Trivalent Chromium Solutions For Applying Chemical Conversion Coatings To Aluminum Alloys or for Sealing Anodized Aluminum

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Corrosion-resistant films were formed on aluminum by immersion in solutions of basic chromic sulfate, plus fluosilicate, with alkali added to near, or slightly beyond, precipitation of insoluble basic compounds. The trivalent chromium films formed on 7075-T6 or 2024-T3 aluminum, when tested in 5-percent NaCl salt spray, provided corrosion resistance in excess of 96 hr. When a post-treatment of peroxide or permanganate solution was applied, corrosion resistance for both alloys almost reached 336 hr and sometimes exceeded this value. In most cases, only a 1 O-min immersion was necessary at 25 °C to obtain a corrosion-resistant film. Trivalent-chromium-treated aluminum served as an effective base for an epoxy paint primer. Anodized aluminum was afforded excellent corrosion resistance, comparable to bichromate, by sealing in dilute basic chromic sulfate solution and post-treated with peroxide.

Chromate conversion coatings have found widespread commercial and military applications on aluminum alloys and zinc or cadmium electrodeposits. Of particular interest to the Navy is the use of chromate coatings on aircraft aluminum alloys, because of excellent corrosion resistance and the ability to serve as an effective base for paint. The baths used to develop this coating contain chromates (hexavalent chromium), and it is the residual chromates in the coating that are largely responsible for the high degree of corrosion inhibition observed. Chromates are highly toxic, however, and their presence in wastewater effluents is severely restricted. It would, therefore, be highly desirable to develop a coating for aluminum alloys utilizing relatively non-toxic chemicals that could serve as an alternative to chromate coating.

Preliminary studies were conducted with molybdate solutions that produced thin colored films (presumably molybdic oxides) on immersed 7075-T6 Al alloy, but that possessed only slight salt spray resistance. With additives, corrosion resistance of about 24 hr salt spray exposure was achieved as, for example, by 5-min immersion at 25 °C in the following bath:

6 g/L Na_2MoO_4
4 g/L Na_2SiF_6
5 g/L $Na_3PO_4 \cdot 2H_2O$
2 g/L Benzotriazole

In another study, 20-min immersion of 7075-T6 Al alloy in 20 g/L Na_2CO_3 + 10 g/L Na_2SO_4 solution at 50 °C produced films of approximately 200 mg/ft^2, but with only a modicum of corrosion resistance. By “sealing” these films in certain aqueous solutions, however, the corrosion resistance was improved. For example, as much as 72 hr salt spray resistance was attained by immersion of the rinsed carbonate film for 5 min in 10 g/L $KMnO_4$ solution at 50 °C.

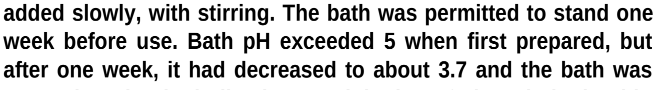
Attention was then directed toward the use of trivalent chromium films, such as have found commercial use on zinc plated surfaces.’ These films offered little corrosion resistance, but imparted an attractive blue-white color to the zinc. It was considered that if trivalent chromium compounds could be formed on aluminum, it might be possible to oxidize part of the film to hexavalent chromium, perhaps by a post-treatment in dilute peroxide or other oxidizing agent. In this way, it might be possible to attain corrosion-resistant films comparable to the chromate without direct use of toxic hexavalent chromium. It should be noted that trivalent chromium is much less toxic than the hexavalent form, as shown in Table 1, compiled by the EPA.

