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SELECTIVE PAINT AND BLACK CHROME COATINGS DEVELOPMENT

Semi-Annual Report for June 5—December 5, 1978

By
R. J. H. Lin
P. B. Zimmer

December 1978

Work Performed Under Contract No. EM-78-C-04-4287

Honeywell Systems & Research Center
Minneapolis, Minnesota

950 1151

U.S. Department of Energy

Solar Energy

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SELECTIVE PAINT AND BLACK CHROME
COATINGS DEVELOPMENT
SEMI-ANNUAL REPORT

For the Period 5 June 1978 - 5 December 1978

K.J.H. LIN and P.B. ZIMMER

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December 1978

Prepared for
The Solar Heating and Cooling
Research and Development Branch,
Office of Conservation and Solar Applications
United States Department of Energy
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FOREWARD

This is the semi-annual report describing the work performed at Honeywell, Inc., Systems and Research Center, for U.S. Department of Energy under Contract No. EM-78-C-04-4287.

The work has been supported primarily by the Solar Heating and Cooling Research and Development Branch, Office of Conservation and Solar Applications, U.S. Department of Energy, and partially by Small Solar Thermal Power Section, Division of Central Solar Technology, U.S. Department of Energy.

The authors acknowledge the guidance provided by Dr. Stanley W. Moore of Los Alamos Scientific Laboratory and Dr. Robert R. Sowell of Sandia Laboratories, who are the Project Monitors.

Dr. R.J.H. Lin is the Project Principal Investigator. The paint coating work was performed by P.B. Zimmer, W.D. McKelvey, G.W. Nelson, and R.L. Bentley. The black chrome coating work was performed by Dr. R.J.H. Lin, S.E. Heckler, L. Fielder, E. Pscheidt, J. Schrenk, K. Sherin, and J. Rogers.

ABSTRACT

Solar selective black chrome and paint coatings were investigated to improve their performance and to develop techniques for large-scale applications.

Formulations and processing conditions for thickness sensitive paint coatings were defined which consistently provide solar absorptance (α) of 0.90 and emittance (ϵ) of 0.10 on low emittance substrates. A significant improvement in abrasion resistance was achieved by decreasing the pigment volume concentration. Addition of aluminum flake to these formulations has resulted in a thickness insensitive coating with $\alpha = 0.90$ and $\epsilon = 0.30$.

The critical bath components of a commercial black chrome plating process have been identified as hexavalent chromium, trivalent chromium, acetic acid and ferric ion. These components were varied and their effect on coating optical properties and durability at temperatures of 350-400°C were studied. Coating thermal stability was significantly improved by reducing the trivalent chromium concentration from the normal 16 g/l to 12 g/l or less.

Initial efforts have begun to optimize black chrome systems on aluminum substrates in terms of cost and durability.

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SECTION 1

INTRODUCTION AND SUMMARY

INTRODUCTION

The objective of this program is to improve the performance of solar selective black chrome and paint coatings and to develop large-scale application techniques for these coatings.

Low cost, environmentally durable, selective paints with solar absorption (α) of 0.92 and emittance (ϵ) of 0.10 have been developed by Honeywell in a previous program for DOE (Reference 1). However, the adhesion and abrasion resistance of the paints still need to be improved, and a large-scale process needs to be developed. The optical properties of the black chrome coating have been very well optimized with process parameters, but little work has been done on the effect of plating bath composition on coating properties. Also black chrome/substrate systems still need to be optimized in terms of cost and durability.

Techniques have yet to be developed to apply both black chrome and paint coatings to aluminum foil as a means of achieving a widely available and easy to use solar selective surface.

SUMMARY

Paint Coatings

Formulations and process conditions for thickness sensitive paint coatings were defined which consistently provide $\alpha = 0.90$ and $\epsilon = 0.10$ on aluminum substrates. Addition of aluminum flake to these formulations has resulted in a thickness insensitive coating with $\alpha = 0.90$ and $\epsilon = 0.30$. A significant improvement in abrasion resistance was achieved by decreasing the pigment volume concentration. New pigments were evaluated, but none has been found which can be used as a substitute for Ferro's F-6331.

Black Chrome Coatings

The critical bath components of a commercial black chrome plating process have been identified as hexavalent chromium, trivalent chromium, acetic acid and ferric ion. These components were varied and their effect on coating optical properties and stability at temperatures of 350-400° C were studied. Coating thermal stability was significantly improved by reducing the trivalent chromium concentration from the normal 16 g/l to 12 g/l or less. Chromic acid and ferric ion had little effect on the coating stability, while high levels of acetic acid tended to decrease the stability. Acetic acid also greatly affected the coating optical properties.

Initial efforts have begun to select an optimal black chrome system for use on aluminum substrates. Various metal undercoats are being utilized in the optimization of the system regarding environmental durability and cost effectiveness.

SECTION 2

PAINT COATINGS

The first six-month efforts for paint coating development have concentrated on defining processing conditions, evaluating new pigments and binders to provide alternate materials, and improving adhesion and abrasion resistance. Investigation of thickness insensitive paint coatings by mixing reflective metal particles in the paint formulation has also begun.

PAINT COATING PREPARATION

Experimental solar paint coating solutions were prepared by ball milling procedures. Pigments, binder, solvent and grinding media were combined in a container of suitable size. The container was rotated to provide the milling action. Pigment agglomerates were reduced to smaller agglomerates and discrete particles by this process. The pigment agglomerate breakdown was monitored periodically during milling by measuring the relative particle dispersion or "grind" of the paint coating solution. Milled paint coating solutions were then "thinned" as required with the appropriate solvent and either spray- or dip-applied to clean aluminum substrates. Coating films were air dried to allow solvent removal, then either force dried to complete solvent removal or cured at elevated temperature.

MEASUREMENTS OF OPTICAL PROPERTIES

Solar absorptance of all paint coatings was measured with a Gier-Dunkle MS-251 solar reflectometer. Emittance reported for paint coatings is the emittance at 100°C, obtained from a Gier-Dunkle DB-100 infrared reflectometer without a filter. The normally manufactured Gier-Dunkle infrared reflectometer includes a polyethylene filter, which can be used to measure room temperature emittance. If a sapphire filter is used, the instrument can be used to measure the emittance at 300°C (Reference 2). Diffuse spectral reflectance was measured with the Honeywell integrating sphere reflectometer.

THICKNESS SENSITIVE COATINGS

Repeatability

A 30 PVC F-6331*/DC-808** coating solution was prepared at 50 percent solids and reduced in solids with xylene for application. Aluminum substrates were dip-coated with the coating solution at 1-5 in./min., air dried, and cured. Absorptance and emittance were measured and recorded in Table 1. These data are compared with data obtained from test panels prepared in a previous program using a coating of the same formulation. This type of test allows the comparison of the coating made previously with the old dip coater with a current batch of the same coating applied with the new dip coater.

From Table 1 it can be seen that the current batch of coating shows somewhat lower absorptance and emittance than the previous batch of coating. The overall optical efficiency of the current batch of coating is about the same as the previous batch of coating.

Comparison of coatings on a sample-to-sample basis shows $\Delta\epsilon = 0.07$ for the previous batch and $\Delta\epsilon = 0.03$ for the current batch of coating. This indicates better control of the withdrawal rate (dip rate) using the new dip coater.

Additional coatings using SR-125 silicone[†] and urethane^{††} in place of DC-808 silicone binder were prepared, applied and measured in a similar manner. These data are shown in Table 2. All of the coatings from the previous program are consistent with the coatings from the current program except the initial replicate coatings using the urethane binder. Urethane coatings prepared later compare well with those from the previous program. The reason for the high emittance value for the first attempted

* Pigment, Ferro Corp., Cleveland, OH.

** Silicone Binder, Dow Corning Corp., Midland, MI.

† General Electric Co., Waterford, NY.

†† Deft Chemical Co., Irvine, CA.

