Development of a thermal control coating optimized for cryogenic space applications

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Abstract. As NASA endeavors to extend the human presence in space beyond low Earth orbit, methods to efficiently store cryogenic propellants in space are required. Current state of the art rigid thermal control coatings absorb approximately 6% of the total solar irradiance, while state of the art thermal control paints absorb approximately 10% of the total solar irradiance. Consequently, radiative heat transfer alone makes passive storage of cryogens in space impossible. A new rigid thermal control coating is in development and has achieved solar absorption values as low as -0.6% (compared to a NIST standard) while maintaining high emissivity. This negative value for a rigid tile of pure yttria has required a new testing method be developed. Rigid tiles are very high performance but have more mass than paints and paper-thin coatings. Tiles must have a metallic substrate and create application challenges. While some use cases may necessarily address the challenges associated with rigid tiles in order to achieve required performance, a similar paint-like coating was also developed. The spray-on version of the new thermal control coating is easily applied to large complex surfaces and is very low mass. This version is also primarily yttria but includes a potassium bromide binder. Application to various substrates shows solar absorption values consistently below 5%, with a minimum of 2.8% achieved. Details of each version of this coating, along with test data is discussed.

1. Introduction
In order to send humans to, and return them from Mars, NASA is planning for the use of cryogenic propellants in space. Long-term storage of cryogenic propellant in space is a challenge due to radiative heat loads from the sun and conductive heat loads from the spaceflight vehicle. The development of a high-performance coating that can block nearly all the energy from the sun while simultaneously emitting infra-red radiation will significantly reduce heat loading on cryogenic tanks in space. This paper will discuss the use of Yttrium Oxide (aka yttria) (Y\textsubscript{2}O\textsubscript{3}), to fabricate two forms of such a coating. One is a rigid tile that has demonstrated higher solar reflectivity than Spectralon\textsuperscript{\textregistered} (the reference material used in solar absorptivity testing) and the other is a thin, spray-on version that will be compared to AZ-93, a common solar reflective paint. The early development of both coating forms, along with theory and discussion, are described in references [1-4].
2. Background
The sun generates a total irradiance of 1366 Watts/m² in space at earth distance (1 AU) [5]. A spherical object that has a flat absorption spectrum from the UV through to the infrared, exposed to that power density, would reach an equilibrium temperature of nearly 400 K (assuming no other heat sources). The sunlit side of the Moon demonstrates this example well. In order for an object exposed to this solar irradiance to become cooler, the fractional amount of solar power absorbed, $\alpha$, must be lowered, while the fractional amount of infrared power emitted (emissivity), $\varepsilon$, must be raised. The ratio of these two quantities, $\alpha/\varepsilon$, has a strong effect on the steady state temperature of an object in space. In practice, the emissivity for most solar reflectors is between 0.8 and 1.0, so this has little effect on the ratio. The solar absorptance, on the other hand, can vary significantly. State-of-the-art solar reflectors based on silver and fused silica have a solar absorptance of 0.06 [6] while white paints, such as AZ-93 from AZ Technology, have a solar absorptance of 0.15+/-0.02 at 5 mils thickness [7].

If a coating can be fabricated with about a 0.01 $\alpha/\varepsilon$ ratio and if this is placed on a sphere at uniform temperature, far from other heat sources, then the sphere will come to a steady state temperature of about 88 K, sufficient to passively store liquid oxygen. One reason this works is the sphere emits infrared from its entire surface, which is 4 times larger than its cross-sectional area, which determines the amount of solar power absorbed. Therefore, the goal of passively storing cryogens is reachable, assuming the solar absorptance limitations of the existing coatings can be overcome. Some of the existing coatings (as well as films) rely on silver or aluminum to reflect the sunlight, both of which have fundamental absorption limitations, preventing the achievement of a 0.01 $\alpha/\varepsilon$ ratio. Another class of coatings is based on using the scattering of small particles held in place by a binder, i.e. white paint such as AZ-93. Many of these coatings are limited by ultraviolet absorption by the binders, though some improvement has been made. AZ-technology has a white paint with an inorganic binder, AZW/LA-II, with a solar absorptance of 0.09+/-0.02 at 10 mils thickness [8]. However, further $\alpha/\varepsilon$ improvements could be realized if the scattering medium were composed of a material with less absorption and the binder were properly chosen.