Experimental Procedure

It was found that baths containing $Cr_2(SO_4)_3$ + Na_2SiF_6 or NaF, when adjusted with NaOH to a pH near or beyond precipitation of basic compounds, were capable of forming light, but visible, films on Al alloys with significant corrosion resistance. When the pH is raised by addition of NaOH, it falls, with time, to considerably lower values. Trivalent chromium salts form coordination compounds of coordination number six. The hydrolysis of coordination complexes is accelerated by addition of alkali and may form successively in the following manner:[2]

$$[Cr(H_2O)_6]Cl_3 \rightarrow [Cr(OH)(H_2O)_5]Cl_2 + HCl$$
$$[Cr(OH)(H_2O)_5]Cl_2 \rightarrow [Cr(OH)_2(H_2O)_4]Cl + HCl$$
$$[Cr(OH)_2(H_2O)_4]Cl \rightarrow [Cr(OH)_3(H_2O)_3] + HCl$$

It is believed that analogous compounds are formed with sulfate, and that liberation of free acid accounts for the observed decrease in pH with time after alkali has been added to the $Cr_2(SO_4)_3$ solution. The molecular weight of the compound may be increased as shown in the example below:[2]



$$2[Cr(H_2O)_5]Cl_2 \rightarrow [(H_2O)_4Cr\begin{matrix}OH\\ \\ OH\end{matrix}Cr(H_2O)_4]Cl_4 + 2H_2O$$

A 12-liter bath was prepared with deionized water, to which was added 4 g/L $Cr_4(SO_4)_5(OH)_2$ [from a commercial preparation:[a] 26 percent Cr_2O_3 and 23 to 24 percent Na_2SO_4] and 0.4 g/L Na_2SiF_6, with continuous stirring for about one hr to dissolve the chemicals. Then 20 mL/L of 0.5 N NaOH was added slowly, with stirring. The bath was permitted to stand one week before use. Bath pH exceeded 5 when first prepared, but after one week, it had decreased to about 3.7 and the bath was somewhat cloudy, indicating precipitation of chromic hydroxide (hydrous chromic oxide). The supernatant liquid of the bath was analyzed by atomic absorption analysis and found to contain 597 ppm Cr or about 64 percent of theoretical.

Aluminum alloy (7075-T6 and 2024-T3) panels, 3x5x0.030 in., were held on titanium racks used for *anodizing aluminum* and prepared as follows:

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[a] Fluka Chemical Corp., Ronkonkoma, NY

Table 1

Water Quality Criteria Summary, Concentrations in μg/L

	CAS #	Priority Pollutant	Carcinogen	Fresh Acute Criteria	Published Criteria: Water & Organisms	Published Criteria: Organisms Only	Recalculated Values using IRIS, as of 9/90: Water & Organisms	Recalculated Values using IRIS, as of 9/90: Organisms Only	Drinking Water MCL	Criteria Federal Register Notice
Chromium (Vi)	7440-47-3	Y	N	16	50		170	3,400	100	50 FR 30788
Chromium (III)	1308-14-1	Y	N	1,700	170,000	3,433,000	33,000	670,000	100	50 FR 30788

- Immersed 30 min in 53 g/L of a proprietary alkaline cleaner[b] at 55 “C with air agitation, followed by room-temperature running water rinses
- Immersed 15 min in 180 g/L of a proprietary non-chromate deoxidizer[c] at 25 °C and followed by room-temperature running water rinses
- Immersed in 12-liter trivalent chromium bath as described earlier at 25 “C, without agitation, for 5, 10, 20 or 40 min and given one of the following post-treatments:
  1. None
  2. 30 sec in 10-mL/L H_20_2 (30%) in deionized water at 25°C and drain-dried without rinsing
  3. 30 sec in 5-g/L $KMnO_4$ at 25 °C; water-rinsed and drain-dried

A scribe mark was made on each panel to ascertain any tendency for self-healing as is observed with chromate conversion coatings. The panels were exposed to 5-percent neutral salt spray, in accordance with ASTM B-117.

Results and Discussion

Visible films were produced on aluminum panels immersed 10 or more min in the trivalent chromium bath; pale tan at 10 min, pale violet at 20 min and pale blue at 40 min. The panels post-treated in permanganate were somewhat darker in color.

Film formation may begin with attack (oxidation) of the aluminum surface by fluoride-containing ions. The pH of the interracial solution is increased, leading to intimate precipitation of hydrous chromic oxides on the surface. However, electrochemical studies indicate that the mechanism is more complex.