Table 1. COMPARATIVE OPTICAL PROPERTIES OF 30 PVC F-6331/DC-808
COATINGS FROM PREVIOUS AND CURRENT PROGRAMS

Dip Rate, In./Min.	Coating Solids, % by Wt.	Previous		Current	
		α	ϵ	α	ϵ
2	30	0.90	0.11	0.88	0.09
		0.91	0.18	0.89	0.12
	29	0.91	0.13	0.88	0.09
		0.91	0.15	0.88	0.10
3	28	0.89	0.12	0.88	0.11
		0.91	0.18	0.89	0.12
	27	0.90	0.13	0.88	0.09
		0.91	0.16	0.88	0.10
4	26	0.90	0.21	0.89	0.11
		0.92	0.24	0.87	0.09
	25	0.92	0.17	0.87	0.08
		0.92	0.17	0.88	0.10
5	24	0.91	0.20	0.89	0.11
		0.91	0.19	0.89	0.11
	23	0.90	0.22	0.88	0.09
		0.91	0.16	0.88	0.10

Table 2. OPTICAL PROPERTIES OF VARIOUS SOLAR PAINT COATINGS DIP APPLIED AT
2 INCHES/MINUTE AND 28 PERCENT SOLIDS FROM PREVIOUS & CURRENT PROGRAMS

Coating Description	Previous		Current	
	α	ϵ	α	ϵ
30-PVC F-6331/SR-125	0.90	0.12	0.90	0.13
30 PVC F-6331/Urethane	0.89	0.10	0.91	0.22
30 PVC F-6331/DC-808	0.90	0.12	0.89	0.12

replication is not apparent at this time.

Variations among replicate coated samples can be seen in Table 3 for coatings prepared in the current program. Larger inconsistencies in emittance values are more evident for samples coated at 1 in./min. and 5 in./min. than for other dip coating rates. It seems that the 1 in./min. and 5 in./min. rates are the low and high limit for the new dip coating equipment.

Pigment Volume Concentration (PVC) and Percent Solids Optimization

A comparative study was performed to optimize optical properties with coating PVC and solid content varying as well as dip coating rate. All of the coatings were based on the F-6331/SR-125 combination. Solar absorptance and emittance were measured and the data recorded in Tables 3 to 8.

It can be seen from Tables 3 to 8 that as PVC decreases (holding dip rate and solids content constant), the emittance increases. This is due to increasing concentration of binder which is absorbing in the infrared. Small differences in solar absorptance can be seen with changes in PVC, but no pattern is evident and therefore, the changes are considered random.

Further examination of the optical data in Tables 3 to 8 shows increased emittance for increased dip coating rate. This is due to increasing coating film thickness with increased dip coating rates. A similar phenomenon occurs with increased coating solids.

Solar selective paint coatings developed to date can be considered as typically providing $\alpha = 0.90$ and $\epsilon = 0.10$.

At 30 PVC the conditions for achieving coatings with these optical characteristics are rather broadly defined as shown in Table 3. If a dip rate of 3 in./min. is selected as the processing condition, it can be seen that a coating with 26

TABLE 3 OPTICAL PROPERTIES OF 30 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

DIP RATE, In/Min	COATING SOLIDS (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE (α) AND TOTAL EMITTANCE (ε)																										
	30%			29%			28%			27%			26%			25%			24%			23%			22%		
	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε
1	1	.91	.16	11	.91	.12	21	.91	.11	31	.90	.10	11	.91	.10	51	.90	.06	61	.89	.06	71	.89	.05	81	.88	.05
	2	.91	.12	12	.91	.10	22	.91	.09	32	.90	.08	42	.90	.08	52	.90	.06	62	.89	.05	72	.88	.05	82	.88	.04
2	3	.91	.17	13	.91	.14	23	.91	.11	33	.90	.10	43	.90	.09	53	.90	.06	63	.89	.06	73	.89	.06	83	.89	.06
	4	.92	.16	14	.91	.16	24	.91	.12	34	.90	.10	44	.91	.10	54	.90	.06	64	.89	.06	74	.89	.06	84	.89	.06
3	5	.92	.22	15	.91	.19	25	.91	.14	35	.90	.13	45	.91	.12	55	.90	.07	65	.90	.08	75	.90	.08	85	.90	.08
	6	.92	.21	16	.91	.19	26	.91	.15	36	.90	.12	46	.91	.11	56	.90	.07	66	.90	.08	76	.90	.07	86	.90	.07
4	7	.92	.28	17	.92	.24	27	.91	.19	37	.91	.17	47	.91	.14	57	.91	.10	67	.91	.10	77	.90	.07	87	.90	.07
	8	.92	.28	18	.91	.25	28	.91	.18	38	.91	.17	48	.91	.13	58	.91	.10	68	.90	.09	78	.90	.09	88	.90	.07
5	9	.92	.33	19	.92	.33	29	.91	.24	39	.91	.22	49	.91	.17	59	.91	.13	69	.91	.12	79	.90	.10	89	.90	.09
	10	.92	.35	20	.92	.32	30	.91	.27	40	.91	.24	50	.91	.18	60	.91	.15	70	.91	.14	80	.91	.12	90	.91	.10

TABLE 4 OPTICAL PROPERTIES OF 28 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

DIP RATE, In/Min	COATING SOLIDS (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE (α) AND TOTAL EMITTANCE (ε)																																
	30%			29%			28%			27%			26%			25%			24%			23%			22%			21%			20%		
	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε			
1	1	.92	.32	11	.92	.30	21	.92	.26	31	.91	.22	41	.91	.19	51	.91	.16	61	.90	.11	71	.90	.10	81	.91	.10	91	.89	.07	101	.88	.06
	2	.92	.28	12	.92	.23	22	.92	.20	32	.91	.18	42	.91	.15	52	.90	.13	62	.91	.11	72	.90	.09	82	.90	.07	92	.89	.06	102	.88	.05
2	3	.93	.36	13	.92	.30	23	.92	.28	33	.92	.28	43	.91	.21	53	.91	.18	63	.92	.14	73	.91	.11	83	.91	.10	93	.90	.08	103	.90	.08
	4	.93	.36	14	.93	.30	24	.92	.28	34	.92	.27	44	.91	.20	54	.91	.17	64	.91	.14	74	.91	.12	84	.91	.12	94	.90	.08	104	.90	.08
3	5	.93	.40	15	.92	.34	25	.93	.33	35	.92	.33	45	.92	.26	55	.91	.22	65	.91	.17	75	.91	.15	85	.92	.14	95	.91	.10	105	.90	.09
	6	.93	.40	16	.92	.34	26	.93	.33	36	.92	.33	46	.92	.26	56	.91	.21	66	.92	.18	76	.92	.14	86	.92	.13	96	.91	.10	106	.90	.08
4	7	.93	.42	17	.93	.38	27	.93	.36	37	.92	.36	47	.92	.30	57	.92	.25	67	.92	.24	77	.92	.19	87	.92	.15	97	.92	.12	107	.91	.11
	8	.93	.42	18	.93	.38	28	.93	.37	38	.93	.37	48	.91	.30	58	.92	.24	68	.92	.23	78	.92	.18	88	.92	.16	98	.91	.13	108	.91	.11
5	9	.94	.44	19	.93	.40	29	.93	.39	39	.92	.41	49	.92	.34	59	.92	.29	69	.92	.28	79	.92	.22	89	.92	.19	99	.92	.15	109	.91	.13
	10	.94	.44	20	.93	.40	30	.93	.39	40	.93	.40	50	.92	.34	60	.92	.28	70	.92	.31	80	.92	.22	90	.92	.21	100	.92	.14	110	.92	.13

TABLE 5 OPTICAL PROPERTIES OF 26 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

