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DEVELOPMENT OF IMPROVED AND NOVEL THERMAL CONTROL COATINGS (Preprint)

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14. ABSTRACT

Thermal control coatings (TCCs) play a critical role in the thermal management of space assets through the reflection of incident solar energy and emittance of infrared heat. The development of new thermal control coatings with improved solar energy reflection, infrared emittance, and reduced weight are essential to the design of future space assets that will reside in harsh environments and have increasing constraints on weight. Optimization of pigment particle size and type can play an important role in the development of improved coatings. Recent improvements in the synthesis and particle size control of zinc orthotitanate pigment for silicate binder coatings have resulted in performance improvements over prior coatings of this type as well as the current zinc oxide based coatings. In addition, a novel pigment concept based on hollow silica particles is continuing to be explored as an extremely space durable and lightweight option for passive thermal control coatings.

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ABSTRACT

Thermal control coatings (TCCs) play a critical role in the thermal management of space assets through the reflection of incident solar energy and emittance of infrared heat. The development of new thermal control coatings with improved solar energy reflection, infrared emittance, and reduced weight are essential to the design of future space assets that will reside in harsh environments and have increasing constraints on weight. Optimization of pigment particle size and type can play an important role in the development of improved coatings. Recent improvements in the synthesis and particle size control of zinc orthotitanate pigment for silicate binder coatings have resulted in performance improvements over prior coatings of this type as well as the current zinc oxide based coatings. In addition, a novel pigment concept based on hollow silica particles is continuing to be explored as an extremely space durable and lightweight option for passive thermal control coatings.

KEY WORDS: Thermal Management/Control, Applications-Space/Spacecraft/Satellite, Microspheres/Microballoons

1. INTRODUCTION

Assets residing in space are subjected to a harsh environment with exposure to intense solar radiation. It is essential for these assets to maintain a certain temperature range to ensure the proper functioning of thermally sensitive components. One key aspect of this thermal management is through the use of thermal control coatings (TCCs) designed to reflect incident solar energy and emit infrared (IR) radiation. TCCs are space-stable white coatings that play a large part in the passive thermal regulation of these systems. The operational environments as well as the performance and design requirements of thermal control coatings can be found in the literature (1-3).

Z-93P and YB-71P, supplied by Alion Science, are two commonly used thermal control coatings. These coatings are composed of dense zinc oxide (ZnO) and zinc orthotitanate (Zn_2TiO_4) pigments, respectively. These TCCs are formulated in a binder of potassium silicate and are designed to reflect visible (VIS) and near infrared (NIR) energy as seen in Figure 1.
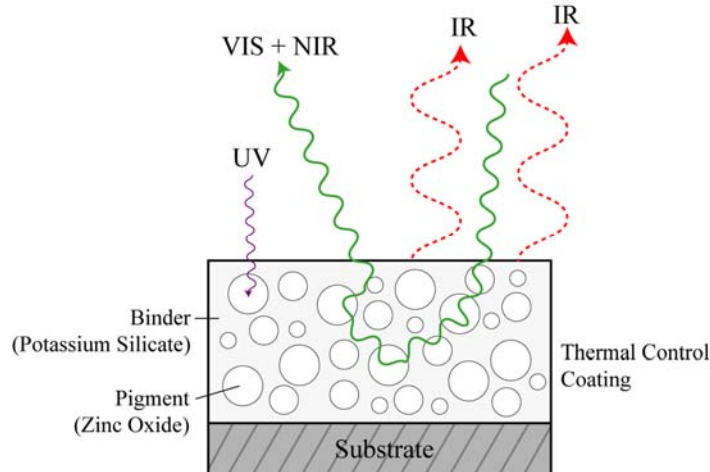

Figure 1. Cross-sectional schematic of a passive thermal control coating utilizing conventional metal oxide pigments such as zinc oxide or zinc orthotitanate.