The film weight of panels, immersed 10 min in the trivalent chromium bath, was determined by stripping the film for 30 min in a solution containing 35 mL/L H_3PO_4 (85%) + 20 g/L CrO_3 at the boiling point, rinsing drying and reweighing. The loss of weight averaged 3.8 mg per panel, or 18 mg/ft^2.

The results of salt spray exposures of panels treated one or more times in a trivalent chromium bath are shown in Figs. 1 and 2, and in Table 2. After 336 hours exposure, the 7075-T6 panels that had been immersed 10,20 or 40 min in a trivalent chromium bath, and given a permanganate post-treatment,

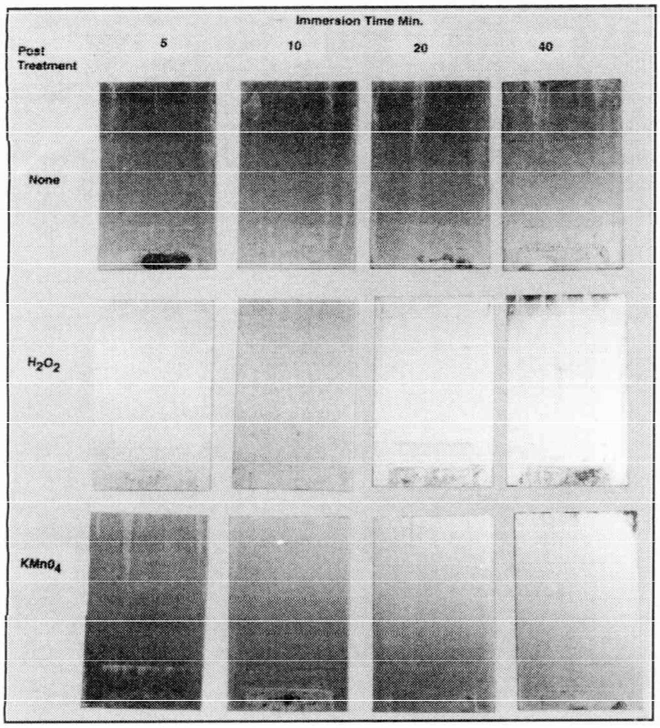

Fig. l—Effects of immersion time in trivalent chromium bath and post-treatments on corrosion resistance of 7075-T6 aluminum panels after 336 hr salt spray exposure.

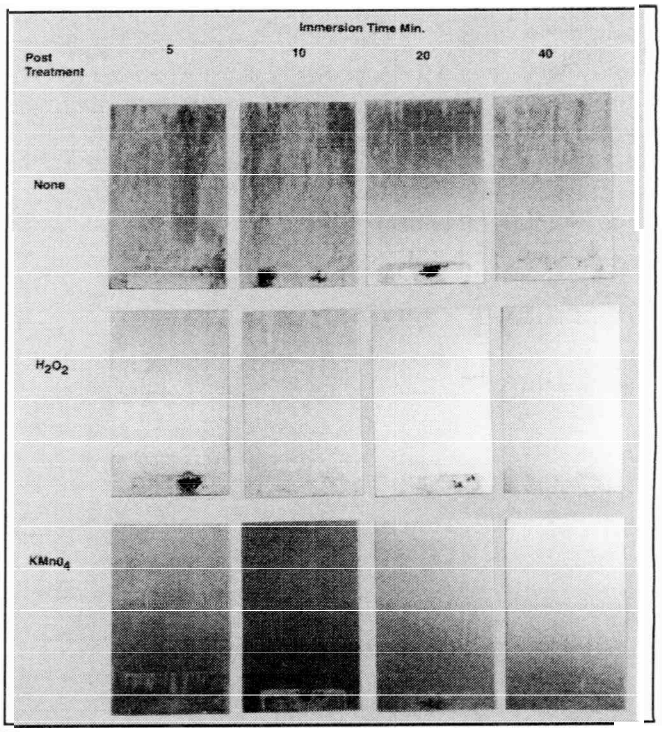

Fig. 2—Effects of immersion time in trivalent chromium bath and post-treatments on corrosion resistance of 2024- T3 aluminum panels after 336 hr salt spray exposure.