DIP RATE, In/Min	COATING SOLIDS (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE (α) AND TOTAL EMITTANCE (ε)																																
	30%			29%			28%			27%			26%			25%			24%			23%			22%			21%			20%		
	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε			
1	1	.92	.32	11	.91	.30	21	.92	.26	31	.92	.20	41	.91	.20	51	.91	.19	61	.92	.14	71	.90	.12	81	.91	.08	91	.90	.09	101	.89	.07
	2	.92	.31	12	.91	.24	22	.92	.20	32	.92	.17	42	.91	.16	52	.91	.14	62	.90	.10	72	.90	.09	82	.90	.07	92	.90	.07	102	.89	.06
2	3	.92	.37	13	.92	.32	23	.92	.28	33	.92	.23	43	.92	.21	53	.92	.19	63	.91	.14	73	.91	.11	83	.90	.08	93	.90	.07	103	.90	.07
	4	.92	.37	14	.92	.32	24	.92	.28	34	.92	.24	44	.91	.20	54	.92	.18	64	.91	.14	74	.91	.12	84	.90	.09	94	.90	.09	104	.90	.07
3	5	.92	.39	15	.92	.36	25	.93	.36	35	.92	.27	45	.92	.25	55	.92	.22	65	.92	.16	75	.92	.15	85	.91	.12	95	.90	.09	105	.90	.07
	6	.92	.40	16	.93	.36	26	.93	.34	36	.92	.26	46	.92	.25	56	.92	.22	66	.92	.19	76	.92	.15	86	.91	.13	96	.90	.09	106	.90	.08
4	7	.92	.42	17	.92	.39	27	.93	.36	37	.93	.32	47	.92	.31	57	.92	.28	67	.92	.21	77	.92	.18	87	.92	.14	97	.91	.12	107	.91	.09
	8	.92	.42	18	.92	.38	28	.93	.37	38	.92	.32	48	.92	.31	58	.93	.28	68	.92	.21	78	.92	.18	88	.92	.15	98	.91	.11	108	.91	.10
5	9	.93	.43	19	.92	.42	29	.93	.41	39	.93	.35	49	.92	.34	59	.93	.32	69	.92	.27	79	.92	.21	89	.92	.18	99	.91	.13	109	.91	.11
	10	.92	.42	20	.93	.41	30	.93	.41	40	.92	.35	50	.92	.34	60	.93	.32	70	.92	.27	80	.92	.21	90	.92	.18	100	.92	.15	110	.91	.11

TABLE 6 . OPTICAL PROPERTIES OF 24 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

DIP RATE, In/Min	COATING SOLIDS (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE (α) AND TOTAL EMITTANCE (ε)																																
	30%			29%			28%			27%			26%			25%			24%			23%			22%			21%			20%		
	ID	α	ε	ID	α	ε	ID	α _s	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε			
1	1	.92	.34	11	.91	.29	21	.91	.26	31	.91	.22	41	.92	.18	51	.91	.16	61	.90	.13	71	.90	.10	81	.90	.10	91	.89	.08	101	.88	.07
	2	.92	.27	12	.91	.20	22	.91	.21	32	.91	.16	42	.90	.14	52	.91	.13	62	.90	.09	72	.90	.09	82	.89	.08	92	.88	.06	102	.87	.05
2	3	.92	.31	13	.92	.26	23	.91	.24	33	.92	.19	43	.91	.17	53	.92	.15	63	.90	.11	73	.90	.10	83	.89	.08	93	.88	.07	103	.87	.05
	4	.92	.31	14	.92	.26	24	.92	.24	34	.91	.19	44	.91	.17	54	.92	.15	64	.90	.12	74	.90	.10	84	.90	.10	94	.89	.08	104	.88	.06
3	5	.92	.36	15	.92	.30	25	.92	.27	35	.92	.23	45	.92	.20	55	.92	.17	65	.91	.14	75	.90	.12	85	.90	.09	95	.90	.10	105	.88	.06
	6	.92	.34	16	.92	.30	26	.92	.26	36	.91	.23	46	.91	.22	56	.91	.17	66	.91	.13	76	.91	.14	86	.90	.10	96	.89	.10	106	.88	.07
4	7	.92	.39	17	.92	.34	27	.92	.31	37	.92	.27	47	.92	.23	57	.91	.21	67	.91	.16	77	.91	.16	87	.91	.13	97	.90	.11	107	.89	.09
	8	.92	.38	18	.92	.34	28	.92	.31	38	.92	.27	48	.92	.24	58	.91	.21	68	.91	.17	78	.91	.16	88	.91	.13	98	.90	.11	108	.89	.08
5	9	.92	.42	19	.92	.38	29	.92	.35	39	.92	.33	49	.92	.28	59	.91	.24	69	.91	.20	79	.91	.17	89	.91	.15	99	.90	.13	109	.90	.10
	10	.92	.41	20	.92	.38	30	.92	.35	40	.92	.33	50	.92	.28	60	.91	.24	70	.91	.21	80	.91	.17	90	.91	.15	100	.90	.13	110	.89	.10

TABLE 7 OPTICAL PROPERTIES OF 22 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

COATING SOLIDS. (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE. (α) AND TOTAL EMITTANCE (ε)																																	
DIP RATE, In/Min	30%			29%			28%			27%			26%			25%			24%			23%			22%			21%			20%		
	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε			
1	1	.92	.34	11	.91	.32	21	.91	.26	31	.91	.22	41	.91	.22	51	.91	.20	61	.91	.16	71	.90	.12	81	.90	.13	91	.89	.10	101	.88	.08
	2	.92	.31	12	.92	.30	22	.91	.22	32	.92	.16	42	.91	.19	52	.91	.15	62	.91	.14	72	.90	.10	82	.89	.11	92	.88	.06	102	.88	.06
2	3	.93	.33	13	.92	.33	23	.91	.26	33	.92	.22	43	.91	.21	53	.92	.20	63	.91	.15	73	.90	.13	83	.90	.11	93	.86	.06	103	.87	.06
	4	.92	.32	14	.92	.31	24	.91	.24	34	.92	.19	44	.91	.19	54	.91	.18	64	.91	.14	74	.90	.11	84	.90	.11	94	.87	.06	104	.88	.06
3	5	.93	.36	15	.92	.34	25	.92	.29	35	.92	.26	45	.92	.23	55	.92	.20	65	.91	.16	75	.91	.14	85	.90	.11	95	.89	.09	105	.88	.07
	6	.92	.37	16	.92	.34	26	.92	.30	36	.92	.25	46	.92	.23	56	.91	.21	66	.91	.16	76	.91	.14	86	.90	.12	96	.88	.09	106	.88	.07
4	7	.93	.40	17	.92	.38	27	.92	.32	37	.92	.29	47	.92	.28	57	.92	.23	67	.91	.19	77	.92	.17	87	.90	.14	97	.90	.11	107	.89	.09
	8	.93	.40	18	.92	.38	28	.92	.33	38	.92	.30	48	.92	.28	58	.92	.25	68	.91	.20	78	.91	.16	88	.91	.14	98	.89	.11	108	.89	.09
5	9	.93	.42	19	.92	.41	29	.92	.36	39	.93	.34	49	.92	.32	59	.92	.27	69	.91	.23	79	.92	.20	89	.91	.16	99	.90	.13	109	.90	.11
	10	.93	.42	20	.92	.41	30	.92	.37	40	.93	.34	50	.93	.31	60	.92	.27	70	.91	.22	80	.92	.18	90	.91	.16	100	.90	.14	110	.90	.11

TABLE 8 OPTICAL PROPERTIES OF 20 PVC F-6331/SR-125 SILICONE SELECTIVE PAINT COATINGS

DIP RATE, In/Min	COATING SOLIDS (% BY WT), IDENTIFICATION (ID), SOLAR ABSORPTANCE (α) AND TOTAL EMITTANCE (ε)																																
	30%			29%			28%			27%			26%			25%			24%			23%			22%			21%			20%		
	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε	ID	α	ε			
1	1	.92	.38	11	.91	.34	21	.90	.27	31	.91	.24	41	.91	.27	51	.90	.24	61	.90	.18	71	.90	.14	81	.90	.14	91	.89	.11	101	.87	.09
	2	.92	.32	12	.91	.25	22	.91	.24	32	.91	.19	42	.91	.21	52	.90	.14	62	.90	.15	72	.90	.12	82	.89	.12	92	.88	.08	102	.88	.06
2	3	.92	.35	13	.92	.31	23	.91	.28	33	.91	.23	43	.91	.22	53	.91	.18	63	.90	.17	73	.90	.12	83	.89	.12	93	.88	.10	103	.87	.07
	4	.92	.35	14	.92	.30	24	.91	.26	34	.91	.22	44	.91	.21	54	.90	.16	64	.89	.15	74	.90	.12	84	.89	.11	94	.89	.09	104	.87	.07
3	5	.92	.39	15	.92	.35	25	.92	.32	35	.91	.26	45	.92	.25	55	.91	.22	65	.90	.17	75	.90	.15	85	.90	.12	95	.89	.10	105	.87	.08
	6	.92	.39	16	.92	.34	26	.92	.32	36	.91	.26	46	.92	.26	56	.91	.22	66	.90	.18	76	.90	.14	86	.90	.13	96	.90	.10	106	.88	.08
4	7	.92	.41	17	.92	.38	27	.92	.36	37	.92	.30	47	.92	.29	57	.91	.24	67	.91	.20	77	.91	.17	87	.91	.15	97	.90	.13	107	.89	.10
	8	.92	.42	18	.92	.38	28	.92	.36	38	.92	.30	48	.92	.30	58	.92	.25	68	.91	.20	78	.91	.17	88	.91	.16	98	.91	.16	108	.89	.10
5	9	.92	.43	19	.92	.42	29	.92	.39	39	.92	.35	49	.92	.34	59	.92	.30	69	.91	.24	79	.91	.20	89	.91	.18	99	.91	.18	109	.90	.13
	10	.92	.43	20	.93	.41	30	.92	.39	40	.92	.35	50	.92	.33	60	.92	.29	70	.91	.25	80	.92	.20	90	.91	.18	100	.91	.17	110	.91	.14

