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ADVANCED TRIVALENT CHROMIUM SEALS FOR HARD-COAT ANODIZED ALUMINUM ALLOYS

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ABSTRACT

Hard-coat (Type III) anodized aluminum alloys have been used by the military, aerospace, automotive, and other industries for applications where superior hardness and wear resistance are required. In recent years there has been a great interest in sealing and dyeing hard-coated aluminum in order to improve the corrosion resistance and appearance of the oxide film. Although hard-coated aluminum has very high wear resistance, it has to be sealed to ensure a desirable level of corrosion resistance. However, conventional industrial seals for hard-coated aluminum cause a dramatic reduction in abrasive wear resistance. A novel room temperature trivalent chromium based seal was found to be an excellent post-treatment for hard-coated aluminum to provide enhanced corrosion resistance without compromising the wear characteristics. In this study, a comparison of post treatments including trivalent chromium based seal, hydrothermal, nickel acetate, sodium dichromate, sodium silicate, nickel fluoride, black dye, black dye and nickel seals was made. The quality of the oxide film was evaluated by microhardness, wear resistance, corrosion resistance, and dielectric strength. The effects and possible mechanisms of the post-treatment processes on the anodic film are discussed.

Keywords: Hard-coat, Anodized Aluminum, Type III, Sealer, Steel.

INTRODUCTION

Aluminum alloys (AA) as light-weight construction materials are commonly used in the military, aerospace, automotive, marine, and civil construction industries. The use of high strength aluminum alloys for oil production is becoming increasingly important because of the technical and economic considerations. Quenched and tempered Cr-Mo steel is the conventional material to produce drill pipes and their connections¹. At many drilling sites for oil production the use of high strength D16T aluminum alloy for the drill string showed reduced loads on hoisting equipment, reduced trip time, lower hydraulic losses, reduced mud pump loads, and lower transportation costs compared to the conventional steel drill pipes¹⁻³. AA D16T (Russian standard GOST 4784, Cu: 3.8 – 4.9, Mg: 1.2 – 1.8) is very similar to AA 2024

– T4 ASTM⁽¹⁾ designation and its yield strength is ~447 MPa. Other high strength AAs with compositions similar to AA 7014 (Zn: 5.5 – 6.0, Mg: 2.4 – 3.0) were also successfully used as the drill pipe material⁴. It has been reported that using AA strings instead of steel, stresses are reduced and strengths are increased in a number of drilling designs⁵. Pervez et al.² investigated the stress and strain levels, expansion force, contact stresses, and hardening parameter when using steel and aluminum Solid Expandable Tubulars in both vertical and horizontal wells. By using aluminum tubulars instead of steel, required expansion force, contact force, hardening parameter, and the equivalent stress generated in aluminum are significantly reduced.

The most important advantages of using aluminum alloy (AA) instead of steel are:

- Lightness (one third the weight of steel) and higher strength to weight ratio,
- Lower modulus of elasticity, about one third of that of steel, provides greater deflection under a given load,
- Suitability for cryogenic applications. AAs are not prone to brittle fracture at low temperatures in the way that steel is because of their face-centered cubic structure,
- Ability to have excellent erosion and/or corrosion resistance after simple and effective surface treatments,
- AA sections can be extruded
- Higher metal removal rates during milling because of the machinability of AAs
- AAs can be welded as readily as steel and the welding speeds are faster.

Any aluminum surface exposed to air develops a hard and protective oxide layer of approximately 2.5 nm⁶. The Pourbaix diagram for aluminum shows that the passivation is mainly due to the Al₂O₃.3H₂O phase comprising neutral and slightly acidic water⁷. Other hydrated forms of Al₂O₃ that may exist in practice give a somewhat narrower passive region. In neutral environments such as the atmosphere, fresh water, and soils, the corrosion reaction consists of combination with water to form aluminum hydroxide and hydrogen gas⁶;



The corrosion regions at higher and lower pH in the Pourbaix diagram extend to very low potentials and thus the corrosion resistance depends on a dense continuous oxide layer. In severe (acidic and alkaline) industrial environments with certain pollutants, localized corrosion occurs in the form of pitting corrosion, intergranular corrosion, stress cracking corrosion or flaking. Deviations from the theoretical Pourbaix diagram is significant when chloride or other aggressive corrosive species destroy the natural passivity and the surface inclusions due to the alloying constituents may cause weak points in the oxide film.

