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EFFECT OF HEXAVALENT CHROMIUM CONTENT ON
PERFORMANCE OF CHROMATE FILMS

Problem Assignment No. 12-79 under Bureau of Naval Weapons
WEPTASK RRMA 05 010/200 1/ROO7 08 01

A. INTRODUCTION

Reference (a) established a problem assignment to determine the corrosion resistance and other surface phenomena related to chemically treated aluminum alloys used in construction of naval aircraft. The non-uniform performance of chemical conversion coatings as paint bases particularly, has led to the need for investigating the various factors which may contribute to the problem.

Reference (b) refers to these coatings as amorphous, consisting essentially of aluminum and chromium chromates. Reference (c) states that chromate conversion coatings contain chromates both as insoluble compounds and as absorbed or adsorbed soluble chromates. Pocock states (reference (d)) that it is fairly well established that these films are gel-like rather than crystalline and some supporting evidence for this was presented in reference (e). Reference (d) states that the chromium in the film is thought to be in the form of chromium chromate or chromic hydroxide plus soluble chromates.

Actually, the only known fact is that hexavalent and trivalent chromium species are present in the coating - the form is still a matter of speculation.

The first parameter studied in this investigation was the effect of the amount of hexavalent and trivalent chromium on unpainted corrosion resistance, paint base properties and electrical resistance of the coating.

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B. EXPERIMENTAL PROCEDURE1. Basis Metals

Chromate coatings were applied to pure aluminum, clad 2024 and bare 2024.

2. Process Details

With a few exceptions, the following processing cycle was used for all the panels:

- a. Non-etching alkaline cleaner - 5 min.
- b. Cold water rinse
- c. Chromic-sulfuric deoxidizer - 2 min.
- d. Cold water rinse
- e. Proprietary chemical film treatment - 3 min.
- f. Cold water rinse - 15 sec.

Following Step f, these variables were included:

- a. effect of drying in air at room temperature
- b. effect of drying in an oven at 180°F for 2 hours
- c. effect of bleaching the newly formed film in hot water at 200°F for 1 minute, then drying in air at room temperature
- d. effect of bleaching as above, then drying in an oven at 180°F for 2 hours

3. Unpainted Corrosion Resistance

Panels were exposed to 5% salt spray at an angle of 6° from the vertical and examined every 24 hours for the first sign of corrosion.

4. Paint Adhesion

Most of the panels were painted with the following system:

- a. 1 coat MIL-C-8514 pretreatment primer
- b. 1 coat MIL-P-7962 lacquer primer
- c. 2 coats of MIL-L-19537 lacquer

In addition, the following systems were applied to several sets of panels:

- a. 1 coat MIL-C-8514 pretreatment primer
 - b. 1 coat epoxy primer
 - c. 1 coat epoxy topcoat
- or
- a. 1 coat epoxy primer
 - b. 1 coat epoxy topcoat

Paint adhesion was evaluated by knife, wet tape test, and the DuPont Scratchmaster, as modified by the Aeronautical Materials Laboratory (reference (g)). The Scratchmaster simulates mechanically the knife adhesion tests and provides quantitative data.

5. Electrical Resistance

The electrical resistance of the various treatments was measured using the method described in reference (h).

6. Analytical Determination of Hexavalent and Trivalent Chromium

Hexavalent chromium was leached from the films by boiling in distilled water. The remaining film was stripped in warm, concentrated HNO₃. Chromium determinations were made colorimetrically. The exact procedure will be described in a report under Problem Assignment No. C 14 RMA 04-1.

In addition, total coating weights were obtained on some of the later sets and compared with the weights of Cr⁺³ and Cr⁺⁶. Freshly formed coatings were stripped in 50-50 HNO₃ and water at room temperature.

C. DESCRIPTION OF RESULTS

1. Determinations of Chromium Content

In the first experiments to determine amounts of chromium in the films, the method described in reference (i) for analyzing chromate films on zinc and cadmium was used. Aluminum, however, reduces the Cr⁺⁶ to Cr⁺³ during the stripping operation so on the first few sets of panels only total chromium could be obtained.

The first factor studied was the effect of immersion time in the chromate bath on amount of chromium in the films using clad 2024 as the basis metal. Results were as follows:

<u>Treatment Time</u>	<u>Total Cr Content (micrograms Cr/in²)</u>	
	<u>Individual Readings</u>	<u>Avg.</u>
30 sec.	65, 71	68
1 min.	108, 114	111
2 min.	152, 176	169
3 min.	191, 203	197
3 min. (bleached 200°F-1 min.)	138, 133	136

As would be expected, the amount of chromium increased with immersion time. The difference of 61 micrograms between the three minute immersion values for bleached and unbleached is assumed to represent the amount of hexavalent chromium present in the film. The reproducibility of the measurements on the duplicate panels is considered to be very good.

