LA-UR-81-3610

LA-UR--81-3610

DE82 006104

Los Alamos National Laboratory is operated by the University of California for the United States Department of Energy under contract W-7405-ENG-36

TITLE: SOLAR-ABSORBER-SELECTIVE PAINT RESEARCH

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SUBMITTED TO: Society of Photo-Optical Instrumentation Engineers,
Los Angeles, CA, January 25-29, 1982

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Los Alamos, New Mexico 87545

FORM NO 836 RM
NO 8629 5/81

INSTRUMENTATION AND OPTICS DIVISION

Solar absorber selective paint research

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Abstract

Research and development effort seeking to develop low cost, high performance solar selective paint has been conducted under government support for approximately eight years. Other investigators have spent many years in bringing various types of selective paint to the market place. This report is intended primarily to focus on the DOE programs that the Los Alamos National Laboratory has the responsibility of monitoring.

Introduction

There is a definite need for low cost, high performance consumer-applied selective coatings for use in both low temperature active and passive applications. In practice these coatings could take the form of attached films or spray-applied paints. Some of the key considerations are performance, cost, durability and ease of site or local installation. Honeywell¹ has been the principal R&D organization involved in developing solar selective absorber paint coatings under DOE contract. Other DOE programs intended to determine the durability of selective coatings have included the testing of the Honeywell selective paints.

Background

The significance of selective absorbers has been well documented for low temperature active systems for years. Performance comparisons based on yearly system performance show that a collector area can be reduced up to 40% for some climates by using selective versus flat black absorbers.²

Selective surfaces have only recently been evaluated for passive systems.³ Figure 1 describes the tradeoffs for a passive water wall system having 1 to 3 layers of glazing when exposed to the Los Alamos, N.M. climatic conditions. The figure describes the solar savings fraction (SSF) as a function of number of glazings and absorber wall optical properties. For a detailed description of SSF or load collector ratio (LCR) see Ref. 3.

Figure 1. A combined plot showing the effect of different values of either wall solar absorptance or wall infrared emittance on performance of a water wall in Los Alamos. The curves labeled α_s show the effect of changing the effective solar absorptance at a constant value of $\epsilon = 0.9$. The curves labeled ϵ show the effect of changing infrared emittance while holding α_s constant at 0.95.

This work was supported by the U.S. Department of Energy, Office of Solar Heat Technologies.

Use of moderately selective absorber-surface paint of $\alpha_s=0.90$ and $\epsilon=0.50$ for a single glazed system will result in approximately a 10% increase in savings fraction over a flat black absorber of $\alpha_s=.95$ and $\epsilon=.70$. A relatively good selective absorber painted surface of $\alpha_s=0.92$ and $\epsilon=0.15$ could result in an overall gain in SSF of approximately 30%. This degree of gain diminishes with multiple glazings configurations much as it does with multiple-glazed flat plate collectors.

Solar paint research and development

Investigations into solar paint concepts can be broken down into two basic types, i.e., thickness-sensitive solar paints and thickness-insensitive solar paints.

Thickness-sensitive solar paint (TSSP) research and development

This type of selective paint can be characterized as obtaining its selectivity by the deposition of an optically thin layer of an absorbing particulate onto a highly thermally reflective substrate. The particulate may be a semiconductor, metal oxide, black pigment or any combination of these. Investigations of particulates have ranged from PbS, Si, Ge, CdSe, CdTe, etc. for semi-conductors through oxides such as CrO_x , FeMnCuO_x , MnCuFeO_x , CrCuO_x , CuCrO_x , CuCrMnO_x , CoFeMnO_x , CoFeO_x , etc., spinels, and into the various organic pigments. Binders or vehicles studied by the various investigators are olefin base polymers, polyethylene, ethylene propylene, ethylene propylene diene materials, silicone resins, fluorocarbons, acrylics, urethanes, etc. Some of the principal investigators involved in these investigations include Mar et al.,⁴ Lin, Zimmer et al.,⁵ Pettit and Sowell,⁶ Van Buskirk,⁷ Löfving,⁸ Telkes,⁹ and Gupta.¹⁰

Of the many combinations investigated by Honeywell the most promising is the Ferro F-6331 Fe-Mn-CuO_x pigment, mixed into G.E. silicone resin SR-125 and dip coated on an aluminum substrate. Laboratory-prepared samples have resulted in properties of $\alpha_s=.92$ and $\epsilon=.10$.

