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MASTER

SELECTIVE
~~SELECTIVE~~ EMITTER

TASK II TOPICAL REPORT

FOR

RADIATIVE-COOLING MATERIALS

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ENERGY MATERIALS RESEARCH COMPANY

2547 EIGHTH STREET
BERKELEY, CA 94710
415/644-2244

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The following report summarizes the work completed at Energy Materials Research Company on selective emitter materials for radiative cooling. Discussed will be 1) Theoretical Basis of Seletive Emitters, 2) Materials Selection, and 3) Acquisition of Materials.

SELECTIVE EMITTER---OPTIONAL MATERIAL

Theoretical Basis

The basis for selective radiative cooling is the spectral radiance of the atmosphere. Figure 1 shows the zenith atmospheric spectral radiance published in 1978 by Berdahl and Martin (1). Inspection of this figure shows that the radiance is depressed in the interval 8-13 microns compared to a black body. The magnitude of the depression correlates inversely with the amount of water vapor present. If a black body is placed on a horizontal surface at night, it will cool below ambient temperature because it initially emits more radiation than it absorbs. The difference is simply the difference in area under the black body curve and under the appropriate atmospheric radiance curve.

An important technique used to improve cooling performance over a black body is the development of a material that emits radiation only in the 8-13 micron interval (see figure 2). By Kirchhoff's law of selective radiation, this selective emitter will be absorbing only in the same wavelength interval. If exposed in a dry climate, such a material will absorb only the depressed 8-13 micron radiation, while emitting at a high rate in the same interval. Another way of looking at this is to note that much of the radiation in the 8-13 micron interval originates from higher altitudes which are cooler. Figure 3 shows that much of the 8-13 micron radiation originates in the upper atmosphere (2).

Material Selection

Our search for a selective emitter began with an extensive survey of absorption spectra in hopes of finding a material with a near ideal absorption curve. Silicides, nitrides, borides, sulfides, and carbides were among the first materials investigated as their Reststrahlen bands looked promising for emissivity in the 8-13 micron range. In addition to spectral criteria, the materials had to be environmentally durable and producible in a

cost effective manner to be selected.

Over a thousand spectra were examined. The most promising materials were two previously studied compounds, polyvinylidene fluoride (Tedlar) and silicon monoxide, and two new candidates, silicon dioxide and silicon nitride. A description of each follows.

Tedlar is available in sheet (film) form from E.I. Dupont De Nemours & Co., Polymer Products Department, Wilmington, Delaware. The primary problem with Tedlar is that its absorption spectrum is different from the ideal. It begins absorbing at 6.5 microns instead of at 8.0 microns, and begins transmitting again at 12 instead of 13 microns (see figure 4). The absorption at 6.5 microns means that more heat will be absorbed from the atmosphere than is theoretically necessary. Likewise, the transmission at 12 microns means that the 8-13 micron 'window' is not being fully used for emission. Another less significant problem is absorption of thermal infrared radiation at 18-30 microns. There is not much atmospheric radiation in this interval, as at shorter wavelengths, but the pigments used for the reflective glazing absorb in this region. This means that the 18-30 micron radiation emitted by the Tedlar will be absorbed by the glazing, heating it, and limiting the system performance. This could possibly be used to advantage to prevent condensation on the glazing, but is generally undesirable because cooling performance is decreased.

Silicon monoxide (SiO) has a very narrow absorption band at 10-12 microns, when prepared 1.0 micron thick. Problems with SiO are that the 10-12 micron absorption does not take full advantage of the 8-13 micron 'window,' and the absorption band is thickness sensitive (see figure 5)(3). Samples 1.2 microns thick show significant absorption between 13-18 microns. The experiments performed to date have used silicon monoxide prepared by vacuum evaporation. Vacuum evaporation processes are used commercially, but the associated costs add up to a dollar per square foot. When compared to approximately five cents per square foot per Tedlar, and about the same price for glazing material, a dollar

or two per square foot is quite expensive. We therefore do not consider SiO to be a commercially practical product.

Silicon dioxide (SiO_2) is a cheap, durable material. The primary problem is that it absorbs 8-11 microns instead of the 8-13 micron ideal. Silicon nitride (Si_3N_4) is not as cheap as SiO_2 but it is relatively inexpensive and is extremely durable. It absorbs from approximately 9-15 microns. Since the SiO_2 absorption cut-off was a little too soon (at 11 instead of 13 microns), and the Si_3N_4 cut-off was a little too late (at 15 instead of 13 microns), it seemed reasonable that a mixture might cut off at the desired 13 microns. This was investigated and absorption spectra published by Chu et al show that a 5% Si_3N_4 95% SiO_2 amorphous film (silicon oxynitride) has an almost ideal absorption spectrum (see figure 6)(4).

The preparation method was discovered via Dr. Bruce Deal of Fairchild Semiconductor, who had previously prepared films of this type by chemical vapor deposition (CVD) (5). CVD is a relatively inexpensive commercial process so the constraint of production capability in a cost effective manner can be satisfied as well. Two production methods become immediately apparent:

- 1) CVD a SiO_xN_y film onto aluminum foil,
- or 2) compound SiO_xN_y powder into polyethylene prepare, film, and laminate to aluminum foil.

The aluminum foil is for solar reflection and low emission in the IR range. This allows the selective emitter material to be the dominant factor in this region. The actual selectivity of the SiO_xN_y can be optimized by careful selection of either film thickness or particle size (depending on the method used) (6, 7 respectively). Doing this allows one to increase the emission slightly in the 8-13 micron range due to interference effects (though the majority of the selectivity is due to bulk material properties).

We see that the silicon oxynitride system has better optical properties than the previously used materials as well as

economic feasibility.

Acquisition of Material

Procuring a sample of the silicon oxynitride has not been as easy as finding the spectra and preparation method. We have as yet to locate a commercial source of the material though an exhaustive search has not been completed. We were able to obtain a small sample from Dr. Deal taken from one of the process reactors at Fairchild. Because the reactor was not set up for high purity production of silicon oxynitride, the level of contaminants (mostly ammonium hydroxide, NH_4OH) rendered our efforts to compound it into polyethylene useless.

Future work could include several alternative paths including:

- 1) Locate a commercial source of SiO_xN_y powder, compound into polyethylene, and make film samples. Wayne H. Thornton of Thomas Publishing Company is confident that he can locate a source of this material if it exists.
- 2) Locate a research laboratory willing to produce sample quantities of SiO_xN_y for our use.
- 3) Construct 'in-house' capability to produce powder and film SiO_xN_y (i.e. CVD reactor). This would be accomplished with the aid of Dr. Deal.
- 4) Obtain samples of SiO_2 and Si_3N_4 amorphous powders and compound mixtures into polyethylene. These later two compounds are readily available commercially.

NOTE: After this report was written a new paper by C.G. Granqvist et. al. was discovered (8). In this paper the use of electron beam evaporated Si_3N_4 as a selective emitter is described. Their samples were not stoichiometric and contained certain amounts of oxygen (i.e. silicon oxynitride!). The published

spectrum (figure 7) shows promise as a selective emitter. These experiments add considerable weight to the need for more work on inexpensive means of producing this material system.

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(FIGURE 1)

IDEAL REFLECTANCE CURVE FOR SELECTIVE EMITTER

(FIGURE 2)

(FIGURE 3)

(FIGURE 4)

(FIGURE 5)

Chu et al.) Infrared spectra of Si_3N_4 - SiO_2 amorphous films. (From

(FIGURE 6)

Reflectance for Si₃N₄ + Al films.

(FIGURE 7)