The next factor studied was the effect of the alloy on amount of chromium. The lower the number of alloying elements present, the more chromium the films contained; i.e., the heavier the film. Results were as follows for 3 minute treatments:

<u>Basis Metal</u>	<u>Total Amount of Cr (micrograms/in²)</u>
Pure Al	375
Clad 2024	197
Bare 2024	129

For the pure aluminum panels, the amounts of hexavalent and trivalent chromium were determined. These were as follows:

$$\begin{array}{r}
 \text{Cr}^{+6} \quad 112 \\
 \text{Cr}^{+3} \quad 272 \\
 \hline
 \text{Total Cr*} \quad 375 \text{ mcg/in}^2
 \end{array}
 \left. \vphantom{\begin{array}{r} 112 \\ 272 \end{array}} \right\} = 384 \text{ mcg/in}^2$$

*determined on separate panel from the one on which Cr⁺³ and Cr⁺⁶ were obtained.

Expressed in terms of percent, 72% of the chromium present in the film was in the trivalent state, 28% in the hexavalent state.

These initial studies indicated that the analytical determination of chromium amounts might provide a significant parameter for characterizing the films, therefore, a correlation with unpainted corrosion resistance and paint adhesion was attempted. A set of panels was treated, triplicate specimens were placed in salt spray and 6 replicates were painted with the wash primer, acrylic lacquer system. Chromium determinations gave the following values:

$$\begin{array}{r}
 \text{Cr}^{+6} - 34 \text{ mcg/in}^2 \\
 \text{Cr}^{+3} - 122 \text{ mcg/in}^2 \\
 \hline
 \text{Total Cr} - 150 \text{ (determined on separate panel)}
 \end{array}$$

The unpainted panels showed no sign of corrosion in 336 hours in salt spray (i.e., this would be a Class 1 film according to the classification of reference (h)). Results of wet tape and Scratchmaster tests were satisfactory and no spalling of the paint occurred when the panels were bent 180°.

The tests described above were repeated on a second set of panels, presumably treated in exactly the same manner. The resultant color was much lighter than that on the previous set. It was discovered that an overload of the electrical circuit tripped the circuit breaker and the temperature of the alkaline cleaner which was being electrically heated dropped considerably below 170°F. It was obvious that the cleaning operation had been incomplete because the mill identification was still visible beneath the chemical film. Tests were made on these panels as planned in order to see the effect of improper cleaning.

Chromium determinations verified the fact that a lighter coating was present, values being as follows:

Cr⁺⁶ - 12 mcg/in²
 Cr⁺³ - 65 mcg/in²
 Total Cr - 80 mcg/in² (determined on separate panel)

These panels exhibited the first sign of corrosion in 192 hours (indicating a Class 2 film as specified in reference (h)). Comparison of paint adhesion to the two sets is given in Table 1. It is interesting to note that only the Scratchmaster detected differences in paint base performance between the two sets, the values for the set inadequately cleaned and with lower chromium content being lower and less uniform than those for the set processed under optimum conditions. The Scratchmaster numbers are related to the weight required to break through the coating; therefore, the lower the number, the poorer the paint adhesion.

2. Effect of Post Treatment on Film Performance

A further attempt was made to study the effect of chromium content on film behavior based on the following assumptions:

a. Both air dried and baked chromate films would contain trivalent and hexavalent chromium compounds, but the hexavalent would be in a soluble form in the air dried and in a largely insoluble form in the film baked at 180°F for 2 hours.

b. Bleaching the newly formed films removed most of the hexavalent chromium in the films leaving only trivalent chromium. Baking of a bleached film would then show the effect of baking on the trivalent species alone.

Both a heavy and a thin film were given some or all of the post-treatments described above. Results are summarized in Table 2.

Salt spray life increased with increasing coating weight and hexavalent chromium content. Baking lowered the salt spray life. Removing the hexavalent chromium by bleaching resulted in slight improvement in salt

spray life over the baked films. Apparently, the effect of heating on the hexavalent chromium is more deleterious to the corrosion protective qualities of the film than is the complete removal of hexavalent chromium by bleaching.

The salt spray life for bleached and baked films varied from being superior to that of the bleached films, to being somewhat inferior, but in all cases, the salt spray requirement of 7 days for Class 2 films was met. The baking treatment used in these experiments apparently has no adverse effect on the corrosion protective qualities of the trivalent portion of this particular proprietary film.

In Sets 1 and 2 where both total coating weight and total chromium were obtained, chromium appears to constitute about one-third of the weight of the coating. Of that chromium approximately 75% is in a trivalent state, 25% in the hexavalent state. This relationship appears to hold whether the films are light or heavy. It is hoped that by electron diffraction, the compounds in which the chromium is present can be determined.

With regard to electrical resistance, the presence of Cr^{+6} in a soluble form appears to be responsible for high resistance values. When it is removed by bleaching or insolubilized by heating, the resistance values are considerably lowered.