The oxide film is dissolved and the pitting corrosion is the most frequent under these conditions. The maximum penetration of pitting as a function of time can be represented by the following semi-logarithmic expression⁸;

$$P_{\max} = A \log t + B$$

where A is a constant, B is the maximum penetration of pitting during the first year, and *t* is the exposure time in years. Both A and B depend on the alloy type and the corrosivity of the atmosphere. As the penetration of pitting corrosion is explained by the logarithmic type law, the

⁽¹⁾ ASTM International (ASTM), 100 Barr Harbor Dr., West Conshohocken, PA 19428.

corrosion rate attenuates considerably with time since the depth of the pits is reported to be less than 10 $\mu\text{m}/\text{year}$ and the loss of mechanical characteristics including yield and tensile strengths represents less than 10% of their original value⁹. Although the severity of the corrosion damage is minimal in technical terms, the appearance of the aluminum tends to deteriorate significantly. In many instances, however, inadequate corrosion properties, deterioration of the appearance, and low surface hardness have greatly restricted the application of aluminum alloys. Thus, the production of hard, corrosion resistant ceramic coatings on aluminum components is of great interest.

In the past, several surface treatment processes have been investigated to produce protective coatings on aluminum components, including Micro-Arc Oxidation, plasma thermal spray, Physical Vapor Deposition, and high temperature glass enameling techniques¹⁰⁻¹⁴. For many applications, anodizing has been favored because of the low cost, aesthetic qualities, and good mechanical properties. Anodic coatings provide both corrosion & wear protection, and anchoring layers for paints.

Anodizing is a special electrochemical process, which forms a very stable thin film of Al_2O_3 on the external surface of aluminum, when it is formed in acidic and alkaline electrolytes. The anodic porous films can be tailored to suit particular applications by appropriate selection of the anodizing electrolyte and the anodizing processing parameters, such as voltage, current density, electrolyte temperature, etc.¹⁵.

The anodic oxide film formed in a sulfuric acid electrolyte consists of a thin compact barrier layer next to the metal, having a thickness of around 1.0 nm/V of applied voltage, overlaid with a thick porous layer containing hexagonally shaped cells with a central pore perpendicular to the metal surface^{16,17}. Sealing as a post-treatment is necessary in order to improve corrosion resistance of the anodized surface. Different sealing techniques such as hot water sealing, dichromate sealing, nickel acetate sealing, cold nickel fluoride sealing, etc. improve the corrosion resistance of the anodized alloys to some extent. In recent years, there has been a growing interest in sealing and dyeing hard-coat anodized aluminum in order to improve the erosion-corrosion resistance and appearance of the oxide^{18,19}. However, unlike Type II anodic coatings (<25 μm), Type III (hard-coat) anodic coatings (>25 μm) of aluminum are typically used without any post-treatment because dyeing or sealing will reduce the abrasion resistance and hardness of the anodic oxide²⁰. A novel trivalent chromium based room temperature sealing, unlike other seals, was found to be very effective in enhancing the corrosion resistance without compromising the wear and hardness characteristics of the hard anodic coating. Among all conventional post treatment processes, only dichromate sealing and silicate sealing processes appear to be able to meet the requirements for the applications of hard anodized aluminum. Unfortunately, hexavalent chromium is a known carcinogen and changing federal regulations dictate the use of environmentally compliant chromate-free anodic coating seals that are capable of meeting new standards. Furthermore, dichromate sealing is not suitable for most dyed parts due to the intrinsic greenish yellow color originating from the incorporation of chromate ions into the micropores of anodic coatings.

The aim of this study is to make a comparative study of the performance characteristics of Type III anodic coatings sealed with eight different post-treatment processes and the novel trivalent chromium based seals. Neutral salt fog spray test (NSFST) measurements were done according to the procedure described in ASTM B117²¹. Wear characteristics and microhardness measurements were performed in order to quantify the effect of each post-

treatment process. Additionally, electrical properties of the sealed anodic coatings were investigated by measuring the breakdown voltages.