TSSP production scale up. A necessary part of the Honeywell contract is the scale up of their laboratory findings into workable production techniques. Studies include determining processing effects on overall coating performance, formulation stability and shelf lives, variations in constituents or substrates, and baking of binders. The final product of this phase of study will be the establishment of high speed mass production techniques.

Reverse roll coating. A series of simulated production runs were made at the United Binding Co., St. Paul, Minnesota using a Revaplast Reverse Roll Laminator manufactured by the Bruderhans Co., Germany to coat 2-ft-wide, 1-mil-thick aluminum foil. The best properties obtained during the run were $\alpha_s=0.93$ and $\epsilon=.14$ at a coating rate of 18 ft/min and 10.7% solids. The basic formulation was the 30% pigment volume concentration (30 PVC) F-6331/SR-125. Some wrinkling of the foil created by the slitting operation was encountered. If this problem cannot be overcome, a heavier foil may be required for this production technique. Oven curing during the run at 270°F provided for solvent removal but did not fully cure the material, which had to be post-production cured at 500°F.

Gravure printing. A more recent process investigated as a potential mass production technique is that of gravure printing. This technique is under investigation at the Reynolds Metal Co., Richmond, Virginia. The paints being tried are shown in Table 1 along with the resulting optical properties.

Table 1. Optical properties of thickness-sensitive solar paint coating applied by gravure printing techniques to 1 mil aluminum foil.

Film Thickness	SR-125		Cargill 6247	
	α_s^*	ϵ	α_s^*	ϵ
0.1 Mil	0.92	0.24	0.91	0.32
0.15 Mil	0.92	0.26	0.92	0.34

Coatings are 30 PVC/F6331 at pigment particle size of 2-4 μm .

*Gier Dunkle MS-251 absorptances have been corrected for machine offset to bring them into agreement with Beckman DK-2A and Beckman 5270 results.

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Coating rates of 400 ft/min were used while applying the 0.1-mil paint thickness. The ovens at Reynolds were able to initiate but not fully cure the silicone modified epoxy binder (Cargill 6247) and only removed the solvent from the silicone system (SR-125). Curing of the SR-125 takes 1 h at 500°F in an air oven. Infrared curing has been accomplished in 3 s.

Scanning electron microscope (SEM) photos of the gravure printed runs are shown in Figures 2 and 3. The texture or pattern associated with the gravure process is shown for the various magnifications. Viscosity and surface tension effects have produced the different patterns, since both runs were conducted on the same equipment. This texturing effect may be an asset in repeatability for high-production-rate coatings; however the texturing may be a liability in achieving the best optical properties.

Figure 2. 20x and 100x SEM photos of the G.E. SR-125 system.

Figure 3. 20x and 100x SEM photos of the Cargill 6247 system.

Spraying. Large sample panels of aluminum 12 in. x 16 in. were spray coated at Honeywell using both an electrostatic pressure-feed spray gun and a pressure feed spray system without the electrostatic feature. The panels sprayed using the electrostatic unit exhibited very good uniformity of coating thickness. Optical properties were $n_s = 0.95$ and $t = 0.48$ at film thickness of 0.1 to 0.12 mils.

When panels were sprayed using the pressure-feed system only, the best developed spraying technique produced a film thickness range of 0.4 - 0.9 mils with optical properties of $n_s = 0.92$ and an t range of 0.30 to 0.40.

Further work will be necessary to confirm the improved optical properties with the electrostatic system, as well as to identify the optimum paint characteristics for

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spraying. The paint formulation used was 30% PVC F-6331/SR-125 diluted with solvent to obtain 15% solids.

Related work

Honeywell has investigated the feasibility of using a transparent material with low index of refraction to reduce the surface reflectance of the selective black coating, and thus improve its absorptance.

The base coating, F-6331/SR-125, was applied to aluminum panels and the optical properties were measured. The panels were then topcoated with FEP Teflon® (DuPont FEP-120) and measurements were again made. The results listed in Table 2 demonstrate the feasibility of this process.

Table 2. Optical properties of thickness-sensitive paint before and after FEP Teflon® topcoat.

Honeywell Panel Code	Before Overcoat		After Overcoat	
	α_s^*	ϵ	α_s^*	ϵ
09787-20-9-13	0.90	0.15	0.93	0.19
09787-20-12-10	0.89	0.12	0.93	0.15
09787-20-13-10	0.90	0.14	0.93	0.18

Thickness insensitive solar paint (TISP) research and development

A number of investigators have attacked the problem of providing a selective paint that can be sprayed or deposited on any type of substrate regardless of emittance. A different approach is required. Either a low emittance base coat must be applied to the substrate or low emittance flake must be included in the paint. The flake can be precoated with pigment⁹⁻¹⁰ or it can be added to a paint that already contains pigment.