D. CONCLUSIONS

1. An analytical method, developed to determine relative amounts of Cr^{+6} and Cr^{+3} in a chromate film makes possible correlative studies of chromium content and film properties such as salt spray life, electrical resistance, and paint adhesion.
2. For the proprietary film studied, salt spray life and electrical resistance increase with increasing soluble Cr^{+6} content. Removing the Cr^{+6} by bleaching or rendering it insoluble by heating, decreases salt spray life and electrical resistance.
3. The salt spray life of a bleached film which has been heated is approximately the same as that of a bleached film which has not been heated.
4. The effect of chromium content and chromium species on paint adhesion is not clear cut as yet. These preliminary tests indicate pre-treatment to be of more significance.

E. FUTURE WORK

1. Further experiments on heating of bleached films varying temperature and time at temperature are planned.
2. Polarization studies of effect of the post treatments described previously on electrochemical behavior are in progress.

3. The radioactive tracer experiments originally planned for the study of reactions between the chemical film and wash primer are being delayed due to higher priority work with the equipment. Since this approach will be employed in the near future by the Alcoa Research Lab under Contract NOW 64-0546F, it may be unnecessary to repeat this phase at the Aeronautical Materials Laboratory.

4. Additional attempts will be made to determine more clearly the relationship between chromium content and paint adhesion.

5. Panels corresponding to Sets 2 and 4 in Table 2 are being exposed with and without paint at Kure Beach, North Carolina, and Miami, Florida.

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 - (d) W. E. Pocock, Metal Finishing, 52, No. 12, 48 (December 1954)
 - (e) S. J. Ketcham, Properties of Chemical Films on Aluminum Alloys, Chapter VI, The Finishing of Aluminum, Reinhold Publishing Co., 1963
 - (f) Federal Test Method Standard 141, Method 6301
 - (g) Report No. NAEC-AMI-2018, Evaluation of "Scratchmaster" Paint Adhesion Tester, dated 17 Aug 1964
 - (h) Military Specification MIL-C-5541A, Chemical Films and Chemical Film Materials for Aluminum and Aluminum Alloys
 - (i) H. K. Katz, K. L. Proctor, and F. Nagley, Performance of Various ~~Chemical~~ at Supplementary Films on Electrodeposited Zinc Coatings, ~~Proceedings~~ Proceedings, Vol. 57, 1957

TABLES

- 1 - Paint Adhesion to Chemical Films
- 2 - Investigation of Effects of Post Treatments

ACKNOWLEDGEMENTS

The contribution of George B. Cook of the Chemistry Branch in developing and applying the method for determination of chromium content in chromate films is gratefully acknowledged; also that of Mary Lyon of the Organic Coatings Branch for the paint adhesion evaluation.

PAINT ADHESION TO CHEMICAL FILMSSet #1 (Optimum Alkaline Cleaning Step)

<u>Panel No.</u>	<u>Scratchmaster Results*</u>		<u>Bend Test</u>	<u>Wet Tape Test</u>
	<u>Dry</u>	<u>Wet</u>		
129	.7	.5	No Spalling	Satisfactory
130	.7	.6	No Spalling	Satisfactory
131	.7	.5	No Spalling	Satisfactory
132	.7	.5	No Spalling	Satisfactory
133	.7	.5	No Spalling	Satisfactory
134	.7	.5	No Spalling	Satisfactory

Set #2 (Inadequate Alkaline Cleaning Step)

135	.56	.34	No Spalling	Satisfactory
136	.58	.26	No Spalling	Satisfactory
137	.50	.24	No Spalling	Satisfactory

*Numbers refer to weight required to break through the coating, therefore, the lower the number the poorer the paint adhesion.

INVESTIGATION OF EFFECTS OF POST TREATMENTS

Set No.	Post Treatment	Coating Weight mc/ft ²	Chromium Weight mc/in ²		Salt Spray Life (Days to first sign of corrosion)	Electrical Resistance microhms/in ²
			Total	Cr+6		
1	Air Dried	50	113	90	13	14,680
	Baked			25	5 (excessive)	4,850
	Bleached & Baked				7	4,130
2	Bleached & Baked				21	4,320
	Air Dried	92	207	158	34	48,150
	Baked			49	6 (excessive)	23,950
3	Bleached*				30	30,730
	Bleached & Baked				9	7,730
	Air Dried	Not Determined	87	65	8	5,050
4	Baked			12	4	
	Bleached				6	3,560
	Air Dried	Not Determined	157	117	21	
	baked			34	6	
	Bleached				14	
	Bleached & Baked				11	

*Due to the heavy coating formed on this set, the 1 minute bleach did not remove all the hexavalent chromium. This explains the excellent salt spray life and high electrical resistance for the bleached and the shorter life for the bleached and baked since baking a film containing hexavalent chromium decreases salt spray life.