3. Materials
Constructing a high reflectivity coating requires small particles of a material that absorbs very little sunlight. These particles, from Mie Theory, should have a circumference approximately equal to the desired peak scattering wavelength. The sun’s peak emission is around 480 nm, so the optimal particle has a diameter of around 150 nm. In early work, barium fluoride (BaF₂) was selected for investigation because it transmits the vast majority of the solar spectrum, as seen in Figure 1. This figure shows the solar spectral irradiance (above the atmosphere, air mass = 0) overlaid on the transmission of a 100-micron thick window of barium fluoride. Also shown is a tile fabricated by pressing a combination of barium fluoride particles and water and then sintering the result to create a foam-like material that scatters light but has no binder. This material performed well in early testing, but as work continued, issues associated with its application on a spacecraft became apparent. The low index of the material, 1.45, means that a relatively thick 5 mm tile would be required to achieve adequate reflectance of the solar spectrum. Also, barium fluoride has a substantial water affinity and water has strong infrared absorption bands; its presence would severely degrade the solar absorptance of the material. Finally, there was evidence of etching on steel parts in the fabrication equipment, which might be due to the formation of hydrogen fluoride (HF), a very dangerous chemical compound.
A transition was made to yttrium oxide (Y$_2$O$_3$) because it is hydrophobic, has a relatively high index (1.8), and is very chemically stable. The spectral transmission band, shown in Figure 2, is not as wide, resulting in a small amount of solar absorptance based on material properties. However, this absorptance is small enough that cryogenic temperatures could still be obtained. Figure 2 also shows a tile composed of this material.

4. Tile fabrication and performance
Tiles are fabricated by mixing 10-parts high purity yttria with 1-part high purity water and blending so that no clumps are formed. The mixture is then transferred to a mold for compaction. A variety of mold materials were tried resulting in the choice of ceramic sides, a sapphire base, and a sapphire ram. The use of sapphire eliminated contamination in the top and bottom surfaces. Compaction pressures of about five Mega-Pascals have yielded the best results, though this can vary with the size of the tile. Next, the compacted tile is sintered in an oven. A variety of sintering profiles were examined in order to optimize the balance between tile strength and optical properties (high temperature sintering results in high strength tiles with poor reflectance while low temperature sintering results in high reflectance tiles that are easily broken). The optimal sintering profile will vary with tile size, but the following profile has demonstrated good results with 1-inch diameter disc-shaped tiles, as shown in Figure 2.

- Ramp oven temp up from room temperature to 250°C at a rate of 10°C/min
- Hold at 250°C for 30 minutes
- Ramp oven temp up from 250°C to 800°C at a rate of 10°C/min
Accurately measuring the solar absorptance of these tiles is complicated because they are better reflectors than the NIST standard reflectors. The accepted approach for measuring solar absorptance is to use in ASTM E903 [9]. A beam of light is aimed at the sample, varied in wavelength from the ultraviolet to the mid-infrared (typically 250 nm to 2400 nm), and a portion of the reflected light is captured by an integrating sphere and measured. The measured radiation is then compared with a reflectance standard (a NIST traceable Spectralon® puck, serial number 3153) to determine the spectral reflectivity of the sample. This reflectivity spectrum is overlapped with the solar irradiance spectrum and integrated to find the solar absorptance. The deep space spectrum (air mass = 0) was used in this analysis, which yields higher absorption values than the typical North American surface spectrum (air mass = 1.5) that considers the solar spectrum accounting for atmospheric absorption and scattering of ultraviolet spectral components.