One key to the performance of these coatings relies on a minimal solar absorptance (α_s) of the film. This is the amount of incident solar radiation that is absorbed by the surface resulting in the addition of heat to the system. Another important parameter of a thermal control coating is the thermal emittance (ε), which needs to be maximized for the best performance. This is a measure of the film's ability to emit heat in the form of infrared energy in the presence of a vacuum. The ratio of α_s to ε has a direct relationship to the absolute temperature (T) of the asset through equation (1):

$$T = \sqrt[4]{\frac{s \cdot \alpha_s \cdot A_s}{\sigma \cdot \varepsilon \cdot A_R}} \propto \frac{\alpha_s}{\varepsilon} \tag{1}$$

where s is a solar constant equal to 0.135 w/cm^2, As is the area in cm^2 exposed to radiation, σ is the Stefan-Boltzmann constant equal to 5.75E^{-12} W·cm^{-2}·K^{-4}, and A_R is the area in cm^2 capable of thermal emittance. In an effort to reduce the temperature, the coating must be designed with the lowest possible α_s/ε value.

There are multiple aspects involved with the development of a novel thermal control coating, one of which is attaining better beginning-of-life (BOL) and end-of-life (EOL) properties to maximize the performance of the coating and the asset by increasing the scattering efficiency and reducing the degradation of the coating. Due to high launch costs and payload capacities, the reduction of coating weight is also another important goal. This can be achieved through the use

of thinner films and less volume of dense pigment. Often times the thermal control systems of an asset are over designed to account for the degradation that will occur over the lifetime in a space environment. It is common for the solar absorptance to increase two-fold in a period of five to seven years. The thermal control subsystems such as radiators must be created to operate efficiently at the highest solar absorptance, adding overall cost and weight. Therefore, improving BOL and EOL optical properties goes hand-in-hand with reduction in weight of both the coating as well as the components of an asset.

Due to the lack of availability of new materials, recent work (4,5) has focused on the improvement of current thermal control coatings originally developed in the 1960's. This work has included the optimization of the pigment particle size of ZnO as well as improved synthesis techniques of Zn_2TiO_4 in an effort to enhance the scattering efficiencies. This work resulted in the introduction of Zinvisible-K and ZOT-P coatings. Even with these improvements, many problems continue to exist with these conventional TCCs. The presence of a dense metal oxide pigment contributes a significant amount of weight to the overall coating. Additionally, these pigments strongly absorb in the ultraviolet (UV) region as dictated by solid state physics (6), leading to extreme optical degradation and decreased performance. Even with the most optimal conditions, high densities and strong UV absorption will always exist with these types of pigments, making it difficult to increase optical properties and reduce weight. One way to avoid these issues is through the use a pigmentless coating.

A novel concept for thermal control coatings has been introduced (5) known as the "virtual" pigment approach by incorporating air voids into the binder systems rather than using high refractive index metal oxides. This concept still relies upon the refractive index difference between the pigment and binder, but utilizes spherical voids of lower refractive index to scatter light rather than traditional white pigment (Figure 2).
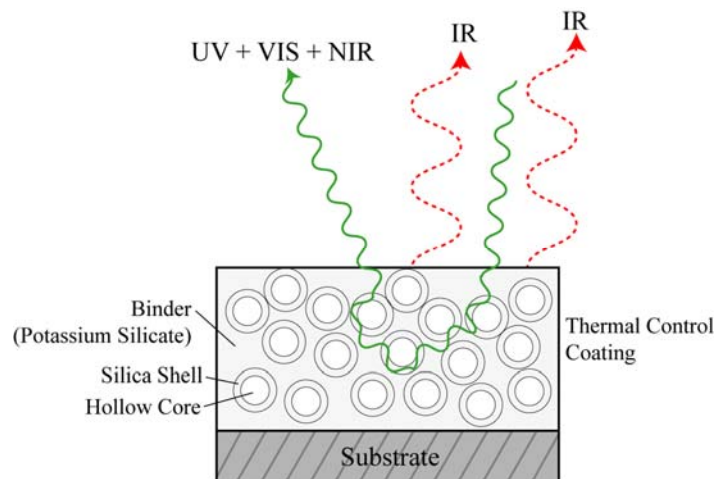

Figure 2. Cross-sectional schematic of a passive thermal control coating utilizing a "virtual" pigment concept through the incorporation of controlled spherical voids.