EXPERIMENTAL

The tested material was a wrought aluminum alloy (6061-T6), with the chemical composition shown in Table 1. Test coupons were degreased and cleaned in alkaline cleaner. Cleaned and degreased coupons were rinsed in flowing tap water for 1 min. After alkaline etching and rinsing, coupons were deoxidized in mixed acids at room temperature and rinsed in flowing tap water for 1 min. A regular anodizing procedure was used to obtain ~50 μm anodic coatings by a DC power supply: 190 g/L H_2SO_4 solution, ~6 g/L Al^{3+} ions at 0 °C, and the current density of 3.23 A/dm².

TABLE 1
CHEMICAL COMPOSITION OF THE ALUMINUM ALLOY (MASS %)

Si	Fe	Cu	Mn	Mg	Cr	Zn	Ti	Al
04-0.8	-0.7	0.15-0.4	<0.15	0.8-1.2	0.04-0.35	<0.25	<0.15	bal.

The anodized coupons were rinsed in flowing tap water for 1 min and room temperature DI water for 1 min. The processing details of the applied post treatment processes are listed in Table 2. All dyeing and sealing solutions were prepared with Deionized water. After sealing

TABLE 2
POST TREATMENT PROCESSING DETAILS

Post Treatment	Chemical Solution	pH	Temperature (°C)	Time (min)
Hydrothermal (A)	DI water + 1 g/L ammonium acetate	6.0	100	30
Hydrothermal (B)	DI water + 1 g/L ammonium acetate	6.0	100	120
Nickel Acetate	4% Nickel acetate Seal	5.8	88	20
Nickel Fluoride	3.5 Nickel fluoride Seal	5.8	32	10
Sodium Dichromate Seal	5 Wt% Sodium dichromate	6.0	95	15
Sodium Silicate Seal	20% Sodium silicate solution	11.2	85	10
Dye	10 g/L black dye	5.0	60	20
Dye + Nickel Acetate	10 g/L black dye and 4% Nickel acetate Seal	5.0 5.8	60 88	20 20
Trivalent Chromium	20% Trivalent chromium Seal	3.8	21	5

and rinsing, the excess water on the surface was removed with oil-free pressurized air. The resultant anodic coating thickness was measured in accordance with ASTM B244²² (Standard Test Method for Measurement of Thickness of Anodic Coatings on Aluminum and of Other Nonconductive Coatings on Nonmagnetic Basis Metals with Eddy-Current Instruments) using a pre-calibrated eddy current instrument. On each sample ten data points were obtained at different locations, and the average value was accepted as the anodic film thickness.

Corrosion resistance testing was done on test coupons for each post-treatment process using a neutral salt fog salt spray chamber maintained in accordance with ASTM B117²¹ (Standard Practice for Operating Salt Spray (Fog) Apparatus). A failure occurred when there were more than five pits developed on a total sample surface area of 193.5 cm² from one or more test samples as stated in MIL-A-8625F²³ (Anodic Coatings for Aluminum and Aluminum Alloys).

Wear resistance testing was performed on eight coupons for each post treatment process using CS 17 wheels, a load of 1000 grams, and a speed of 70 rpm for 10,000 revolutions in accordance with FED-STD-141²⁴, Method 6192. The CS 17 wheels were resurfaced after every 10,000 revolutions by running them for 50 revolutions over S-11 abrasive discs. The recorded temperature was 23 ± 2 °C and the relative humidity was 22 ± 3 %. The wear resistance was measured on both sides of each conditioned coupon. The microhardness of each test coupon was examined by a microhardness tester (HV_{0.05}; load 50 g, duration 15 sec). The average value of three measurements was taken as the microhardness of the anodic film.

Voltage breakdown testing was performed on two coupons for each post-treatment process using the methods described in ISO 2376²⁵ with a single ball electrode and a 500 g load. The voltage was increased 25 V/s with breakdown defined as passing 10 mA current. The average value of ten measurements was taken as the breakdown voltage of the anodic film. Test coupons were cured at ambient conditions for more than 48 hours prior to testing. Tests were performed at 23 ± 2 °C and 22 ± 3 % relative humidity.