ASTM E903 has several shortcomings, but the most serious is that it is a relative, not an absolute, measurement, as shown in the following example. The reflectivity curve (NIST) of the Spectralon® puck is shown in Figure 3 (solid line). Using a Jasco V-670 reflectance spectrometer with an ISN-723 integrating sphere accessory, the reflectance versus wavelength of a disk of sintered Y$_2$O$_3$ was measured and its spectral reflectivity calculated by comparison with the measured reflectance of the Spectralon® standard and its NIST reflectivity data. The result is shown in Figure 3 (dashed line) displaying a broad region with reflectivity greater than one, which is not possible. The calculated solar absorptivity of the Spectralon® standard is 1.16% and -0.68% for the Y$_2$O$_3$, a negative absorptivity, demonstrating the measurement problem in using ASTM E903.

![Figure 3. Reflection spectra of Spectralon (solid line) and a sintered yttrium oxide tile (dashed line).](image)

The measured solar absorptance of Y$_2$O$_3$ tiles varies, primarily due to differences in vendor supplied material, but calculated negative values are commonly found. Consequently, a direct measurement of solar absorption is needed to assess the performance of highly reflective materials. This can be done...
by placing a sample in vacuum, with very cold surroundings, and measuring its steady-state temperature when a solar simulated light source is impinged onto it. The development of a system to perform this measurement is described by Swanger, et al [10]. A TESA 2000 portable emissometer/reflectometer and solar reflectometer was used to measure the emissivity of the Y$_2$O$_3$ tiles yielding a value of 0.92, close to the theoretically determined expectation.

Another limitation of the ASTM E903 standard for measuring solar absorptance is that it covers a limited region of the solar spectrum and misses approximately 3% of the solar irradiance at wavelengths longer than 2500 nm. Yttrium oxide has minimal absorption out to about 8 microns (see Figure 2); however, theory shows that mid-IR radiation (4-8 microns) may not scatter effectively and may pass through the tiles (long waves will not see the small scattering particles). Consequently, a thin metallic coating is placed onto the back of the tiles, using vapor deposition, to reflect this radiation. Silver backings did not adhere properly, so aluminum was used instead; an example is shown in Figure 4. Figure 4 also shows that the aluminum coated tiles can be attached to an aluminum plate using a strain isolation pad resulting in a bond strongly enough that the plate can be lifted by the tile.

5. Spray-on Formulation and Application

The performance of low absorptance solar reflectors is partially dictated by the thickness of the coating. Thicker coatings reflect more light; like needing more than one coat of paint for optimal coverage. Consequently, the tiles, being approximately 3 mm thick, provide very good reflection. However, they are difficult to apply to a spacecraft or tank due to their small, rigid, construction and contribute more mass than a paint-like coating would. Many users would be willing to sacrifice some thermal control performance in exchange for ease of application. With this in mind, a yttrium oxide based spray-on paint that uses potassium bromide as a binder was also generated. Potassium bromide has essentially no solar absorption, making it worth considering as the basis for a solar reflector, except that it dissolves easily in water and has low index of refraction (about 1.56). However, these properties are what make it an ideal choice as a binder. By dissolving it in a mixture of water and alcohol (for better wetting of the paint) and then mixing in yttria particles, a white paint is achieved. This can be sprayed onto a surface and, as it dries, the potassium bromide comes out of solution and forms a thin, crystalline layer of material that holds the yttrium oxide particles in place, creating a white, broadband, solar reflector.

The spray-on yttrium oxide/potassium bromide coating has been applied to a variety of materials, resulting in optimal formulations that vary with substrate (steel and aluminum have different alcohols for example). In addition, it has been found that many (typically 10) light sprays yield a more uniform and rugged coating than a few thick coatings do. The result is a coating that is about 5 mils thick,
similar to that of AZ-93, enabling a direct comparison between them. Figure 4 shows photos of aluminum, silver, and multi-layer insulation (MLI) that have been coated with 10 layers of the spray-on coating. Note, only the outer layer of the MLI was coated. In addition, stainless steel and spray-on foam insulation (SOFI) have also been tested.