The refractive index of ZnO is approximately 2.0 at a wavelength of 500 nm and about 1.5 for potassium silicate, yielding a difference of 0.5. The refractive index difference between a vacuous or air void (n = 1) and potassium silicate is also 0.5. Therefore, properly sized air voids should be as effective as ZnO pigment at scattering solar radiation. Interestingly, thermal control coatings are sometimes formulated above the critical pigment volume concentration (CPVC) in an attempt to incorporate naturally occurring voids into the coating to aid in scattering efficiency. This increase occurs because the refractive index difference between ZnO and a void is significantly greater than that of ZnO and potassium silicate (Figure 3).
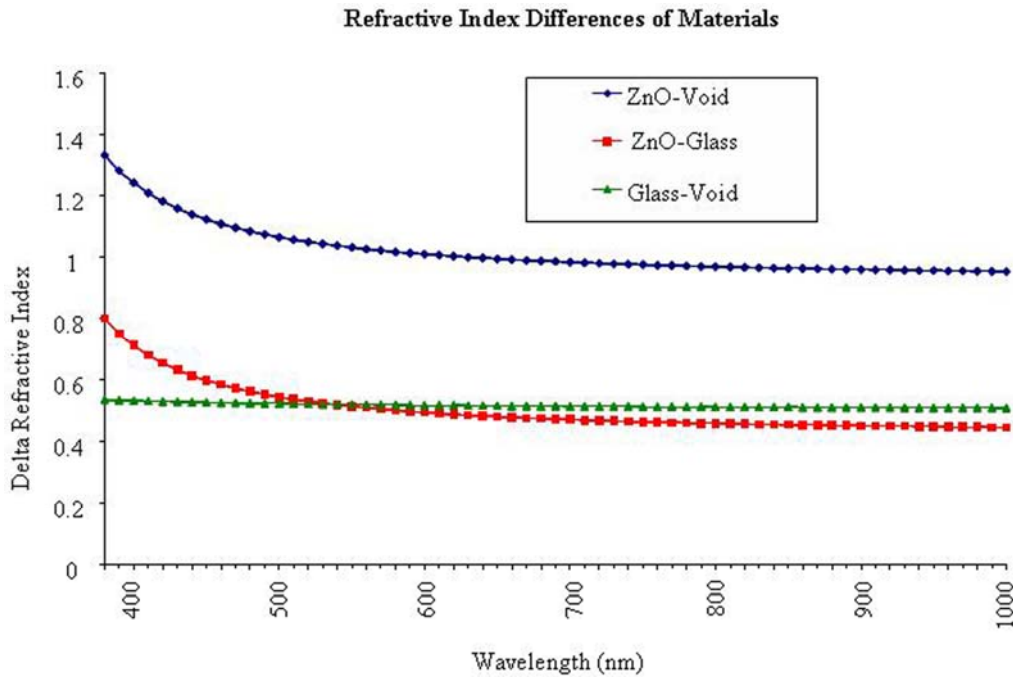

Figure 3. Refractive index differences between zinc oxide, glass, and voids.

Unfortunately, films formulated above the CPVC usually have poor mechanical properties. Above the CPVC, the coating becomes significantly less flexible. This increase in brittleness can cause delamination and cracking of the coating. The porosity also increases considerably above the CPVC due to the presence of these air voids that are not filled with binder material. Increased porosity can allow the permeation of foreign material and debris that can lead to coating contamination and degradation. Formulating thermal control coatings at very high PVCs also adds a greater amount of pigment to the system. This pigment causes a notable increase in the weight of the coating and it also provides more UV absorbing material that will optically degrade. Rather than formulating above the CPVC, the resolution is to incorporate controlled air voids into the coating through the use of hollow microparticles composed of a stable optically transparent material such as silica.

Spheres consisting primarily of an air core with a very thin casing composed mainly of silica should have a density much less than that of zinc oxide at 5.6 g/cm3, leading to a dramatic decrease in the weight of the coating. Being that these spheres are composed of silica they