percent solids or less is required to achieve these optical properties. From Tables 4 to 8 it can be seen that when formulations with 28 to 20 PVC are used, 21 percent solids or less is required to achieve these optical properties. From these data, it would appear that there is a significant advantage in using coatings with 30 PVC instead of 28 PVC as far as latitude in processing is concerned. However, further testing of the coatings for abrasion resistance shows that 30 PVC coatings are significantly less durable than coatings with 20 to 28 PVC. (See page 29.)

New Pigments

One of the goals of this development effort is to evaluate new pigments which could provide a backup for the F-6331 material either to replace it altogether or to be used with it to enhance its properties. This effort primarily involves three manufacturers' products as shown in Table 9.

The prime pigment candidate F-6331 comes from Ferro. Variations of this material with higher absorptance (01-114-8 extra black) and differences in particle size (IP-671A, IP-671B) have been evaluated. Virtually all of the pigments from Harshaw were evaluated in the previous program using spray coating techniques. Sufficient material was supplied for the current program to evaluate them using dip coating techniques. The CrO_2 from Dupont is a material of needle (acicular) shape having magnetic poles at opposite ends of about $0.1 \mu\text{m} \times 0.6 \mu\text{m}$ size and is capable of being magnetically oriented.

Test coatings using each of these materials have been prepared by dip coating, and evaluated. The best optical properties from coatings using these pigments is shown in Table 10.

The CrO_2 pigment could not be applied by dip coating due to the behavior of the pigment as a permanent dipole. The particle-to-particle attraction of acicular CrO_2 was so strong that substrate wetting would not take place by dip coating techniques.

Table 9. PIGMENTS SELECTED FOR EVALUATION

Manufacturer's Name	Trade Designation	Chemical Composition	Status
Harshaw	L-4815-12-1	CuFeMn Oxides	Completed
	L-4815-12-1	CuFeMn Oxides	Completed
	L-4815-12-3	CuFeMn Oxides	Completed
	L-4815-12-4	CuFeMn Oxides	Completed
	Meteor 7890	CuCr Oxides	Completed
Ferro	F-6331 (01-114-8) Extra Black	FeMnCu Oxides	Completed
	V-302	CrCu Oxides	Completed
	V-717	MnCuFe Oxides	Completed
	F-6331 (IP-671A)	FeMnCu Oxides	Completed
	F-6331 (IP-671B)	FeMnCu Oxides	Completed
Dupont	S-6	CrO ₂	In Process

Table 10. BEST OPTICAL PROPERTIES TO DATE FOR 30 PVC SELECTIVE
PAINT COATINGS USING VARIOUS PIGMENTS AND SILICONE BINDERS

Pigment	Binder	Dip Rate, In/Min	Solids, % by Wt.	α	ϵ
L-4815-12-1	DC-808	-	-	-	-
L-4815-12-2	DC-808	10	30	0.70	0.18
L-4815-12-3	DC-808	10	30	0.73	0.15
L-4815-12-4	DC-808	5	29	0.86	0.29
Meteor 7890	DC-808	5	28	0.88	0.16
Meteor 7890	SR-125	5	30	0.87	0.16
F-6331 (01-114-8)	DC-808	2	24	0.90	0.11
F-6331 (01-114-8)	SR-125	2	24	0.90	0.08
V-302	DC-808	4	26	0.81	0.12
V-717	DC-808	4	27	0.57	0.10
F-6331 (1P-671A)	SR-125	1	25	0.92	0.09
F-6331 (1P-671B)	SR-125	2	22	0.90	0.07
F-6331 Standard Matl	SR-125	4	25	0.91	0.10
F-6331					
S-6	DC-808	-	-	-	-

This area of development will be further pursued. Harshaw is attempting to reduce the particle size of their materials at our request. Attempts will be made to apply coatings containing CrO_2 by techniques other than dip coating. Previous work with coatings containing CrO_2 show that the pigment can be oriented vertical to the substrate by a magnetic field. This technique will be used to develop a light trap effect to alter optical properties.

New Binders

Both SR-125 and DC-808 silicones have been used successfully as binders for solar selective paint coatings and offer two sources. Additional work with binder materials was considered advantageous to minimize processing cost and improve the optical and durability properties. The aliphatic urethane binder previously evaluated requires the addition of a catalyst to cure. This reduces the useful life of the coating to be impractical for dip coating applications but allows the material to cure at room ambient temperatures. Although not as thermally stable as the silicones, the aliphatic urethane offers a significant advantage in application methods such as spray coating which do not require a long shelf life. In addition to this, urethane materials would be expected to have better abrasion resistance than silicones.

Additional binders were selected as shown in Table 11 and are in various stages of evaluation. Silicones from Dow Corning have been measured for transmittance in the solar region. The silicones from General Electric have not been received. The two-component aliphatic urethane from Deft Chemical meets the requirements of MIL-C-83286 and is being used in various experimental paint coatings.

Table 11. BINDERS SELECTED FOR EVALUATION

Chemical Type	Manufacturer's Name	Trade Designation	Status
Silicones	Dow Corning	DC-804	In Process ↓
		DC-805	
		DC-806	
		DC-840	
		DC-62230	
	General Electric	SR-82	Not Started ↓
		SR-112	
		SR-141	
		SR-182	
		SR-240	
		SR-422	
		SR-6777	
Urethane	DEFT	MIL-C-83286	In Process ↓
		03-X-59	

THICKNESS INSENSITIVE COATINGS

Coatings developed to date have depended on the aluminum substrate and good thickness control to achieve low emittance. Thickness control by dip coating techniques is no longer a problem. The usefulness of the coating material and technique is somewhat limited. A coating independent of either thickness or substrate offers considerably wider applicability and is thus more versatile. It was believed that incorporation of highly reflective metallic particles in the existing solar paint might accomplish this.

A number of aluminum flake pigments were selected to provide a wide range of particle sizes. The 30 PVC F-6331/SR-125 solar selective paint coating was selected as the starting coating. Combinations of the 30 PVC F-6331/SR-125 coating and aluminum flake were made so that from 10 to 30 percent flake aluminum was used. One set of samples was prepared by spraying and the other by brushing. Coatings were applied so that thick coatings resulted. Solar absorptance and emittance were measured and the data recorded in Table 12.

Spray coated substrates showed decreased absorptance and emittance with increased aluminum flake concentration as shown in Table 12. This effect is minimized with coatings containing 2468, the largest aluminum flake. The coating containing 30 percent 2468 aluminum flake showed $\alpha = 0.90$ and $\epsilon = 0.31$. Replicate samples verified these data.

Brush coated substrates showed less dramatic effects from increasing the concentration and size of aluminum flake. Again however, coatings containing 2468 showed better properties than those with smaller flake. The coating containing 30 percent 2468 aluminum flake showed $\alpha = 0.90$ and $\epsilon = 0.48$ when brush coated.

