Organic Sealant for Anodized Aluminum-Corrosion Protection Without Chromate

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Sealing of anodized aluminum with long chain carboxylic acids, preferably isostearic acid, can provide corrosion resistance greater than that imparted by chromates. Resistance to ASTM B-117 salt spray is excellent (1000 to 4000 hours for 1100, 2024, and 7075 alloys, longer for more resistant alloys). Other accelerated corrosion tests gave poor to marginal results. These phenomena are understandable in light of the different chemistry of organic seals from hot water seals. The action of the organic seals mimics that of chromates, i.e. they form a hydrophobic surface with reactive ingredients to repair damage. Sealing by immersion through a layer of acid floated on water can be employed. Corrosion protection of steel and other metals can be achieved by coating with aluminum, anodizing and sealing with organic acid.

Long chain carboxylic acids can be used to seal anodized aluminum[1]. Previous patents[2,3] and papers[4] based on our work have described the excellent corrosion resistance attainable, as measured by ASTM B-117 Salt Spray. The method can be used with most types of alloys (Table I).

Table I. Testing of Alloys by Salt Spray

Alloy	Time To Failure (hrs)	Treatment
380	500+	isostearic
1100	900	emulsion
2024	2000	isostearic
5354	3500	isostearic
6061	4000+	stearic-IPA
7075	3000	stearic-IPA

The oxide coating formed by anodizing, a process of oxidation at the aluminum anode of an electrolytic cell, consists of a porous layer of boehmite, an aluminum oxyhydroxide, over a thin continuous barrier layer. Conventional sealing uses boiling water, hot dilute solutions of nickel, cobalt, or magnesium salts (usually acetates), or at room temperature, a solution of nickel fluoride. All of these cause conversion of aluminum oxyhydroxide to the trihydroxide. During the process the coating swells, closing the pores. Organic acid seals react with the surface to form an aluminum soap. The pores remain open, but filled with acid. Damage to the anodized layer is instantly repaired by reaction of the freshly exposed surface with acid to form a soap. Being liquid, isostearic acid is more mobile. Thus it is able to migrate more readily to the site where repair is needed and gives somewhat better resistance to corrosion and fatigue than solid acids.

Because a different chemistry applies to organic seals, some of the conventional tests for seal quality should not be applied. Acid Dissolution (ASTM B-680) and Dye Stain (ASTM B-136) tests generally fail. These essentially measure the available surface area of the oxide layer and require closure of the pores to pass. Exposure of an aluminum soap to the strong acids used in these tests instantly destroys the soap, liberating free carboxylic acid. The acids then attack the highly porous (ca. 50% void) surface. An acid dissolution rate of 416 mg/dm^2 was observed - substantially equivalent to an untreated surface.

In contrast to these tests, electrical impedance spectroscopy gives results in an intermediate range of 26 to 27 megohm/cm^2. Galvanic current between dissimilar metals is comparable to that resulting from chromate treatment. Most important, salt spray resistance 4 to 5 times better than that obtained using chromates results.

The action of organic sealants mimics that of chromates. The aluminum soap and the chromium oxyhydroxide barrier layer are both hydrophobic. Repair of insults to the protective layer is due to the presence of free acid in the organic seal or of residual hexavalent chromium in the chromate seal[6].

A number of different formulations have been used. All are based on use of isostearic acid. This commercial material is a mixture of many isomers of stearic acid, which lowers the melting point to 10°C (50°F). It is relatively non-toxic (LD_{50}=25 g/kg), non-flammable (Flash Point 182°C), and not corrosive. Boiling point is well in excess of 300°C at atmospheric pressure.

The several formulations are tailored to specific applications. The standard is Isostearic acid 99.9%, Benzotriazole 0.1%. A water emulsion is used for application over oil-based inks and dyes without smudging. Substitution of citric acid for benzotriazole gives a material acceptable for incidental food contact. When bath life is not a factor, isostearic acid can be used without additives. Other chelates, such as 8-hydroxyquinoline and dithizone have been used. Figure 1 shows the effect of benzotriazole chelating agent on salt spray life. In spite of the negative effect, a small amount should be added to enhance bath stability, particularly when copper containing alloys are used. Other chelating agents extend salt spray corrosion resistance.