should also be able to reflect more energy in the UV spectrum, leading to better EOL optical properties. Exposure results have confirmed that the optical degradation that occurs with current coatings is in fact due to ZnO pigment degradation and not the potassium silicate binder material. After 570 hours in a simulated space environment known as the Space Combined Effects Primary Test and Research (SCEPTRE) facility (7), there was no degradation of Kasil 2135, the silicate binder material (Figure 4).
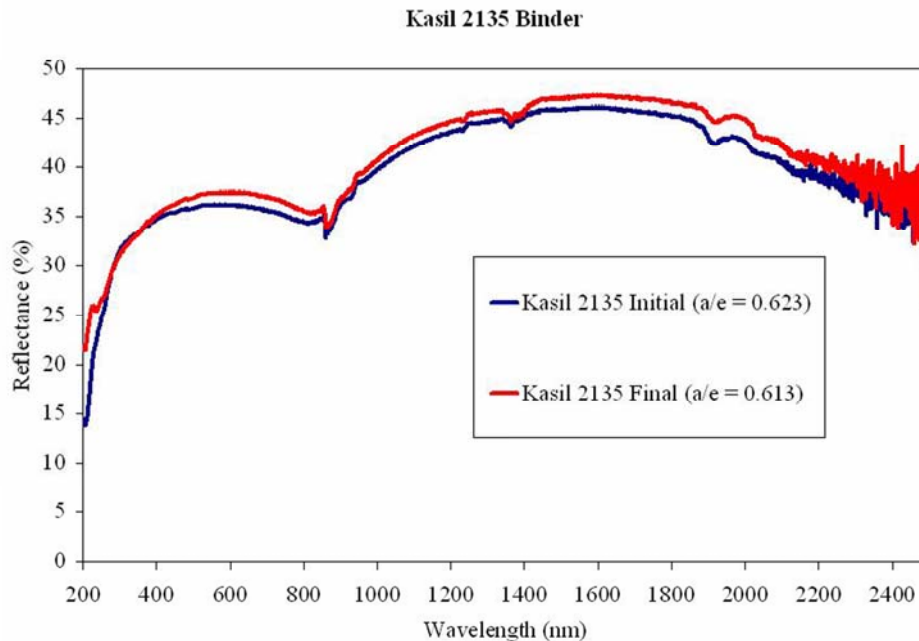

Figure 4. Reflectance of potassium silicate binder before and after 570 hours of simulated space exposure with no degradation.

Previous modeling of optimal void scattering (4,5) was used to determine the void diameter that would result in the highest amount light scattering. Any voids above 1 μm would not be effective at scattering between the wavelengths of 400 nm and 1000 nm according to this literature data. The only void materials available commercially were either too large in diameter or composed of material that would not withstand the harsh space environment. Two of these materials were selected to be used in formulations as proof-of-concept materials, and their reflectance was measured using a Perkin-Elmer Lambda 9 UV/VIS/NIR spectrophotometer. These results were plotted along with a ZnO-based coating (Figure 5). A product offered by the 3M Corporation composed of hollow soda-lime borosilicate spheres with diameters ranging from 20 μm to 70 μm was used in addition to a hollow polymeric material sold by Rohm and Haas know as Ropaque with a 0.40 μm outer shell diameter and a 0.25 μm inner void diameter. The 3M film had to be applied at a very large thickness to obtain reflectance because its large void diameter was not optimal for scattering light from 400 nm to 1000 nm. The most important aspect of this reflectance data is the evident enhancement of the UV reflectance properties with the void coatings compared to Z-93P.
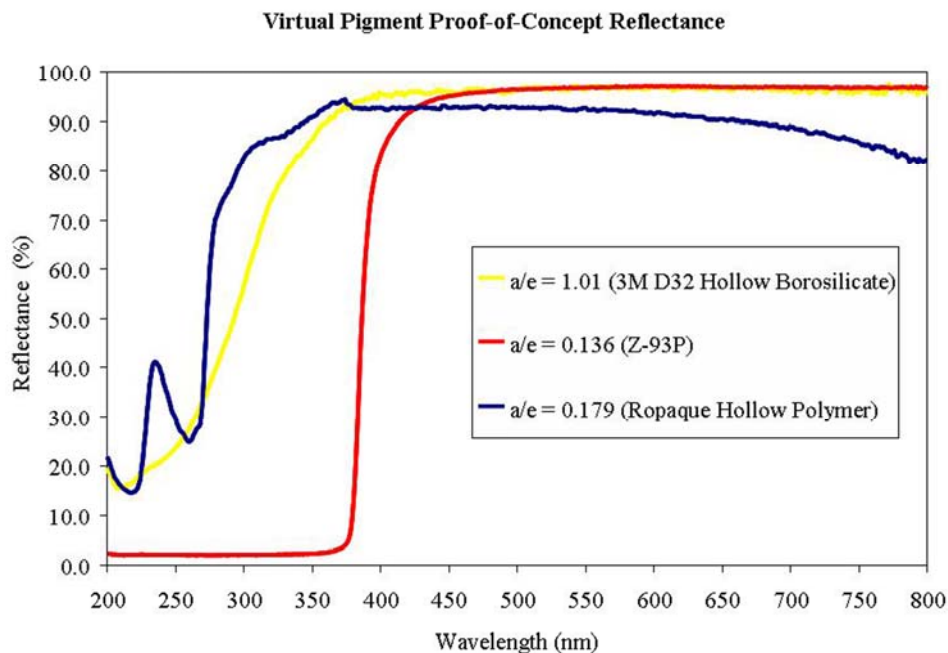
Figure 5. Reflectance of "virtual" pigment proof-of-concept films utilizing hollow particles vs. the reflectance of conventional Z-93P.