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[b] 4215NC-LT, Turco Products Co., Westminster, CA

[c] Smut-Go, Turco Products Co., Westminster, CA

Table 2

Corrosion Ratings* of Panels Treated in Trivalent Chromium Bath After 336 Hr Salt Spray Exposure

Immersion Time, Min	None	Post-Treatment: 30 sec, 10 mL/L H_2O_2 (30%) No rinse	Post-Treatment: 30 sec, 5 g/L $KMnO_4$ Water-rinsed
Al 7075-T6 Alloy			
5	3	3+	3+
10	3	3+	5
20	2+	3	4+
40	2+	3	4+
Al 2024-T3 Alloy			
5	0+	3	2
10	1	3	5
20	1+	2+	5
40	1	2+	5

*Rating key
5—No corrosion
4—Traces of corrosion (incipient)
3—Slight corrosion (<1% area affected)
2—Moderate corrosion (1–5% area affected)
1—Considerable corrosion (5–25% area affected)
0—Extensive corrosion (>25% area affected)

were free of corrosion or had only faint traces of corrosion (Fig. 1, Table 2). All 7075-T6 panels given the peroxide post-treatment were only slightly corroded. Even panels immersed in a trivalent chromium bath 5 or 10 min without any post-treatment showed only slight corrosion, while those immersed 20 or 40 min were somewhat more corroded. In general, the best corrosion resistance was obtained when panels were immersed for 10 min. There was little evidence of self-healing at the scribe mark made in the 7075-T6 panels.

The 2024-T3 panels, after 336 hours salt spray exposure, were completely uncorroded when trivalent-chromium-treated for 10 minor more and given the permanganate post-treatment (Fig. 2). There was only slight corrosion on panels treated 5 or 10 min and given the peroxide post-treatment somewhat more corrosion was seen on the panels treated 20 or 40 min in trivalent chromium. In general, as with the 7075-T6 panels, the best corrosion resistance was obtained after 10 min treatment in trivalent chromium. With 2024-T3 panels that were not given a post-treatment, corrosion resistance was poor with considerable white salts. Even the poorest of these, however, were not nearly as badly corroded as bare (untreated) panels, which were 95-percent covered with heavy white salts. The 2024-T3 panels did show self-healing properties at the scribed areas when a post-treatment was applied to those treated in trivalent chromium for 10 min or more.

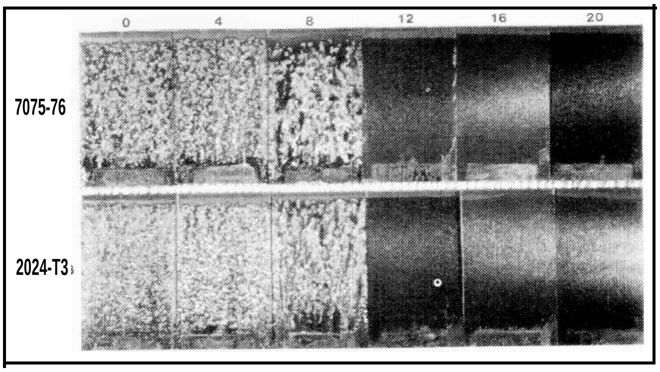

Fig. 3-Effect of 0.5 M NaOH additions in mL/L to trivalent chromium bath on corrosion behavior of treated aluminum alloys after 168 hr salt spray exposure.

Self-healing is believed to be a function of hexavalent chromium introduced into the coating by the peroxide or permanganate post-treatment. A panel treated for 10 min in the trivalent chromium bath and post-treated with peroxide was leached for 30 min in 200 mL of boiling water. The water was found to contain 0.05 ppm of hexavalent chromium. A control panel, not peroxide post-treated, had no hexavalent chromium. Total chromium in the coating was determined by dissolving the films for 5 min in 25-percent (vol.) HCl at 25 °C and analyzing for Cr by atomic absorption spectroscopy. The solution contained 3.36 ppm Cr, or 0.73 mg Cr removed per panel. This would indicate that only about 19 percent (0.73/3.8 X 100) of the films contained Cr. Hydrous chromic oxide would not account for more than about 40 percent of the film; it is therefore considered likely that aluminum compounds constitute much of the films' weight.