TABLE 12. OPTICAL PROPERTIES OF 30 PVC F-6331/SR-125
COATING WITH ALUMINUM FLAKE SPRAY AND BRUSH
APPLIED

TYPE	ALUMINUM FLAKE ¹	% BY WT	Spray		Brush	
	RELATIVE SIZE		α	ϵ	α	ϵ
6205	Small	10	.90	.65	.90	.60
		15	.85	.60	.88	.56
		20	.78	.54	.85	.53
		25	.67	.49	.77	.49
		30	.58	.45	.73	.47
6230	Medium	10	.84	.54	.91	.65
		15	.75	.48	.90	.59
		20	.64	.42	.89	.59
		25	.54	.36	.89	.56
		30	.43	.32	.83	.50
6231	Medium	10	.88	.60	.89	.54
		15	.84	.54	.87	.55
		20	.79	.51	.89	.59
		25	.68	.44	.85	.49
		30	.66	.42	.85	.53
6091	Large	10	.88	.61	.89	.50
		15	.84	.54	.89	.59
		20	.73	.45	-	-
		25	.65	.41	.85	.51
		30	.57	.35	.85	.51
2468	Extra Large	10	.93	.57	.91	.55
		15	.92	.52	.91	.55
		20	.92	.44	.90	.45
		25	.91	.39	.90	.48
		30	.90	.31	.90	.48

¹ Aluminum Company of America, Pittsburgh, PA

Figure 1 compares the absorptance/emittance response of 30 PVC F-6331/SR-125 coatings containing small aluminum flake (6230) with coatings containing large aluminum flake (2468). It can be seen that there is very little decrease in solar absorptance of coatings with increasing concentration of the large aluminum flake 2468. Decreasing solar absorptance occurs with increasing concentration of small aluminum flake 6230.

The spectral reflectance of the coatings containing 2468 flake aluminum applied by spray and brush shown in Figures 2 and 3 respectively. Increases in the aluminum flake content result in increased reflectance in the infrared.

These tests demonstrated the feasibility of using low emissivity metallic particles in the standard coating to eliminate the need for thickness control and low substrate emittance.

IMPROVEMENT OF ADHESION AND ABRASION RESISTANCE

The effect of PVC on the optical properties of solar selective paint coatings had previously been reported but the effect on abrasion resistance was not known. A number of observations of the 30 PVC F-6331/SR-125 coating indicated a problem in its resistance to handling.

Solar selective paint coatings with 20-30 PVC F-6331/SR-125 were prepared by dip coating. Absorptance and emittance were measured before and after exposure to abrasion. The abrasion test consisted of rubbing cheesecloth over the coated surfaces for 1750 cycles. The cheesecloth was in layers over a stiff bristle brush under 28.4 g/cm^2 (4.4 oz./in^2). The results are shown in Table 13.

There appears to be a dramatic difference in abrasion resistance between the 30 PVC coating and any of the other coatings based on the data in Table 13. At 30 PVC the solar absorptance decreases from $\alpha = 0.90$ to $\alpha = 0.66$ while 20-28 PVC coatings decrease from $\alpha = 0.90$ to $\alpha = 0.85$. None of the coatings showed

FIGURE 1. OPTICAL PROPERTIES OF SPRAY APPLIED 30 PVC F-6331/SR-125 WITH VARIOUS CONCENTRATIONS OF ALCOA 2468 AND 6230 ALUMINUM FLAKE

FIGURE 2. SPECTRAL REFLECTANCE OF SPRAY APPLIED 30 PVC F-6331/SR-125 WITH VARIOUS CONCENTRATIONS OF ALCOA 2468 ALUMINUM FLAKE.

FIGURE 3. SPECTRAL REFLECTANCE OF BRUSH APPLIED 30 PVC F-6331/SR-125 WITH VARIOUS CONCENTRATIONS OF ALCOA 2468 ALUMINUM FLAKE.

TABLE 13. ABRASION RESISTANCE OF F-6331/SR-125
SOLAR SELECTIVE COATINGS (1750 CYCLES)

PVC	BEFORE		AFTER	
	α	ϵ	α	ϵ
30	0.90	0.08	0.66	0.07
28	0.92	0.14	0.85	0.15
26	0.91	0.12	0.86	0.12
24	0.90	0.09	0.85	0.10
22	0.90	0.11	0.86	0.13
20	0.90	0.12	0.86	0.14

dramatic changes in emittance resulting from abrasion. The significant decrease in abrasion resistance may indicate the presence of excess pigment for the silicone binder. Further testing with the urethane binder will be pursued in an attempt to identify PVC limits for this combination. The data to date shows that coatings between 20-28 PVC provide better abrasion resistance than do coatings with higher concentrations of pigment.

SECTION 3

BLACK CHROME COATINGS

INTRODUCTION

The development of black chrome coatings includes two major areas. The first area is to study the effects of bath composition on coating properties. This is primarily to improve the thermal stability of black chrome for high temperature (300°C-400°C) applications, and to determine the concentration limits of bath components to provide a bath control guide for platers. The second area is to optimize coating/substrate systems based on cost and durability. This is basically for flat plate collector applications. Black chrome with different intermediate metallic coatings on aluminum, steel and aluminum foil are being studied. Efforts for the first six months have concentrated on the study of the effects of bath composition. Black chrome on aluminum has just begun.

MEASUREMENTS AND TESTS

Optical Measurements

The solar absorptance was measured with a Gier-Dunkle MS-251 solar reflectometer. The emittance at 300°C was measured with a Gier-Dunkle DB-100 infrared reflectometer with a sapphire filter and then converted into the total hemispherical emittance, $\epsilon_{t,H}$ (300°C), using the calibration equation reported by Pettit (Reference 2). The emittance at 100°C was obtained from the Gier-Dunkle DB-100 infrared reflectometer without a filter.

Thermal Tests

Black chrome samples for high temperature applications were subjected to temperatures of 350°C and 400°C in air. The stability was determined by comparing the optical properties (α , ϵ) of the coating before and after the high temperature tests.

Environmental Tests

Two types of environmental tests were used, accelerated humidity test and weathering test. The humidity test used is the MIL-STD-

810B, Method 507, Procedure I. This test consists of a thermal and humidity cycle, from room temperature to 71°C (160°F) at 95 percent relative humidity and from 71°C to room temperature at greater than 85 percent RH, over a 24-hour period. This is one of the most severe accelerated environmental tests. The test conditions impose a vapor pressure on the samples that forces moisture penetration and migration.

The accelerated weathering test used is the Federal Test Method Standard (FTMS) 141A, Method 6152. This test consists of 102 minutes of carbon arc light without water at $145^{\circ}\text{F} \pm 5^{\circ}\text{F}$, and 18 minutes of light and water spray. The light is filtered to produce radiation similar to that of June sunlight at noon. The water spray is deionized or distilled water finely sprayed such that it wets the entire surface on impact. A two day rest period after 5 days of testing is not used although this rest period is specified in the FTMS.

EFFECTS OF BATH COMPOSITION ON COATING PROPERTIES

An extensive study was performed to determine, quantitatively the critical components of the black chrome bath, and the effect of each component on coating durability, at temperatures of $350\text{-}400^{\circ}\text{C}$.

The plating process currently being used is the Harshaw ChromOnyx Black Chromium process (Reference 3), the critical components of which have been identified as chromic acid, trivalent chromium, acetic acid, and ferric ion (Reference 4). Each of these components was varied and the resultant coatings were subjected to temperatures of 350°C and 400°C . The stability was determined by comparing the optical properties of the coating (α , ϵ) before and after the high temperature tests. Some samples were also subjected to environmental tests and evaluated in the same manner.

Conventional Bath Composition

According to a Harshaw Technical Bulletin (Reference 5) a typical formulation used in a black chrome bath is as shown in Table 14.

Table 14. Typical Black Chrome Bath Formulation

Chromic Acid	340 g/l
ChromOnyx Make-Up Addition Agent	270 ml/l (27 vol. %)
ChromOnyx MR Addition Agent	26 g/l
Barium Hydrate or Carbonate	11 g/l

Analytical results obtained by Sowell (Reference 6) on conventional black chrome baths are shown in Table 15.

Analytical Methods

Methods of analysis for each bath component are described in the Appendix which is a reprint of the Sandia analytical procedures reported by Erickson (Reference 4). The procedures for chromic acid and addition agent (or acetic acid) analysis are essentially the procedures recommended by Harshaw. Cr^{+3} is determined by the difference in Cr^{+6} content between the original bath and after all Cr^{+3} has been oxidized by ammonium persulfate. Consequently, one large number is subtracted from another large number producing a relatively large error of approximately 2 g/l Cr^{+3} . However, the methods are in general reliable and adequate for the purpose of black chrome bath control. "Round Robin" samples taken from the same bath by Sandia were sent to Honeywell and Harshaw and analyzed by the procedures used by the participating laboratories. The results are shown in Table 16. Reasonable agreement among laboratories confirms the reliability of the methods.