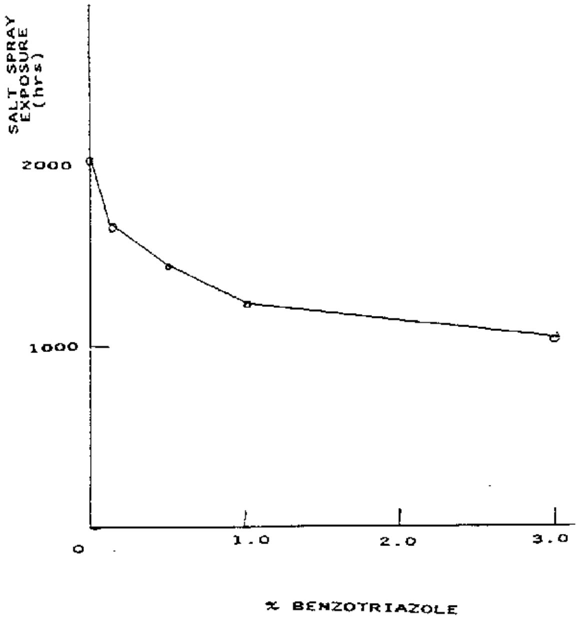

Figure 1. Effect of Benzotriazole on Corrosion Resistance

TABLE II. TESTING OF PANELS SEALED WITH ISOSTEARIC ACID SOLUTIONS IN N-METHYLPYRROLIDONE

ISOSTEARIC ACID (%)	TIME TO FAILURE (B-117 SALT SPRAY) (hours)	PAINTABILITY (WET TAPE TEST) (EPOXY PRIMER)
10	300	pass
15	500	pass
25	1400	pass
50	----	fail
100	2050	fail

Dipping in full strength isostearic acid leaves an oily residue on the metal surface. In the laboratory this can be removed by wiping with cotton cloths or paper towels. On production scale, excess can be removed by tumbling with absorbents or by immersion in N-methylpyrrolidone (NMP) Water mixtures.

Following up on the use of NMP for removal of excess, a series of experiments was conducted to provide a paintable surface. As shown in Table II, application of Isostearic acid as a 15 to 25% solution in NMP gives a surface which accepts epoxy primer, paint (and presumably adhesives), without dropping salt spray life below 336 hours. Recovery of isostearic acid and NMP is accomplished by adding excess water, skimming the acid from the surface for re-use, then evaporating water to leave either NMP/water mixture or pure NMP (Figure 2).

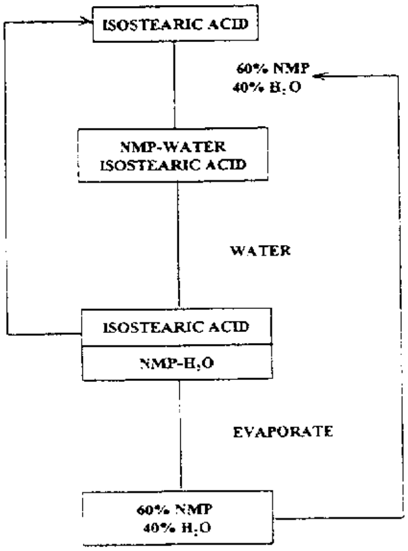

Figure 2. Recycling of Isostearic Acid and N-methylpyrrolidone

To reduce the cost of initially filling a tank with these sealants, experiments were conducted to take advantage of the fact that the sealants (except the emulsion) are oily liquids which float on water. Parts were coated by immersing through the oily layer into water. Salt spray panels (3x10 in. 2024) were sealed after anodizing using a tank containing 2.5 gallons of water and 1 quart of isostearic acid. Salt spray testing was discontinued at 1938 hours with no pitting observed.

Corrosion protection of steel (and any other metal that can be coated with aluminum) can be accomplished by subjecting the aluminum coated part to anodizing and isostearic acid sealing. Ion Vapor Deposition and Flame Spray can not be used because porosity of the coatings allow current flow to the steel. For example, a 3x10 inch panel of IVD aluminum on steel showed an initial current of 350 amp, compared to the usual 20 to 30 amp, since no high resistance oxide coating forms on exposed steel. Panels cut from a dip-coated sheet (0.8 mil thickness of 5000 series aluminum on steel) were masked with organic polymer coating at the edges. Anodizing was successful, isostearic acid sealant was applied, and a panel sent for salt spray testing. After 900 hours the test was discontinued. The center of the panel was intact, but corrosion (white rust) was spreading from the masked edges.

Small panels, 2.5x2.5 inch were electroplated using the SIGAL process[6,7], to a thickness of 24 microns (1 mil). Anodizing produced an 8 micron (0.3 mil) oxide layer which was sealed with Isostearic acid. The salt spray test is in progress, with no corrosion after 960 hours. We believe that aluminum applied by thermal decomposition coating from iodides or alkyls could also be anodized and used for corrosion protection.

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