RESULTS AND DISCUSSION

Corrosion Resistance

After exposure to the neutral salt fog spray test (NSFST) in accordance with ASTM B 117²¹, test coupons were visually examined to determine the total number of pits. Table 3 shows the salt spray corrosion results for all post-treated anodic coatings. When the test coupons had more than five pits in a total of 193.5 cm² from one or more test pieces, corrosion test stopped. Bare anodic coating without any dye or seal application failed within 48 hours. Dyed test coupons failed during the first day of testing, even when the parts were sealed in nickel acetate seal at 88 °C for 20 minutes. Cold nickel fluoride sealed anodic hard-coats failed at 70 hours.

Hydrothermally sealed test coupons failed between 320 and 380 hours. Test coupons sealed in nickel acetate bath failed at 495 hours. The best NSFST performance was observed for sodium dichromate (95 °C, 15 min.), sodium silicate (85 °C, 10 min.) and trivalent chromium (21 °C, 5 min.) seals.

Comparative salt spray performance results clearly show that hard-coated samples sealed at room temperature with environmentally friendly trivalent chromium passed the corrosion requirement of MIL-A-8625F²³ even at 1000 hours.

Unlike Type II anodized (<25 μm) aluminum, hard-coated (~ 50 μm) samples had much lower localized corrosion resistance. For instance, both unsealed and nickel acetate sealed Type II anodized 6061-T6 aluminum exceeded 4000 hours of NSFST before failure. Li et al.,²⁶ observed that hard-anodized aluminum has small cracks and pores caused by the internal

TABLE 3
NEUTRAL SALT FOG SPRAY TEST (NSFST) RESULTS FOR HARD-COATED AND POST TREATED ALUMINUM

Post-Treatment	Hours	Number of Pits
Black Dye	21	>5
Black Dye + Nickel Acetate	23	>5
Bare Hardcoat	43	>5
Nickel Fluoride	70	>5
Hydrothermal (B)	327	>5
Hydrothermal (A)	374	>5
Nickel Acetate	495	>5
Sodium Dichromate Seal	1000	<5
Sodium Silicate Seal	1000	<5
Trivalent Chromium Seal	1000	<5

stresses generated by the growth of the oxide at the substrate/oxide interface. Such a surface with cracks may be responsible from the poor corrosion resistance of the hard-anodized samples, even though the coating was thicker. Additionally, fissures and voids can form when the parts are transferred from the 0 °C anodizing bath to a room temperature rinse tank²⁰. These fissures and voids may be too large to be filled and closed with the post-treatment processes investigated in this study. However, localized corrosion resistance of hard-coated samples was significantly improved by using sodium silicate, sodium dichromate, and trivalent chromium seals. Further studies are required to verify the presence of surface defects formed on the hard-coated samples.

Wear Characteristics

Wear resistance of sealed and unsealed hard-anodized aluminum is shown in Figure 1. The military specification, MIL-A-8625F²³ states that a hard-anodized aluminum have a maximum weight loss of 1.5 mg/1,000 cycles. The unsealed hard-coated aluminum surface had an average wear index of 0.84 mg/1,000 cycles. Trivalent chromium sealed samples did not change the wear resistance and outperformed the sodium silicate (0.92 mg/1,000 cycles) and sodium dichromate (0.98 mg/1,000 cycles) seals.

The change in wear resistance after these post processes can be explained by the sealing mechanisms and the formation of end products on the surface. Hydrothermal, nickel acetate, and black dye with nickel acetate post treatments sealed the pores by hydrating the aluminum oxide layer to the softer boehmite-like complexes and resulted in a large decrease in wear resistance (see Figure 1). On the other hand, those processes that plug the pores with a

precipitate of some form, like trivalent chromium, nickel fluoride, sodium silicate, and sodium dichromate sealing had a weight loss that still met the MIL-A-8625F²³ specification.