Effect of Cr^{+3} Concentration

The Cr^{+3} concentration was varied from 8 g/l to 16 g/l. Analyzed results for these baths are shown in Table 17.

It was possible to produce coatings with high α at all concentrations, but it must be noted that the $\epsilon_{t,H}(300^\circ\text{C})$ increased as much as 0.09 as the concentration was lowered to $\text{Cr}^{+3} = 8$ g/l. Table 18 shows the initial α and ϵ and the thermal test results.

Coatings produced in baths of lower Cr^{+3} concentrations are significantly more stable under thermal testing than those produced in a standard bath ($\text{Cr}^{+3} = 16$ g/l). The standard bath coating degraded from $\alpha = 0.95$ to $\alpha = 0.82$ after 1000 hours at 400°C whereas the $\text{Cr}^{+3} = 8$ g/l coating showed an α decrease of only 4% (from $\alpha = 0.95$ to $\alpha = 0.91$) after the same test. In all cases the emittance ($\epsilon_{t,H}(300^\circ\text{C})$) decreased with increased hours

Table 15. Typical ChromOnyx Black Chrome Bath Composition*

Used in Bath	Found	
	Bath 1	Bath 2
CrO ₃ , 340 g/l	331	335
Make-Up Additive, 270 ml/l (27 vol. %)	27	27
MR Additive, 26 g/l	-	-
Cr ⁺³ (g/l)	16	18
Fe (g/l)	8	8

*Reference 6

Table 16. Round Robin Results: ChromOnyx Black
Chrome Bath

Component	Sandia	Honeywell	Harshaw (Cleveland)	Harshaw (Los Angeles)
CrO ₃ (g/l)	324	326	327	317
Make-Up Additive (vol. %)				
a) Harshaw Eq. (Ref. 5)	-	23.9	23.1	24.9
b) Sandia Eq. (Appendix)	26	24.6	-	-
Cr ⁺³ (g/l)	13.2	14.8	13.8	12.9
Fe (g/l)	10.4	10.5	9.5	10.2

Table 17. Analytical Results of Trivalent Chromium Variations of Black Chrome Plating Solution

Components	Trivalent Chromium Variations		
	16 g/l	12 g/l	8 g/l
Total Acid (N)	10.02	9.94	10.13
Make-Up Addition			
Agent (Vol. %)	26.9	25.8	26.2
Chromic Acid (g/l)	316.1	320.3	327.0
Trivalent Chrome (g/l)	15.6	11.5	8.6
Ferric Ions (g/l)	7.6	7.5	8.3

Table 18. Effects of Trivalent Chromium Concentration on Thermal Aging of Electroplated Black Chrome

Cr ⁺³ Concentration	Test Temperature	Test Time (Hr)	α^*	$\epsilon_{t,H}$ (300°C)*	Plating Time
16 g/l	As Plated 350°C	0	0.94	0.15	3.5 min
		150	0.88	0.12	
		1000	0.87	0.11	
	400°C	150	0.83	0.10	
		1000	0.82	0.12	
12 g/l	As Plated 350°C	0	0.95	0.19	3.5 min
		150	0.93	0.16	
		1000	0.93	0.15	
		1250	0.92	0.15	
	400°C	150	0.94	0.14	
		1000	0.90	0.12	
		1250	0.90	0.13	
8 g/l	As Plated 350°C	0	0.95	0.24	3.5 min
		150	0.93	0.19	
		1000	0.92	0.20	
	400°C	150	0.94	0.20	
		1000	0.91	0.18	

All samples plated on bright nickel at 175 amp/ft², 18-30°C.

*Average of 3 samples.

at high temperatures. These results are in agreement with those reported by Sowell and Pettit (Reference 7).

Results from the environmental testing are shown in Table 19. The Cr^{+3} concentration does not significantly alter the coating stability in these tests. Degradation of the coatings in both the humidity and weathering tests, was similar for all Cr^{+3} concentrations with α decreasing 1-3% and $\epsilon_{t,H}(300^\circ\text{C})$ changing also 1-3% after 1000 hours of tests.

Effect of Cr^{+6} (CrO_3) Concentration

The concentrations of Cr^{+6} (as CrO_3) studied ranged from 260 g/l to 390 g/l. Results of bath analysis are shown in Table 20. Thermal aging results are shown in Table 21. Coatings with high solar absorptance ($\alpha = 0.93 - 0.96$) were produced at all levels of Cr^{+6} but the emittance ($\epsilon_{t,H}(300^\circ\text{C})$) was high in the $\text{CrO}_3 = 390$ g/l and $\text{CrO}_3 = 370$ g/l baths.

This component of the bath does not appear to significantly affect the stability of the coatings during thermal testing. The α decreases 2-3% in all of the coatings and, as in the Cr^{+3} variations, the $\epsilon_{t,H}(300^\circ\text{C})$ decreases with increased time at high temperatures. An important note is that all of the Cr^{+6} variations were made holding the Cr^{+3} concentration constant at 8 g/l. This is the Cr^{+3} concentration which produced the most thermally stable coatings in the previously discussed experiments.

Effect of Acetic Acid Concentration

The acetic acid (HAc) concentration was varied from 13% to 38% expressed as volume percent of make-up addition agent. The Cr^{+3} concentration was again held constant at 8 g/l for all baths. The baths compositions are given in Table 22.

Table 19. Effects of Trivalent Chromium Concentration on Environmental Stability of Electroplated Black Chrome

Cr ⁺³ Concentration	Test Type	Test Time (Hr)	α^*	$\epsilon_{t,H}(300^{\circ}\text{C})^*$	Plating Time
16 g/l	-	0	0.94	0.15	3.5 min
		24	0.92	0.14	
		48	0.92	0.14	
		1000	0.91	0.15	
	Weathering	24	0.93	0.15	
		48	0.92	0.14	
		1000	0.91	0.18	
12 g/l	-	0	0.95	0.19	3.5 min
		24	-	-	
		48	-	-	
		1000	0.94	0.18	
	Weathering	24	-	-	
		48	-	-	
		1000	0.93	0.17	
8 g/l	-	0	0.95	0.24	3.5 min
		24	0.95	0.24	
		48	0.95	0.25	
		1000	0.93	0.27	
	Weathering	100	0.93	0.24	
		500	0.93	0.25	

All samples plated on bright nickel at 175 amp.ft², 18-30°C.

*Average of 2 samples.

Table 20. Analytical Results of Chromic Acid Variations of Black Chrome Plating Solution

Components	Chromic Acid Variations				
	390 g/l	370 g/l	330 g/l	290 g/l	260 g/l
Total Acid (N)	11.09	10.90	10.13	9.09	8.60
Make-Up Addition Agent (Vol. %)	24.60	25.80	26.20	24.40	24.90
Chromic Acid (g/l)	386.00	369.00	327.00	287.50	259.00
Trivalent Chrome (g/l)	7.20	7.4	8.6	7.50	8.40
Ferric Ions (g/l)	7.60	8.3	8.3	8.60	7.70
Cr ⁺⁶ /Cr ⁺³	28	26	23	20	16

Table 21. Effects of Hexavalent Chromium Concentration on Thermal Aging of Electroplated Black Chrome

Cr ⁺⁶ (as CrO ₃) Concentration	Cr ⁺⁶ /Cr ⁺³ Ratio	Test Temperature	Test Time (Hr.)	α^*	$\epsilon_{t,H}(300^\circ\text{C})^*$	Plating Time
390 g/l	28	As Plated 350°C	0	0.93	0.32	4.5 min
			150	0.89	0.26	
			1250	0.89	0.27	
		400°C	150	0.91	0.22	
			1250	0.91	0.21	
370 g/l	26	As Plated 350°C	0	0.96	0.27	4.0 min
			150	0.92	0.20	
			1250	0.93	0.22	
		400°C	150	0.94	0.20	
			1250	0.93	0.19	
330 g/l	23	As Plated 350°C	0	0.95	0.24	3.5 min
			150	0.93	0.19	
			1000	0.92	0.20	
		400°C	150	0.94	0.20	
			1000	0.91	0.18	
290 g/l	20	As Plated 350°C	0	0.94	0.19	4.0 min
			150	0.93	0.15	
			1250	0.93	0.16	
		400°C	150	0.94	0.15	
			1250	0.92	0.14	
260 g/l	16	As Plated 350°C	0	0.95	0.21	3.0 min
			150	0.93	0.16	
			1250	0.94	0.18	
		400°C	150	0.93	0.17	
			1250	0.93	0.16	

All samples plated on bright nickel at 175 amp/ft², 18-30°C, Cr⁺³ = 8 g/l.