There was significant benefit in corrosion resistance with use of permanganate post-treatment compared to peroxide; however, the latter is simpler and less polluting and is preferred when optimum corrosion resistance is not required.

After the 12-liter bath was used to treat approximately 150 panels (2.6 ft^2 per liter processed), it was reduced in effectiveness for providing corrosion resistance. It was found, however,

Table 3

Effect of Sodium Hydroxide Addition on the Corrosion Resistance of Aluminum Alloys Treated in Trivalent Chromium Bath: All Panels Post-Treated in Peroxide

Volume, mL N/2 NaOH added/L	pH after standing 2 weeks	Corrosion Rating* After Salt Spray Exposure: 7075-T6 96h	7075-T6 168h	7075-T6 336h	2024-T3 96h	2024-T3 168h	2024-T3 336h
0	3.36	0	0	0	0	0	0
4	3.51	0	0	0	0	0	0
8	3.61	0	0	0	0	0	0
12	3.64	5	3+	3	4	3	2
16	3.68	5	4	3+	4	3	2+
20	3.71	5	4	4	4	3	2+

*See Table 2 for rating key

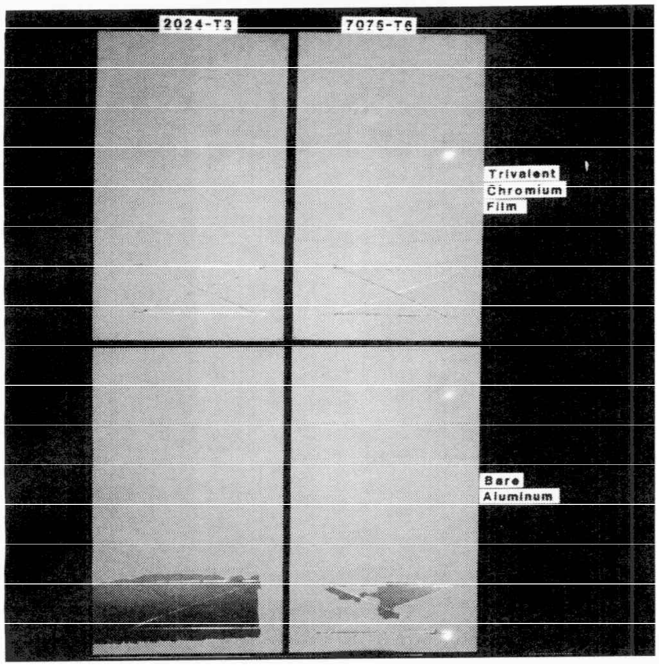

Fig. 4—Paint adhesion properties of bare and trivalent-chrornium-fteated aluminum, showing results of tape pull test in scribed area.

that addition of 0.4 g/L of Na_2SiF_6 and a small amount of NaOH, rejuvenated the bath to previous effectiveness. The bath is also reduced in effectiveness by extended periods of non-use; however, bath activity is enhanced by addition, with agitation, of a small amount of alkali (e.g., 0.3 mL/L of 0.5 N NaOH) prior to operation.

The bath is not yet considered fully optimized. There are indications that additions, such as boric acid or a non-ionic Surfactant, may be beneficial. Also, increasing the Na_2SiF_6 concentration from 0.4 to about 0.8 g/L appears beneficial for 7075-T6, but not for 2024-T3, aluminum alloys.

It is interesting to note that bath control by pH is insufficient to ensure good operation. Instead, the amount of alkali added is critical. Various amounts of alkali were added to one-liter baths of the composition given earlier; namely, 4 g/L $Cr_4(SO_4)_5(OH)_2$ + 0.4 g/L Na_2SiF_6. The baths were allowed to stand two weeks; the pH was measured and the panels were immersed for 5 min at 25 °C and given the peroxide post-treatment. The results are as shown in Table 3.