Microhardness

The microhardness ($HV_{0.05}$) results are shown in Figure 2. The microhardness values range from 357 to 403 $HV_{0.05}$ for all samples and the variation is well within the repeatability of the microhardness test method. A correlation of microhardness test data between laboratories is reported in ASTM E384²⁷ (Standard Test Method for Microindentation Hardness of Materials). The repeatability, differences due to test error between two test results in the same laboratory on the same material, is ± 65 HV for non-ferrous samples with a load of 50 gf and a Vickers hardness of 375 $HV_{0.05}$. On the other hand, the repeatability, differences in test results for the same material in different laboratories, is ± 75 HV for non-ferrous samples with a load of 50 gf and a hardness of 375 $HV_{0.05}$.

The data in Figure 2 suggests that there are no differences in microhardness ($HV_{0.05}$) for unsealed and sealed samples because the range of microhardness data (46 HV) is well within the error of the test method. Similar results with no differences in microhardness values between sealed and unsealed aluminum samples were reported by other research groups²⁸.

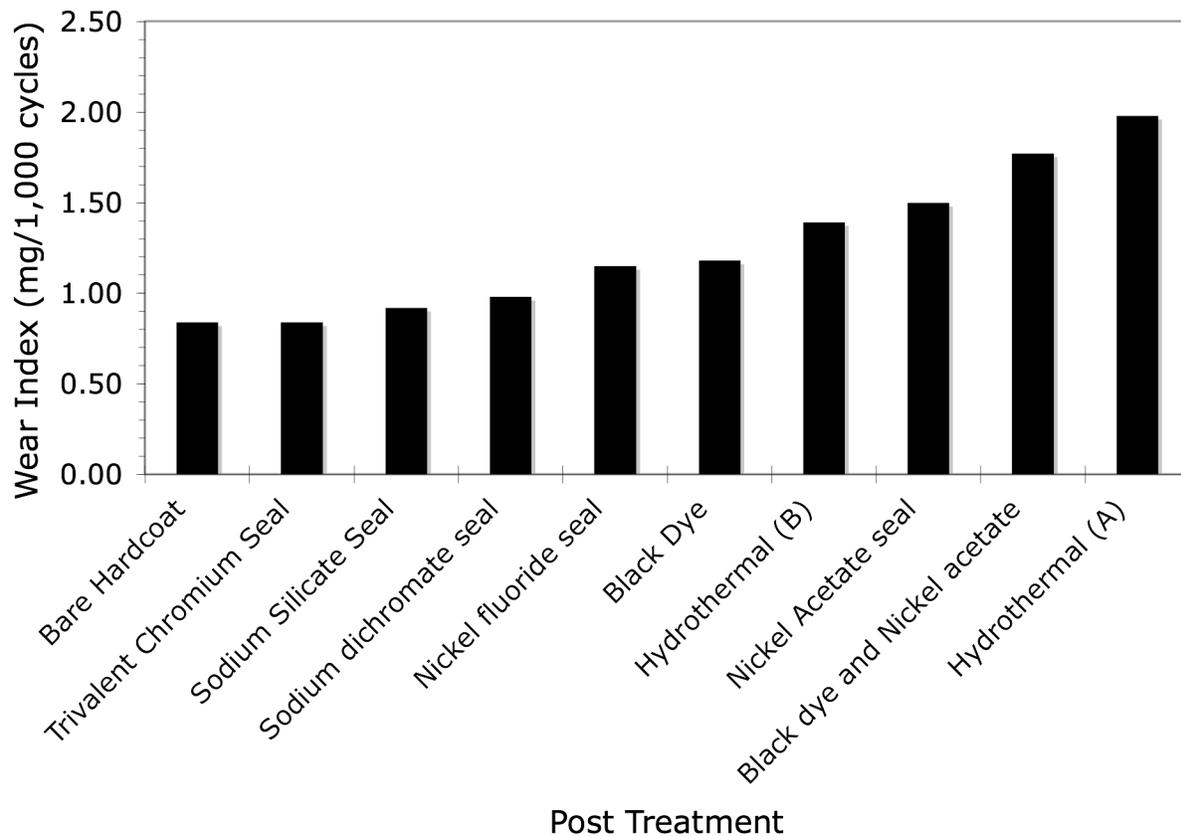


FIGURE 1 - The effect of sealing on wear resistance of hard-anodized aluminum.