*Average of 2 samples.

Table 22. Analytical Results of Acetic Acid Variations of Black Chrome Plating Solution

Components	Acetic Acid (Make-Up Additive) Variations				
	38%	30%	26%	22%	13%
Total Acid (N)	11.98	11.06	10.13	9.48	8.34
Make-Up Addition Agent (Vol. %)	37.90	30.40	26.20	21.50	12.5
Chromic Acid (g/l)	338.80	344.60	327.00	324.90	330.70
Trivalent Chrome (g/l)	7.10	6.90	8.60	6.60	6.60
Ferric Ions (g/l)	8.20	7.80	8.30	8.30	7.90

Table 23 shows the results of thermal tests. Except for HAC = 38%, coatings plated at other HAC concentrations were rather stable, with the maximum loss in α being 4% after 1000 hours at 400°C. Contrary to other coatings, the ϵ of HAC = 30% coating increased during the thermal tests. The reason for this is not clear. Based on the data of initial optical properties and thermal stability, the appropriate range of HAC concentration appears to be within 20% to 30%. More samples with HAC concentrations within this range will be prepared and tested to establish a better defined HAC concentration range.

Effect of Fe^{+3} Concentration

The ferric ion (Fe^{+3}) concentration was varied from 4 g/l to 20 g/l in increments of 4 g/l. The standard Fe^{+3} concentration is 8 g/l. The Cr^{+3} concentration was held at 8 g/l for all the baths. The analytical data of the baths are listed in Table 24. The thermal tests results for the coatings are shown in Table 25.

Generally, the optical properties of the resultant coatings are not greatly affected by the Fe^{+3} concentration unless it is very high (e.g. $\text{Fe}^{+3} = 20$ g/l). The coating samples have only been thermally tested for 150 hours at 350°C. Preliminary results indicated that coatings made with all concentrations were stable at 350°C with the loss of α by 1-2% after 150 hours of testing.

It should be noted that the plating break-in period required decreases as the Fe^{+3} concentration increases. For $\text{Fe}^{+3} = 16$ g/l the break-in time is ~ 15 min. which is one half that for $\text{Fe}^{+3} = 8$ g/l, the standard concentration.

Discussion

Because of the number of bath components involved, it was very difficult to maintain the concentrations of the components which were not being varied, at a constant level. In order to assure reliability and validity in the test results, care has been taken to keep the components to be held constant within a critical concentration range which was established from the evaluation of various coatings. Within this critical range,

Table 23. Effects of Acetic Acid Concentration on Thermal Aging of Electroplated Black Chrome

Acetic Acid Concentration	Test Temperature	Test Time (Hr)	α^*	$\epsilon_{t,H}(300^{\circ}\text{C})^*$	Plating Time
38 (% by Volume Addition Agent)	As Plated 350°C	0	0.80	0.10	4.0 min
		18	0.67	0.10	
		275	0.66	0.10	
	400°C	18	0.63	0.12	
		275	0.61	0.08	
30	As Plated 350°C	0	0.89	0.29	3.5 min
		18	0.89	0.35	
		275	0.89	0.38	
	400°C	18	0.89	0.37	
		275	0.89	0.38	
26	As Plated 350°C	0	0.95	0.24	3.5 min
		150	0.93	0.19	
		1000	0.92	0.20	
	400°C	150	0.94	0.20	
		1000	0.91	0.18	
22	As Plated 350°C	0	0.93	0.32	3.5 min
		18	0.92	0.28	
		300	0.94	0.27	
	400°C	18	0.93	0.28	
		300	0.92	0.28	
13	As Plated 350°C	0	0.83	0.30	6.5 min
		18	0.84	0.20	
		275	0.83	0.18	
	400°C	18	0.83	0.21	
		275	0.83	0.17	

All samples plated on bright nickel at 175 amp/ft², 18-30°C, Cr⁺³ = 8 g/l.

*Average of 2 samples.

Table 24. Analytical Results of Ferric Ion Variations of Black Chrome Plating Solution

Components	Ferric Ion Variations				
	4 g/l	8 g/l	12 g/l	16 g/l	20 g/l
Total Acid (N)	10.16	10.13	9.89	10.60	10.20
Make-Up Addition					
Agent (Vol. %)	27.60	26.20	25.5	29.20	27.80
Chromic Acid (g/l)	319.10	327.00	319.50	328.50	319.30
Trivalent Chrome (g/l)	8.40	8.60	7.90	9.30	8.30
Ferric Ion (g/l)	4.40	8.30	11.40	15.30	20.10

Table 25. Effects of Ferric Ion Concentration on Thermal Aging of Electroplated Black Chrome

Fe ⁺³ Concentration	Test Temp.	Test Time (Hr)	α^*	$\epsilon_{t,H}(300^{\circ}\text{C})^*$	Plating Time
4 g/l	As Plated	0	0.95	0.19	3 min.
	350°C	150	0.94	0.18	
8 g/l (STD)	As Plated	0	0.95	0.24	3.5 min.
	350°C	150	0.93	0.19	
12 g/l	As Plated	0	0.94	0.15	3.5 min.
	350°C	150	0.94	0.17	
16 g/l	As Plated	0	0.94	0.15	3.5 min.
	350°C	150	0.92	0.15	
20 g/l	As Plated	0	0.91	0.11	4.5 min.
	350°C	150	0.89	0.11	

All samples plated on bright nickel at 175 amp/ft², 18-30°C, Cr⁺³ = g/l.

*Average of 2 samples.

all coatings produced had similar optical properties and thermal stability.

The most significant improvement in coating thermal stability was achieved by reducing the level of trivalent chromium from 16 g/l to 8 g/l. Chromic acid and ferric ion had little effect on the coating stability, while high levels of acetic acid tended to decrease the stability. Acetic acid also greatly affected the coating optical properties.

To produce coatings with acceptable α and ϵ and also stable at 350°C-400°C, all bath components have to be closely monitored, especially trivalent chrome and acetic acid. The process parameters - current density, time, and temperature - must also be carefully controlled if consistently optimal coatings are to be produced.

Black Chrome on Aluminum

The main purpose of this task is to prepare samples of different black chrome/intermediate metallic layers systems on aluminum substrates for environmental stability testing and cost evaluation. Efforts on this task have just begun.

The coating systems to be studied include:

- 1) Aluminum/Black Chrome
- 2) Aluminum/Zinc Flash/ Black Chrome
- 3) Aluminum/Nickel/Black Chrome
(Ni = $\frac{1}{4}$, $\frac{1}{2}$, 1 mil)
- 4) Aluminum/Zinc Flash/Nickel/Black Chrome
(Ni = $\frac{1}{4}$, $\frac{1}{2}$, 1 mil)
- 5) Aluminum/Zinc Flash/Copper Flash/Nickel/Black Chrome
(Ni = 1/10, $\frac{1}{4}$ mil).

Samples of each of these systems will be delivered to Los Alamos Lab for outdoor exposure tests and will also be tested at Honeywell in the MIL-STD-810B and accelerated weathering chambers to determine their environmental durability.

Preparation of these samples is not straightforward. Aluminum requires special pretreatments to make it receptive to electroplated coatings. In the Aluminum/Nickel/Black Chrome system a process patented by J. Lowery of NASA-MSFC (Reference 8) was used to prepare the aluminum for the nickel plating. This method involves anodic etching of the aluminum in a phosphoric acid bath. It was very difficult to plate the nickel smoothly and evenly over the aluminum surface. Samples with nickel thicknesses of $\frac{1}{4}$, $\frac{1}{2}$ and 1 mil have been prepared, but they all showed parallel ridges over most of the surfaces.

