the two materials (Figure 3). While the literature primary particle size of SP-500C is reported at 0.5 µm, it was shown to have aggregates and agglomerates in a Gaussian distribution up to 14 µm. The Zinvisible™ product was developed as a nano-fine grade ZnO for use in transparent sunscreen formulations, touting a primary particle size below 0.15 µm, too low to efficiently scatter visible light. However, in our application we were interested in maximizing this material's light scattering capabilities. This required that complete dispersion to the primary particle size be avoided and the agglomerates be used as scattering particles. Particle size analysis of Zinvisible™ processed in this manner is shown in Figure 3. Validation of aggregate size was performed using scanning electron microscope (SEM) analysis, which indicated the presence of 1-2 µm agglomerates composed of fused 50-150 nm primary particles. The presence of some very small primary particles is observable as a secondary peak in the particle size distribution measurement. The effective size distribution of Zinvisible™ agglomerates is still not within the optimal range desired of 0.25 - 0.45 µm. However, when compared to the size distribution of SP-500C, it was expected to have greater scattering efficiency. In addition, the presence of some smaller aggregates and primary particles within this optimal size range would also contribute to scattering. To date, AFRL has not identified a source of ultra-high purity ZnO with an effective size distribution centered in the theoretical optimal size range.

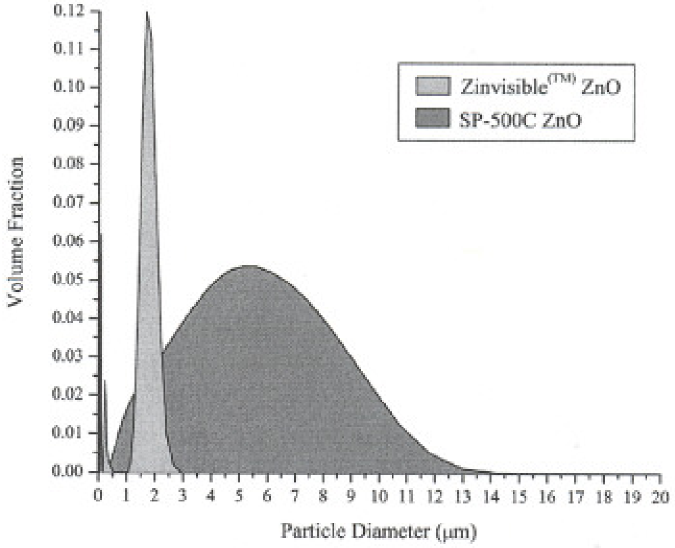

FIGURE 3. Particle size distribution of large (SP-500C) and small (Zinvisible™) particle size zinc oxide pigments evaluated.

Use of the smaller Zinvisible™ particle size ZnO resulted in thermal control coating films that displayed greater reflectance values per unit dry film thickness than SP-500C, thus indicating that scattering efficiency was indeed increased via smaller particles. Figure 4 displays the minimum film thickness required for each formulation to obtain its maximum reflectance values; further increases in film thickness did not improve reflectance values and thus only contribute to additional weight. Of significant importance is the fact that the smaller particle size ZnO film achieved very nearly the same reflectance values at a film thickness 18% less than that of SP-500C, directly correlating to a weight savings of 18% as well. Both film reflectance spectra track nearly identical until approximately 900 nm wavelength, at which there appears to be some inherent difference between the two pigment materials. The smaller particle size ZnO tended to show very slight absorption from 900 nm to 1900 nm, followed by a crossover in which SP-500C begins to show comparatively more absorption. Since the film compositions were essentially identical except in regard to pigment particle size, this could be a result of a difference in surface roughness affecting the measured reflectance. In addition to the film reflectance values, the measured reflectance of the uncoated black glass substrate is included for reference. Note that the ~5% broadband reflectance of the substrate is due to Fresnel surface reflection as a result of its smooth surface and does not contribute after being coated.

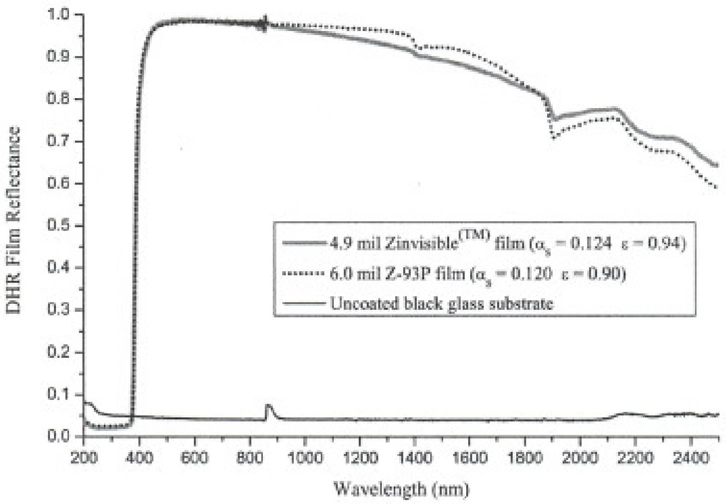

FIGURE 4. Direct hemispherical reflectance spectra of Zinvisible™ and SP-500C pigmented thermal control coatings at 65.1% PVC and optimum film thickness.