There is, evidently, a critical transition between 8 and 12 mL/L of 0.5 N NaOH addition (see Table 3 and Fig. 3). Solutions with 8 mL/L or less NaOH addition were incapable of providing protection to aluminum, while those with 12 mL/L or more provided effective protection; the difference in pH was minimal (3.61 vs. 3.64). It is interesting to note that there was no precipitation in the bath with 12 mL/L of 0.5 N NaOH, slight precipitation with 16 mL/L and moderate precipitation with 20 mL/L. Results of salt spray exposure on the corrosion ratings are shown in Table 3. There appeared to be some increase in corrosion resistance with increase of 0.5 N NaOH from 12 to 20 mL/L, although the bath with 12 mL/L added has the benefit of no loss of trivalent chromium through precipitation.

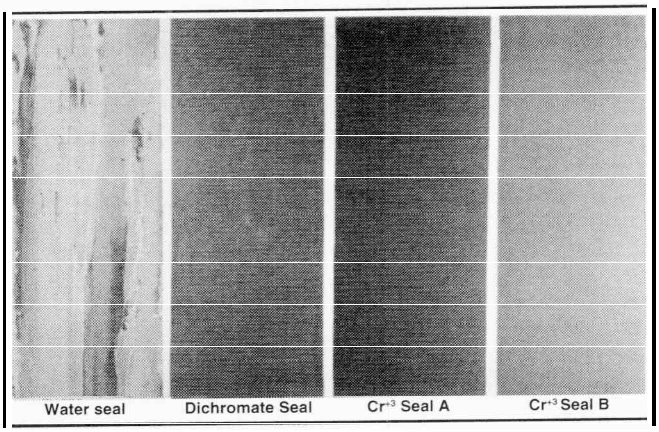

Fig. 5-Sulfuric-acid-anodized 2024- T3 aluminum sealed in various solutions at boiling point and exposed over 3000 hr to salt spray.

Additional panels were treated in the solutions containing 12, 16 or 20 mL/L of 0.5 N NaOH for only 2.5 min at 25 °C. The baths were then heated to 42 °C and the tests repeated. The results of salt spray exposure tests on these panels are shown in Table 4.

Panels immersed 2.5 min at 25 °C in the trivalent chromium baths were generally poor, although the bath containing 20 mL/L 0.5 N NaOH provided substantially greater corrosion resistance than baths containing lesser amounts. Increasing the bath temperature to 42 °C considerably improved the corrosion resistance of panels immersed 2.5 min. Immersion of panels for 2.5 min at 42 °C provided approximately the same corrosion resistance as panels immersed 5 min at 25 °C, evidence that increasing the trivalent chromium bath temperature can substantially reduce the required treatment time.

Anions Other than Sulfate

Trivalent chromium solutions other than sulfate have been studied briefly; chloride, nitrate and acetate were not as effective as sulfate. A simple solution of 2.5 g/L CrF_3. $9H_20$, however, adjusted to proper pH with alkali, showed some promise.

Table 4

Effects of Trivalent Chromium Bath Temperature on Corrosion Resistance of Treated Aluminum

Volume, mL/L 0.5 N NaOH added	Corrosion Rating* After 168 Hr Salt Spray Exposure			
	2.5 min at 25 °C		2.5 min at 42 °C	
	7075-T6	2024-T3	7075-T6	2024-T3
12	0	0	3	2+
16	1	0	3+	3
20	2+	2	3+	3

*See Table 2 for rating key

Wiping-on Procedure

Preliminary tests showed that corrosion-resistant films can be applied to aluminum by a wiping-on procedure, using absorbent material soaked with trivalent chromium solution. Post-treatment was applied, after rinsing, by a fine spray of dilute peroxide solution to cover the surface, which was then allowed to dry. These results indicate that the process can be used effectively for treating large surfaces for which an immersion process is impracticable.

Electrolytic treatment

It was found that application of a 2-min cathodic treatment of aluminum in the trivalent chromium bath, followed by a 10-sec anodic treatment, produced films with good corrosion resistance. This process may be explored further; the advantages of an immersion process are apparent, although involving longer processing times.