The zinc flash was applied using a non-electroplating, immersion process (Reference 9). Because the immersion time was very short and the coating is very difficult to appraise visually, it was also very difficult to produce an aluminum/zinc/black chrome sample on which there were no imperfections in the black chrome coating. The samples chosen for testing were cut from panels which had the most uniform black chrome coatings.

Samples were also prepared with nickel plated over the zinc flash. The nickel on zinc-plated-aluminum was much smoother than on bare aluminum. The attempt to plate black chrome directly on aluminum was not successful. The preparation of aluminum/zinc/copper/nickel/black chrome is in process.

SECTION 4

FUTURE PLANS

The following future plans are for the next four months.

PAINT COATINGS

Thickness Sensitive Selective Paints

The effect of pigment particle size on optical properties will be verified. The investigation of new pigments and binders will be completed. The foil coating using spray techniques will be investigated. The thermal stability of silicone and urethane binders will be evaluated.

Thickness Insensitive Selective Paints

The mechanism of the dependence of optical properties on the type of aluminum flakes used will be studied. The effects of application techniques on coating optical properties will also be investigated.

Black Chrome Coatings

Better defined acceptable acetic acid concentration range will be established by concentrating the study of HAc variation on the 20-30 vol. % range with finer increments. Effects of coating thickness and plating parameters, including current density and plating time, on coating thermal stability will be studied. The thermal stability, humidity and weathering tests for samples plated with varied black chrome baths will be completed. Coatings surface compositions will be analyzed. Combined environmental testing, including temperature $\geq 250^{\circ}\text{C}$ and moisture and simulated solar radiation, will be conducted.

Preparation of different black chrome/intermediate metallic layers systems on aluminum substrates will be completed. Samples will be tested at Honeywell and delivered to Los Alamos Lab. Different black chrome coating systems on steel, including intermediate layers of copper flash and chrome flash, will also be prepared and evaluated.

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APPENDIX

ANALYTICAL PROCEDURES FOR CHROMONYX BLACK CHROME PLATING SOLUTIONS

Sampling

The important first step, sampling, is done by removing, by pipette, a 20 ml aliquot from the well mixed bath contents, placing the aliquot in a 500 ml volumetric flask, and diluting the aliquot to 500 ml with water. Suitable aliquots are taken from the volumetric flask for each of the following tests:

1. Cr^{+6} as CrO_3 (grams per liter)
2. Cr^{+3} (grams per liter)
3. Make-up addition agent (vol %)
4. Fe (grams per liter)

Chromic Acid

Scope

This method describes the procedure for determining the amount of hexavalent chromium (CrO_3) in a ChromOnyx plating solution.

Apparatus

Burette, 50 ml
Pipette, 10 ml
Flask, Erlenmeyer, 250 ml

Reagents

Ferrous ammonium sulfate - 0.1N, accurately standardized
against Bureau of Standards $\text{K}_2\text{Cr}_2\text{O}_7$

Sulfuric acid, 1:1 - one volume of sulfuric acid is carefully
mixed with one volume deionized water

Phosphoric acid - reagent grade orthophosphoric acid (85%-87%)

Ferroun indicator - tris (1,10-phenanthroline) iron(II) sulfate
solution, 0.025M

Procedure

Transfer, by pipette, 10 ml diluted plating bath solution (20 ml diluted to 500 ml) to a 250 ml Erlenmeyer flask. Add 100 ml deionized water, 15 ml 1:1 sulfuric acid, 5 ml phosphoric acid, and 2 drops ferroin indicator. Titrate the solution with standard ferrous ammonium sulfate to the salmon orange endpoint.

Calculation

$$\text{CrO}_3 \text{ (g/l)} = M \times N \times 83.317$$

where M = ml standard ferrous ammonium sulfate
N = normality of ferrous ammonium sulfate

Scope

This method describes the procedure for determining the amount of trivalent chromium (Cr^{+3}) in a ChromOnyx plating solution.

Apparatus

Hot plate
Burette, 50 ml
Pipette, 10 ml and 2 ml
Flask, Erlenmeyer, 500, with Speedyvap cover
Magnetic stirrer and Teflon stirring bars

Reagents

Ferrous ammonium sulfate - 0.1N, accurately standardized against
Bureau of Standards $\text{K}_2\text{Cr}_2\text{O}_7$

Sulfuric acid - reagent grade, concentrated

Phosphoric acid - reagent grade orthophosphoric acid (85-87%)

Ammonium persulfate - reagent grade

Silver nitrate solution (1%) - 10 grams AgNO_3 are dissolved in
1000 ml deionized water

Hydrochloric acid (25%) - 25 ml concentrated HCl are diluted to
100 ml with deionized water

Procedure

Transfer, by pipette, 10 ml diluted plating solution (20 ml diluted to 500 ml) to a 500 ml Erlenmeyer flask. Add 175 ml dionized water, 8 ml sulfuric acid, and 2 ml silver nitrate solution. Add 5 g ammonium persulfate and a magnetic stirring bar, cover with a Speedyvap and boil 8-10 minutes. Remove from heat and cool for a few minutes. Dilute to about 200 ml with water and add 2 g ammonium persulfate. Boil without a cover for 10 minutes. Add 2 ml 25% HCl and boil for an additional 15 minutes. Cool to room temperature, add 5 ml phosphoric acid, add 2 drops ferroin indicator, and titrate with standard ferrous ammonium sulfate to the salmon endpoint.

Calculation

$$\text{Cr}^{+3} \text{ (grams/liter)} = (M \times N \times 43.33) - (0.52 \times C)$$

where M = ml ferrous ammonium sulfate used

N = normality of ferrous ammonium sulfate

C = grams/liter CrO_3 determined in the CrO_3 analysis

ChromOnyx Make-Up Addition Agent

Scope

This method describes the procedure for determining the amount of ChromOnyx make-up addition agent (or ChromOnyx addition agent when used to make up a bath) in a ChromOnyx plating solution.

Apparatus

Burette, 50 ml

Pipette, 25 ml

Flask, Erlenmeyer, 250 ml

Reagents

Sodium hydroxide - 0.5N, accurately standardized against Bureau of Standards potassium acid phthalate

Phenolphthalein indicator - one gram phenolphthalein is dissolved in 100 ml methanol

Procedure

Transfer, by pipette, 25 ml diluted plating solution (20 ml diluted to 500 ml) to a 250 ml Erlenmeyer flask. Add 100 ml deionized water and several drops phenolphthalein indicator. Titrate with standard 0.5N sodium hydroxide to a strong pink-red endpoint which persists for one minute.

Calculation

$$\text{*Addition agent (vol \%)} = \frac{100}{A} \left[\frac{(M \times N) - C}{50} \right]$$

where A = molarity of pure addition agent (usually near 14)
M = ml of 0.5N sodium hydroxide used
N = normality of standard sodium hydroxide
C = grams/liter CrO_3 determined in the CrO_3 analysis

*Calculation formula provided by Harshaw is:

$$\text{Addition agent (vol \%)} = \text{TA} \times 7.02 - (1.05 \times \text{oz/gal } \text{CrO}_3)$$

where TA = ml NaOH x normality of NaOH

Fe

Scope

This method describes the procedure for determining the amount of iron in a ChromOnyx plating solution.

Apparatus

Burette, 25 ml
Flask, Erlenmeyer, 250 ml
Pipette, 25 ml

Reagents

EDTA solution - 0.01M ethylenediaminetetracetic acid, disodium salt, in deionized water, accurately standardized against primary standard Zn or calcium carbonate

Eriochrome cyanine R indicator - undiluted solid

Procedure

Transfer, by pipette, 25 ml diluted plating solution (20 ml diluted to 500 ml) to a 250 ml Erlenmeyer flask and dilute to

approximately 125 ml with deionized water. Add a small amount of Eriochrome cyanine R--the color should be brownish green. Start a titration with standard EDTA, titrate slowly, but continue until the bright orange endpoint is reached.

Calculation

$$\text{Fe}^{+3} \text{ (grams/liter)} = T \times M \times 55.847$$

where T = ml of EDTA solution used
M = molarity of EDTA solution