![Figure 4](image_url)

**Figure 4.** From left to right, an aluminum substrate prepared for Y$_2$O$_3$ spray-on application, an aluminum substrate with 10 layers of Y$_2$O$_3$ spray-on, a silver foil with 10 spray-on layers, and the outer surface of a piece of multi-layer insulation with 10 spray-on layers.

### 6. Spray-on Coating Performance Results

Table 1 summarizes some of the results when spraying different surfaces. The underlying substrate condition can greatly affect the results, especially if it results in an uneven coating. Note the difference between the smooth and scuffed silver substrate and between the unfinished and the machined aluminum substrates. All the solar absorption calculations were performed as described in the previous sections comparing the reflectance spectrum to that of the NIST Spectralon puck and then integrating over the deep space solar irradiance spectrum.

| Substrate                     | Number of Layers | Solar Absorption |
|-------------------------------|------------------|------------------|
| Unfinished Aluminum Panel     | bare             | 31%              |
|                               | 4 spray-on layers| 15%              |
|                               | 10 spray-on layers| 6%              |
| Unfinished Stainless Steel Panel | bare           | 53%              |
|                               | 4 spray-on layers| 18%              |
|                               | 10 spray-on layers| 8.5%            |
| Silver Foil (smooth)          | bare             | 16%              |
|                               | 10 spray-on layers| 5%              |
| Silver Foil (scuffed)         | bare             | 25%              |
|                               | 10 spray-on layers| 5.5%            |
| Multi-Layer Insulation (MLI) Substrate | bare | 11% |
|                               | 10 coats         | 5.5%             |
| 7075 machined Aluminum Substrate | bare           | 35%              |
|                               | 10 coats         | 4%               |

**Table 1.** Solar absorption values of various substrates quantifying the improvement obtained by applying multiple layers of spray-on coating.

Figure 5 shows a finely machined 7075 aluminum disk with 0, 3, and 10 layers of spray-on coating. The combination of a smooth surface and a uniform spray coating caused this sample to have the lowest solar absorptance of any of the spray-on specimens, achieving a solar absorptance of only 4%. The
particular sample shown in Figure 5 was fabricated for use on an upcoming cube-sat whose goal is to compare the performance of the \( \text{Y}_2\text{O}_3 \) based spray-on coating to AZ-93 in low earth orbit. The cube-sat will contain two spray-on samples and two AZ-93 samples, designed to point away from the earth and its infrared emissions, allowing the samples to be exposed to just the sun’s irradiance.

![Figure 5](image)

**Figure 5.** A 7075 aluminum disk with no spray (left, \( \alpha = 31\% \)), 3 spray layers (center, \( \alpha = 10\% \)), and 10 spray layers (right, \( \alpha = 4\% \)).

### 7. Space Environment Testing

In addition to a cube sat experiment, there are several tests both underway and planned to examine the space environment effects on the yttrium oxide tiles and the spray-on coating. The first is the use of the Materials International Space Station Experiment (MISSE) where samples can be placed outside of the International Space Station (ISS) for long-term exposure to the low earth orbit environment. One of the original BaF\(_2\) tiles was placed on MISSE-10 and has returned to earth, but evaluation of this sample has been delayed by COVID lab restrictions. Several packaged \( \text{Y}_2\text{O}_3 \) tiles, shown in Figure 6, were delivered for MISSE-11, one of which is currently on the ISS.

![Figure 6](image)

**Figure 6.** Four \( \text{Y}_2\text{O}_3 \) tiles fabricated and packaged for MISSE-11. From left to right these are the flight sample, the flight backup, the control sample, and a second backup.