2. HOLLOW SILICA PARTICLE SYNTHESIS

The reflectance results were encouraging enough to pursue the synthesis of space-stable, optimally-sized hollow microspheres. The synthesis of these types of materials for various unrelated applications has been a strong focus in recent literature (8-12). Hollow silica spheres were chosen to be prepared by a variation on the procedure published by Zoldesi and Imhof entitled, "Synthesis of Monodisperse Colloidal Spheres, Capsules, and Microballoons by Emulsion Templating," (8). These spheres were synthesized from a silicone oil-in-water emulsion by adding 10% ammonia by volume to distilled water. A volume fraction of 0.01 dimethyldiethoxysilane (DMDES) monomer was then added to this solution with shaking. This solution was permitted to sit undisturbed for 24 to 48 hours (depending on the desired particle size) before the oil droplets were encapsulated through the addition of 0.043 M tetraethoxysilane (TEOS). This took place through 10 additions overall at intervals of 10 minutes with mild stirring in an effort to reduce agglomerations. Stirring was continued for approximately 96 hours before the spheres were removed from solution by centrifugation and suspended in ethanol for 18 hours to dissolve the inner oil-core. The product was then washed two final times with ethanol and permitted to dry for 24 hours before it was calcined for 2 hours at temperatures ranging from 200°C to 600°C.

The particles were characterized using Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), and SEM Focused Ion Beam (FIB). The product was confirmed to be spherical and very monodisperse using SEM imaging. The spheres ranged in diameter from batch to batch at 0.9 to 1.4 μm depending on the growth time selected after the addition of DMDES (Figure 6). SEM FIB was used to make multiple cross-sectional slices into the spheres,

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providing confirmation that they were composed of a hollow inner core with an outer shell diameter on the order of 0.1 μm (Figure 7).
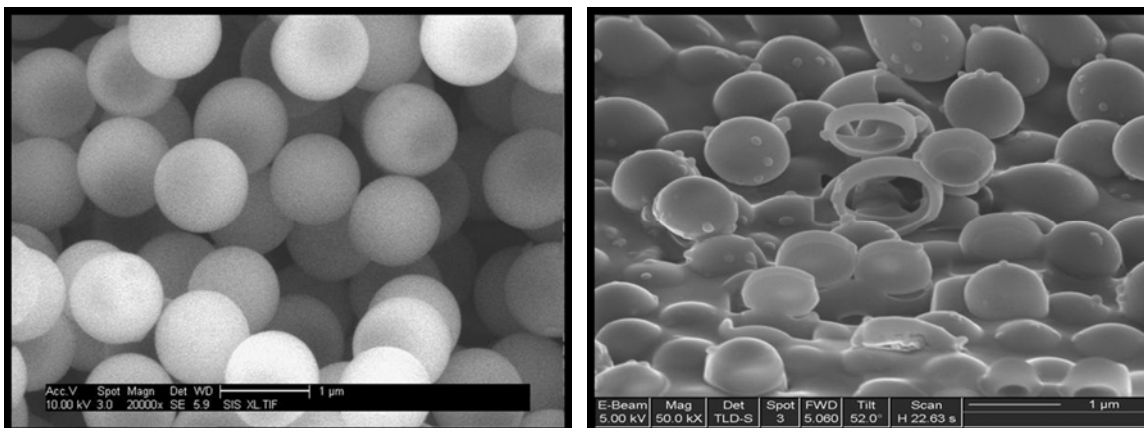
Figures 6 and 7. SEM and SEM FIB images of AFRL synthesized hollow silica spheres.