Painted Panels

Panels treated in the 124-liter trivalent chromium bath for 5 or 20 min, with or without peroxide post-treatment, were painted with strontium chromate inhibited epoxy primer (MIL-P-23377), aged one week, immersed in distilled water 24 hr at room temperature, dried, scribed and tape-tested, in accordance with ASTM D3359, Standard Method A. Bare panels failed the tape-test, but all trivalent-chromium-treated panels, with or without post-treatment, passed the paint adhesion tests (see Fig. 4).

Sealing Anodized Aluminum

Aluminum 2024-T3 alloy panels were anodized in 15-percent (weight) sulfuric acid solution for 30 min at 21 “Cat 18 V. A trivalent chromium bath was prepared containing 5 g/L $Cr_4(SO_4)_5(OH)_2$ [26 percent Cr_20_3 and 23 to 24 percent Na_2SO_4], plus about 20 mL/L 0.5 N NaOH for use as a seal. The following seals were applied to the anodized aluminum:

- Water Seal—15 min in boiling deionized water
- Bichromate Seal—15 min in 50 g/L Na_2Cr2O_7. $2H_2O$ (boiling).
- Trivalent Chromium Seal
    - A—Two min in above bath (boiling); rinse; two min in 10 mL/L H_20_2 (30%)
    - B-1 5 min in above bath (boiling); rinse; two min in 10 mL/L H_20_2 (30%)

The panels were exposed to salt spray for over 3000 hr (see Fig. 5 for results). The water-sealed panels exhibited considerable corrosion, but the bichromate or trivalent chromium seals were completely uncorroded. This demonstrates the effectiveness of trivalent chromium sealing. When anodized aluminum is sealed in a trivalent chromium bath at room temperature, corrosion resistance is far superior to water-sealed panels, but not quite as resistant as those sealed with bichromate. Also, deletion of the peroxide post-treatment did not seriously reduce the corrosion resistance of anodized aluminum sealed with trivalent chromium.

Findings

Corrosion-resistant films can be applied to highly corrosion-susceptible 2024T3 and 7075-T6 aluminum alloys by immersion in a bath containing 4 g/L $Cr_4(SO_4)_5(OH)_2$ [26% Cr_2O_3 and 23 to 24 percent Na_2SO_4] + 0.4 g/L Na_2SiF_6 + 20 mL/L 0.5 N NaOH. The amount of NaOH maybe reduced to 12 to 16 mL/L to retard precipitation of hydrous chromic oxide in the bath, but at the expense of somewhat reduced corrosion resistance. Corrosion resistance is enhanced by post-treatment in peroxide or permanganate. Ten min immersion in the trivalent chromium bath is optimum; however, immersion time can be reduced further by moderate heating of the bath. Trivalent chromium films on aluminum alloys serve as an effective base for adhesion of epoxy paints. The trivalent chromium films are suggested as an alternative to chromate conversion coatings.

Sulfuric-acid-anodized aluminum (2024-T3) sealed in dilute chromic sulfate solution and post-treated in peroxide solution, provided corrosion resistance comparable to that of dichromate-sealed anodized aluminum. A collateral finding was that a trivalent chromium seal applied to chromic-acid-anodized panels was even more effective than bichromate for improving corrosion resistance.

In separate determinations, it has also been found that chromium sulfate, $Cr_2(SO_4)_3$, offers the same protection as $Cr_4(SO_4)_5(OH)_2$, but with greater amounts of alkali required, and that the trivalent chromium bath treatment is even more effective for protection of aluminum alloy 6061-T4 than for 7075-T6 or 2024-T3.

Editor's note: Licenses for the techniques described in this paper are obtainable from the U.S. Government. Contact Patent Counsel, Naval Air Warfare Center (Code NAWC-AD) Warminster, PA 18974-5000.

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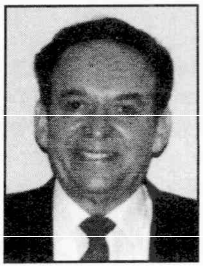

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