In the coming year, after COVID lab restrictions have been lifted, both atomic oxygen and ultraviolet exposure testing of the tiles and spray-on coating are planned to be performed at the Glenn Research Center. In addition, solar wind interaction with the spray-on coating will be performed at the Goddard Space Flight Center. No significant degradation of \( \text{Y}_2\text{O}_3 \) is expected since this is the most thermodynamically stable compound in the group of metal oxides. However, there is some concern about the potassium bromide (KBr) in the spray-on coating. KBr may decompose in the presence of atomic oxygen or solar wind. In addition to the in-space environment testing, larger tiles are currently being constructed from which Mohr bars can be cut, which will allow the measurement of the material breaking strength. Making quantitative measurements of strength is important in ensuring survival of the tiles under handling and launch conditions.

### 8. Interest

Several aerospace companies have shown interest in the tiles and the spray-on coating. A recently awarded cryogenic focused NASA Tipping Point Project is considering coating one of the flight tanks with the spray-on version of this coating. The goal is to demonstrate the adherence of the coating...
under both launch conditions and cryogenic thermal contraction of the tank. In addition, work is ongoing to develop manufacturing processes for both the tiles and the spray-on coating working with the Thermal Protection System Facility at the Kennedy Space Center.

9. Conclusions
A new class of low absorptivity solar reflectors is under development, including both a tile and a spray-on version. The tiles are composed of yttrium oxide particles that have been wetted, pressed, and then sintered to form a ceramic. They have a solar absorptance less than a NIST reflectance standard, Spectralon®, making them a potential option for achieving passive storage of cryogens, such as liquid oxygen and liquid methane, in deep space. The spray-on coating, composed of yttrium oxide particles bound in place by potassium bromide, trades off thickness and absorptivity for ease of application. It can be sprayed over relatively large areas but has a higher solar absorptivity than the thicker tiles (highly dependent on the optical properties of the underlying substrate). Work is underway to test the environmental degradation of these reflectors and to transition them to a state where they can be applied to spaceflight vehicles.

10. References
[1] Youngquist, Robert C., and Mark A. Nurge. "Achieving cryogenic temperatures in deep space using a coating." Optics letters 41, no. 6 (2016): 1086-1089.
[2] Youngquist, Robert C., Mark A. Nurge, Wesley L. Johnson, Tracy L. Gibson, and Jan M. Surma. "Cryogenic deep space thermal control coating." Journal of Spacecraft and Rockets 55, no. 3 (2018): 622-631.
[3] Youngquist, Robert C., Mark A. Nurge, “Cryogenic Selective Surfaces,” NIAC Phase 1 Final Report, 2/2016. Cryogenic Selective Surfaces - NASA Technical Reports Server (NTRS)
[4] Youngquist, Robert C., Mark A. Nurge, “Cryogenic Selective Surfaces,” NIAC Phase 2 Final Report, 9/2018. Cryogenic Selective Surfaces - NASA Technical Reports Server (NTRS)
[5] ASTM E490 – 00a(2019) “Standard Solar Constant and Zero Air Mass Solar Spectral Irradiance Tables,” ASTM International, West Conshohocken, PA, 2019, www.astm.org
[6] “Optical Solar Reflectors Leaflet,” Qioptiq, http://www.qioptiq.com/download/QST_Datasheet_SolarReflectors%20v3.pdf [retrieved 24 March 2017]
[7] AZ Technology, “AZ-93 White Thermal Control, Inorganic Paint/Coating,” http://www.aztechnology.com/products/paints/az-93.html
[8] AZ Technology, “AZW/LA-II Ultra-Low Solar Absorptance White Thermal Control Paint/Coating,” http://www.aztechnology.com/products/paints/azw-la-ii.html
[9] ASTM E903-20, “Standard Test Method for Solar Absorptance, Reflectance, and Transmittance of Materials Using Integrating Spheres”, ASTM International, West Conshohocken, PA, 202, www.astm.org
[10] Swanger, A. M., A. Krenn, R. Youngquist, and T.L. Gibson, “Development of a Space Irradiance Simulator for Advanced Studies and Materials Research,” presented at the 2021 Cryogenic Engineering Conference and International Cryogenic Materials Conference.

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