The bulk powder reflectance values were also measured for batches with external diameters of 1.1-1.2 μm as well as 1.3-1.4 μm (Figure 8). The bulk reflectance for both sizes provided very similar and promising data with excellent reflectance in the UV region. Unfortunately, the bulk reflectance was not able to be obtained for the 0.9-1.0 μm sized particles.
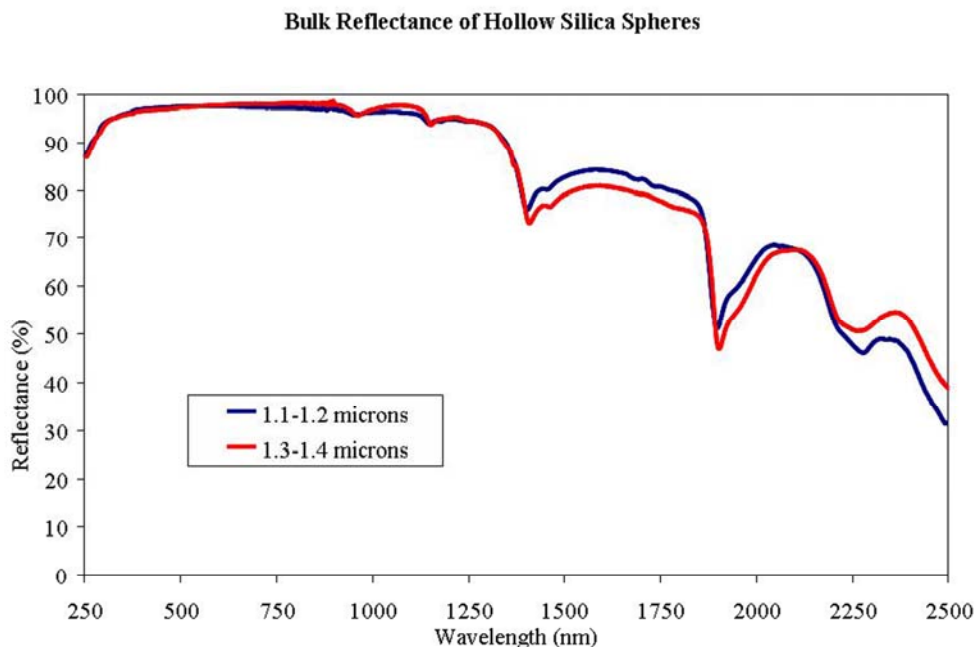

Figure 8. Bulk reflectance of AFRL synthesized hollow silica spheres of different size.