Using the reflectance data obtained from the DHR spectrophotometer, the resultant solar absorptance values (α_S) for Zinvisible™ and SP-500C films were calculated to be 0.124 and 0.120, respectively. Not surprisingly, both films had nearly equivalent solar absorption characteristics. However, an important difference in measured emittance between the two coatings was observed. While emissivity is an inherent property of a material, the roughness of the material's surface can have a significant impact on the overall measured emittance since there is more emissive surface area exposed. The emittance of Zinvisible™ films averaged 0.94, while those of the SP-500C films measured only 0.90. Thus, the thinner Zinvisible™ films actually resulted in a slight overall α_s/ε performance advantage over SP-500C films of greater thickness; 0.132 versus 0.133, respectively.

Scanning electron microscopy (SEM) of the film surfaces clearly resolves the structural morphology differences between the two formulations investigated (Figure 5). The class of thermal control coatings investigated in this study are intentionally formulated with minimal potassium silicate binder so that voids are present in the film, assisting greatly in scattering the incident radiation. The large agglomerate size of the SP-500C pigment resulted in much greater film pore sizes as a result in the inherently larger interstitial volume associated with random dense packing of larger particles. The smaller size ZnO pigmented films displayed a surface that appeared much more uniform in both pore size and roughness. Direct comparison between the two SEM micrographs resolves the greater surface area present in the Zinvisible™ films and much fewer numbers of deep pore cavities that would contribute less to measured emittance. It is also obvious from the micrographs that the primary particle size is smaller for the Zinvisible™ films, which also directly results in a greater surface area of exposure, further contributing to higher emittance values. There are some specialty applications in which emittance is of greater importance than the α_s/ε ratio. In these cases, the smaller sized pigmented formulations would provide enhanced performance.

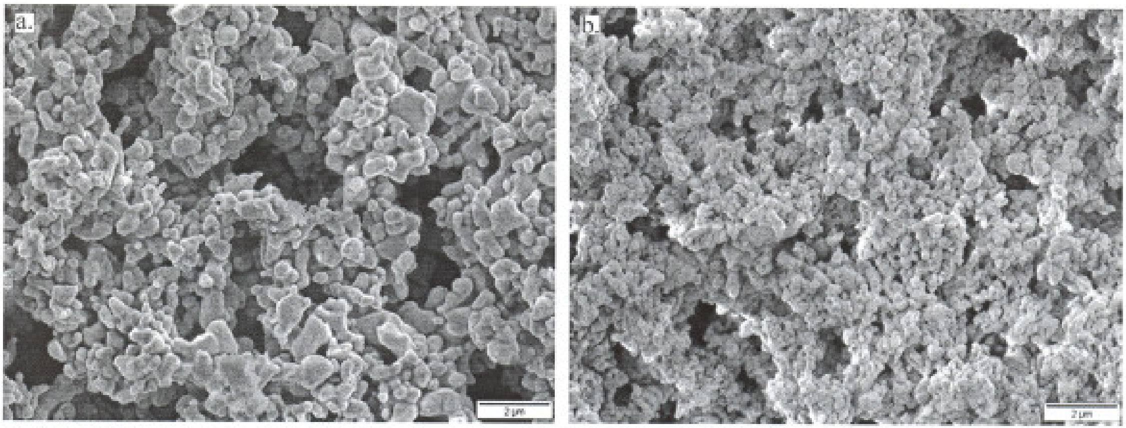

FIGURE 5. Scanning electron microscope images that reveal the greater primary pigment diameter and pore size of (a.) SP-500C based films in comparison to (b.) Zinvisible™ films (scale bar is 2 μm).

4. CONCLUSIONS

The utilization of a smaller particle size ZnO pigment (Zinvisible™) in the formulation of thermal control coatings for space assets results in slightly improved α_s/ε value of 0.132 in comparison with the currently used large particle size pigment. Furthermore, this improved value was obtained at a dry film thickness 18% thinner (4.9 mils) than the current state of the art, which translates to weight savings without sacrifice in thermal management properties. The smaller particle size formulations also display a marked improvement in emittance values (0.94), likely due to a more uniform surface roughness of smaller amplitude and fewer macroscopic pores. While the smaller particle size pigment employed in these experiments is still larger than optimal for improving the scattering efficiency of the system, the results indicate that there are potential gains to be found in developing such pigments for use in thermal control coatings. Furthermore, in applications where high emittance is of critical importance, the results indicate that use of a smaller particle size ZnO pigment results in improved performance.

5. ACKNOWLEDGMENTS

The authors would like to gratefully acknowledge financial support for this project under NRA-8-31, NASA Space Environmental Effects (SEE) Program, Marshall Space Flight Center, Huntsville, AL.

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