Honeywell has approached the problem by adding aluminum-flake material to the TSSP system. Figure 4 shows a photomicrograph of a TISP coating at 1000X. The figure shows the interleaved aluminum flake. Small bumps on the flakes are believed to be particles of F-6331 pigment correlating to a grind of 2-4 μ m. The dark area on the flakes is believed to be composed of a thick layer of smaller particles of F-6331 pigment in SR-125 silicone binder.

Figure 4. Scanning electron micrograph of 30PVC F-6331/Al 2468/SR-125 paint coating at 1000X showing the large aluminum 2468 flakes and the smaller F-6331 pigment particles uniformly distributed on the flakes.

*Gier Dunkle MS-251 absorptances have been corrected for machine offset to bring them into agreement with Beckman DK-2A and Beckman 5270 results.

Honeywell's current effort is to define the size, size distribution and PVC of F-6331 and concentration of aluminum pigments. The application procedure is known to have a significant effect on both α_s and ϵ and must be carefully controlled for test purposes. Figure 5 shows the same coating at 200X giving a better view of the exposed coating surface. Other aluminum flake materials that have been investigated are shown in Figures 6 through 8. The optical properties obtained from these systems are described in Table 3. Nickel particles were also investigated but resulted in poorer properties than the aluminum.

Table 3. Optical properties of aluminum leafing flake materials.

Flake/Pigment/Binder/Base Composition	10% PVC α_s/ϵ	30% PVC α_s/ϵ
AlCan 462/F6331/SR125/Al	0.93/0.74	0.87/0.68
AlCan 565/F6331/SR125/Al	0.91/0.70	0.88/0.62
AlCan 769/F6331/SR125/Al	0.91/0.66	0.88/0.53
Alcoa 2468/F6331/SR125/Al	0.95/0.57	0.92/0.31

Figure 5. SEM of 30 PVC F-6331/Alcoa 2468/SR-125/Al showing extent of interleaving of aluminum particles.

Figure 6. SEM of 30 PVC F-6331/Alcan 462/SR-125/Al.

Figure 7. SEM of 30 PVC F-6331/Alcan 565/SR-125/Al.

Figure 8. SEM of 30 PVC F-6331/Alcan 769/SR-125/Al.

An interesting result was obtained from samples pressure sprayed at Los Alamos using a Honeywell TISP formulation mixed more than 2 years previously. The paint, F-6331/Alcoa 2468/ SR-125 formulation, was sprayed on an etched aluminum substrate for 1, 3 and 5 passes to determine the effects of light to heavy coverage of the substrate and any effects of high shelf life. Table 4 describes the results where the thinner coating benefits from the low emittance substrate.

Table 4. Shelf life/multiple pass results.

	Aluminum Substrate	No. of spray passes		
		<u>1</u>	<u>3</u>	<u>5</u>
α_s	0.07	0.90	0.91	0.92
ϵ	0.03	0.21	0.32	0.38

SEM photos of the heavier coatings were very similar to Figs. 4 and 5. Shelf lives of this nature would probably never be recommended by a supplier but are extremely encouraging.

Durability studies

Honeywell has conducted accelerated weathering and humidity durability tests of the thickness-sensitive paint coatings.⁵ Accelerated weathering tests have resulted in a change in emittance of 7-12% and a change in absorptance of 2-8% for etched substrate materials when exposed to 3051 hours of accelerated weathering per Fed. Test Method Standard 141, Method 6152. Optical changes resulting from 4968 h of MIL-STD-810B humidity testing were normally less than those resulting from the accelerated weathering tests.

Lockheed Palo Alto Research Laboratory test results

The effects of short-term and extended environmental stresses on the operational properties of selective coatings were studied by means of accelerated laboratory simulation techniques.¹¹ Test parameters included UV radiation, elevated temperature and humidity, thermal cycling, and stagnation heating. In addition to many metal/metal oxide selective surfaces, the Honeywell-produced selective paints were studied.

Table 5 describes the optical properties of these paints before and after exposure.

Table 5. Humidity, thermal cycling and UV effects.