3. DEVELOPMENT OF VIRTUAL PIGMENT COATINGS

The bulk reflectance results led to the need to determine which of the three particle sizes would yield the greatest light scattering with the thinnest film. Each of the diameters was formulated into a coating utilizing a potassium silicate binder at an estimated pigment volume concentration of 65%, including void volume. The reflectance was measured for each sample on black glass because it is an optically absorbing substrate that will not interfere with the scattering measurements (Figure 9), and the film thickness was measured using a KLA-Tencor P-15 stylus profilometer. The 1.1-1.2 µm particles had the lowest reflectance with a film thickness of 108 microns, so it was determined that this was not the optimal diameter. The 0.9-1.0 µm and 1.3-1.4 µm particles had very similar reflectance values, but the film thickness of the smaller spheres (70 microns) was 3.5 times thinner than that of the larger spheres (250 microns). From these results it was determined the optimal sized virtual pigment was slightly less than 1 µm. Although the reflectance of the virtual pigment does not meet that of Z-93P, an increase in the film thickness should result in more comparable results.
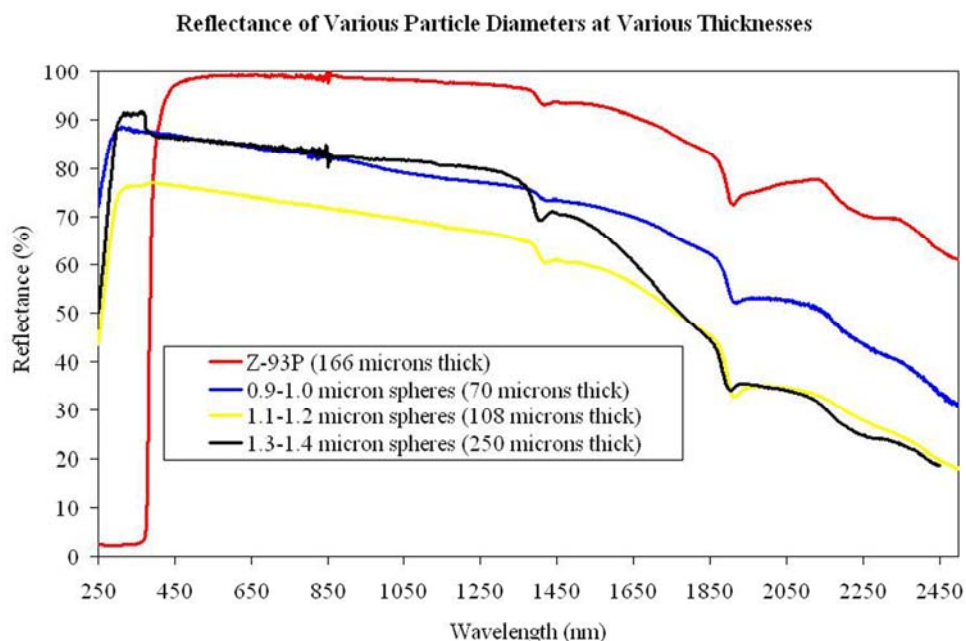

Figure 9. Reflectance of "virtual" pigment films utilizing hollow silica spheres of various sizes in comparison to Z-93P.

Along with the particle size determination, another study was conducted to determine the optimal pigment volume concentration of the coating. Up to this point, all of the coatings had been formulated at 65% because this was the PVC of Z-93P, the most commonly used thermal control coating. The medium sized spheres (1.1-1.2 µm) were formulated into coatings with pigment volume concentrations of 55%, 65%, and 75% in a potassium silicate binder. The reflectance of each film was measured on black glass at the same film thickness (1.18 mils). Figure 10 shows

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that the PVC of 75% has significantly higher reflectance values than the other two concentrations. It should be noted that the pigment volume concentrations are based upon an estimated hollow silica density. The experimental density if this material is still unknown.
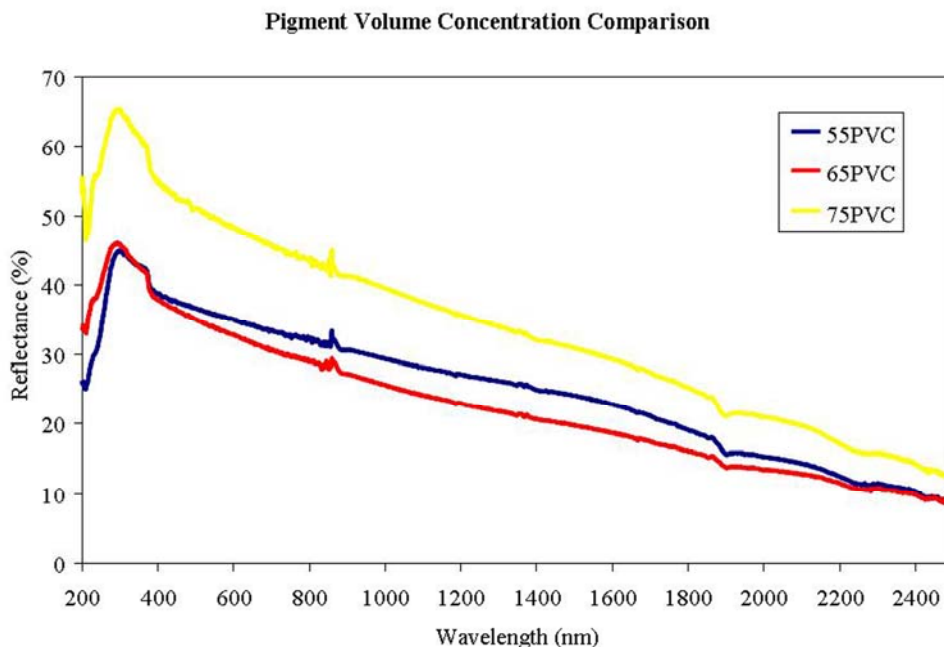

Figure 10. Reflectance of "virtual" pigment films with various pigment volume concentrations of hollow silica microspheres.