Material	Sample	Initial Properties		Post Exposure 1		Post Exposures 1 & 2		Post Exposures 1, 2 & 3	
		α_s	ϵ	α_s	ϵ	α_s	ϵ	α_s	ϵ
Honeywell Paint	1	0.92	0.11	0.92	0.11	0.92	0.11	0.92	0.10
Silicone, Thickness	2	0.93	0.15	0.92	0.15	0.90	0.13	0.88	0.12
Sensitive	3	0.92	0.16	0.92	0.16	0.90	0.13	0.89	0.12
Honeywell Paint	1	0.91	0.17	0.89	0.18	0.89	0.17	0.90	0.20
Urethane, Thickness	2	0.90	0.11	0.88	0.13	0.87	0.13	0.88	0.15
Sensitive	3	0.90	0.11	0.88	0.14	0.88	0.13	0.88	0.14
Honeywell Paint	1	0.92	0.44	0.91	0.45	0.90	0.44	0.91	0.49
Silicone, Thickness	2	0.90	0.30	0.90	0.30	0.90	0.30	0.90	0.35
Insensitive	3	0.82	0.40	0.81	0.41	0.81	0.41	0.83	0.43
Honeywell Paint	1	0.82	0.37	0.80	0.40	0.78	0.44	0.74	0.40
Urethane, Thickness	2	0.84	0.42	0.81	0.43	0.79	0.49	0.76	0.46
Insensitive	3	0.84	0.42	0.81	0.43	0.79	0.49	0.76	0.46

Exposure 1 - 30 days at 95% R.H. at 86°F.

Exposure 2 - Thermal cycling, - 104°F to 248°F, 60 cycles.

Exposure 3 - Ultraviolet Irradiation - 12000 equivalent sun hours.

Berry Solar Products (BSP) test results

Berry Solar has a DOE contract¹² to investigate selective and nonselective coatings for solar collectors. Many paints have been evaluated as a part of this program. Optical properties of coatings were tested before and after being subjected to a combined temperature and solar cycle. The thermal cycle consisted of 8 cycles per day of heating and cooling from 200°F to 450°F.

The test boxes were covered with ASG Sunadex A[®] glazing and exposed to sunlight. An auxiliary heater provided the thermal cycle. Optical results from this test for varying cycles and exposures are shown in Table 6.

Table 6. Selective/semi-selective paints.

Manufacturer	Binder/Pigment/ Substrate	Initial α_s/ϵ	Exposure 1 α_s/ϵ	Exposure 2 α_s/ϵ	Exposure 1 & 3 α_s/ϵ
Honeywell	Si/F-6331/Al	0.915/0.10	0.905/0.10 (3)	0.910/0.15 (4)	0.93/0.15
DuPont	(2)/(2)/Al	0.930/0.38	0.935/0.39	0.920/0.43	-
DuPont	(2)/(2)/Cu	0.925/0.39	0.945/0.39	0.930/0.43	-
(1)	Si/(2)/Al	0.940/0.59	0.950/0.62	0.945/0.62	-
(1)	Si/(2)/Cu	0.940/0.59	0.938/0.68	0.945/0.61	0.87/0.70

Exposure 1 21,851 ly and 78 cycles.

Exposure 2 42,307 ly and 161 cycles.

Exposure 3 156,307 ly done at Desert Sunshine Exposure Tests, Inc.

(1) Name withheld upon request or not available.

(2) Material unknown or proprietary.

(3) Exposed at 21,672 langley and 73 cycles.

(4) Exposed at 41,361 langley and 161 cycles.

Durability Conclusion

In general and under the test conditions, the Silicone/F-6331/Al systems have shown quite good durabilities. The urethane TISP has shown considerable degradation. This degree of degradation would eliminate it from active collector applications; however, it might still be a potential candidate for use in passive solar applications. Fluoropolymers should also result in good durabilities.

Summary

By mid-1982 the advanced thickness-sensitive selective paint (TSSP) coating is expected to be producible under various factory conditions. Commercial exploitation is expected to follow as a function of market acceptance and supply and demand. A coating with $\alpha_s=0.9$ and $\epsilon=0.1$ at a material cost of 5¢/ft² may soon be a reality.

Thickness-insensitive selective paint (TISP) coatings should be at the point of optimization soon. Further effort will be needed to bring these coatings to demonstrated production feasibility and commercialization. These coatings have significant potential for many diverse applications outside of their use on flat plate collectors. Selectivity of $\alpha_s=0.9$ and $\epsilon=0.3$ at a material cost of 6¢/ft² is expected.

Acknowledgements

The author wishes to thank all the DOE Contractors for their support in providing information for the paper. Particular thanks go to Mr. Paul Zimmer of Honeywell for the excellent material provided.

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