The emittance of the films was measured using an AZ Technology Temp 2000A Emissometer. All of the films with various sized particles and pigment volume concentrations resulted in emittances in the range of 0.88 to 0.94, which are comparable to both ZnO and Zn_2TiO_4 coatings.

SEM was completed on the cross-section of one of the films (Figure 11). This image confirms that the addition of hollow silica spheres leads to the incorporation of uniformly-sized air voids into the film. This well controlled incorporation provides a mechanism for successfully scattering light in the VIS and IR regions as well as in the UV.
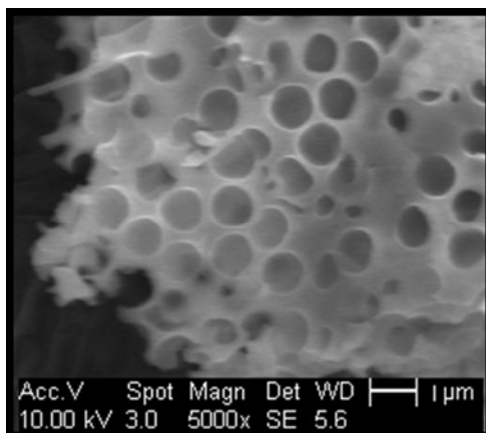

Figure 11. SEM cross-section of a film incorporating hollow silica microspheres.

4. CONCLUSION

Due to the limitations of white metal oxide pigments, the concept of a "virtual" or pigmentless coating was explored. This concept was developed from proof-of-concept films into a tangible and functional thermal control coating with a decreased weight as well as better optical properties in the UV region. The incorporation of well-controlled and optimally-sized air voids via introduction of hollow silica microspheres has allowed for improved characteristics, which could potentially lead to an increased performance in a space environment in addition to significant money savings in the areas of design and launch costs. The size of the air voids as well as the pigment volume concentration of the virtual pigment were also able to be optimized for the best optical performance. Initial reflectance and emittance values have proven promising enough to prepare samples for preliminary screening in the SCEPTRE facility (7) for an initial 775 ESH. These results will provide valuable solar absorptance and degradation data.

5. REFERENCES

1. D. G. Gilmore, ed., Spacecraft Thermal Control Handbook Volume 1: Fundamental Technologies, American Institute of Aeronautics and Astronautics, Reston, VA, 2002.
2. R. M. Van Vliet, Passive Temperature Control in the Space Environment, The MacMillan Company, New York, 1965.
3. Y. Harada and G. A. Zerlaut, "Stable White Coatings," IIT Research Institute IITRI-C207-205, 1963.
4. J. A. Johnson, J. J. Heidenreich, R. A. Mantz, P. M. Baker, and M. S. Donley, Progress in Organic Coatings, **47**, 432 (2003).
5. J. A. Johnson, C. A. Cerbus, A. I. Haines, and M. T. Kenny, Proceedings of the 43rd AIAA Aerospace Sciences Meeting and Exhibit, (2005).
6. J. H. Braun, FSCT Federation Series on Coatings Technology, Federation of Societies for Coatings Technology, Blue Bell, PA, 1995.
7. C. A. Cerbus, 20th Space Simulation Conference Proceedings, NASA/CR-1998-208598 Preprint (1998).
8. C. I. Zoldesi, and A. Imhof, Advanced Materials, **17**, (7), 924 (2005).
9. J. H. Hoe, J. S. Kin, B. J. Jeon, S. M. Koo, and Y. E. Lee, Chemical Communications, 1712 (2003).
10. I. Tissot, J. P. Reymond, F. Lefebvre, and E. Bourgeat-Lami, Chemical Materials, **14**, 1325 (2002).
11. G. Dubois, J. J. L. M. Cornelissen, V. Y. Lee, E. F. Connor, T. Magbitang, H. Kim, W. Volksen, and R. D. Miller, Polymer Preprints, **45**, (1), 616 (2004).
12. K. P. Velikov and A. Van Blaaderen, Langmuir, **17**, (16), 4779 (2001).