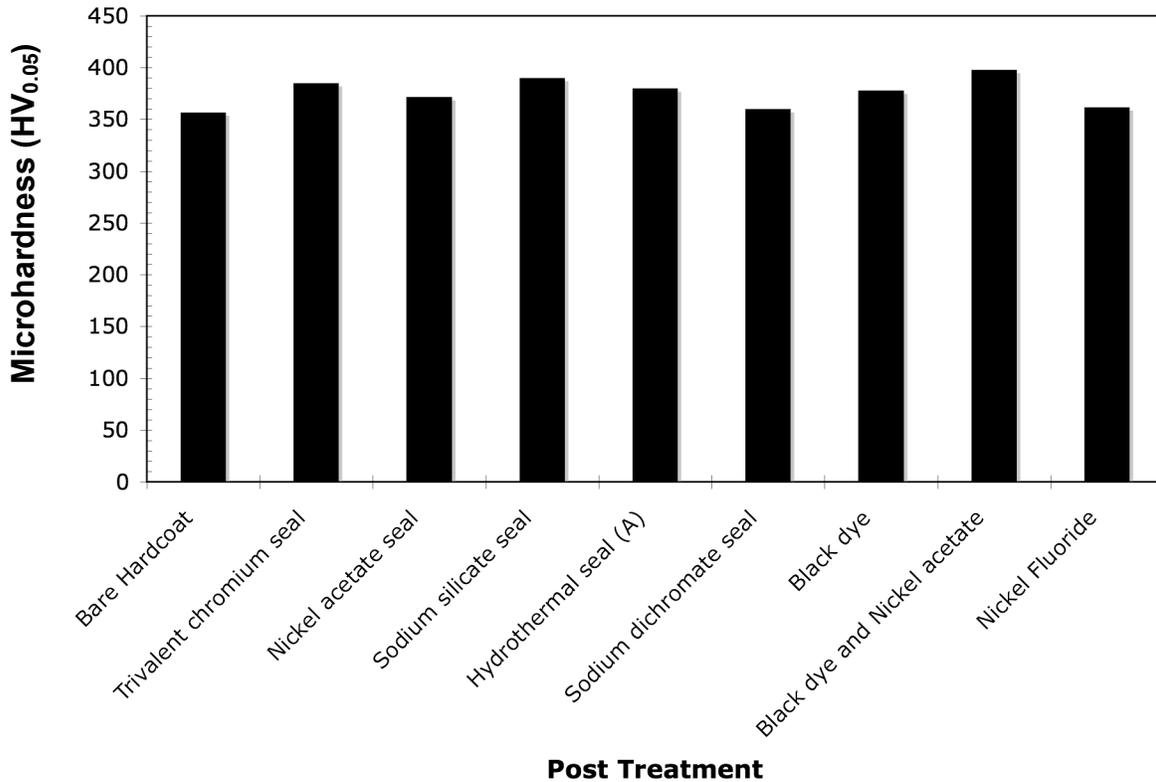


FIGURE 2 - The effect of sealing on the microhardness (HV_{0.05}) of hard-anodized aluminum.

Electrical Properties

Breakdown voltage per micron (V/ μm) for unsealed and sealed samples are shown in Figure 3. Unsealed hard-coats had a breakdown voltage of 29 V/ μm . It is important to mention that sealing with sodium silicate significantly reduced the breakdown voltage to 19 V/ μm . All other sealing processes increased the breakdown voltage. Hydrothermally sealed samples had breakdown voltages close to 40 V/ μm . Breakdown voltage values of trivalent chromium sealed hard-anodized samples are comparable to hydrothermally sealed samples and averaged around 36 V/ μm .

As shown in Figure 3, hydrothermal sealing in boiling Deionized water enhances the dielectric strength of anodic coatings. Increasing the hydrothermal sealing time from 30 minutes to 120 minutes does not improve the corrosion resistance (see Table 3) and dielectric strength while substantially deteriorating the abrasion resistance of hard-anodic coatings (see Figure 1).

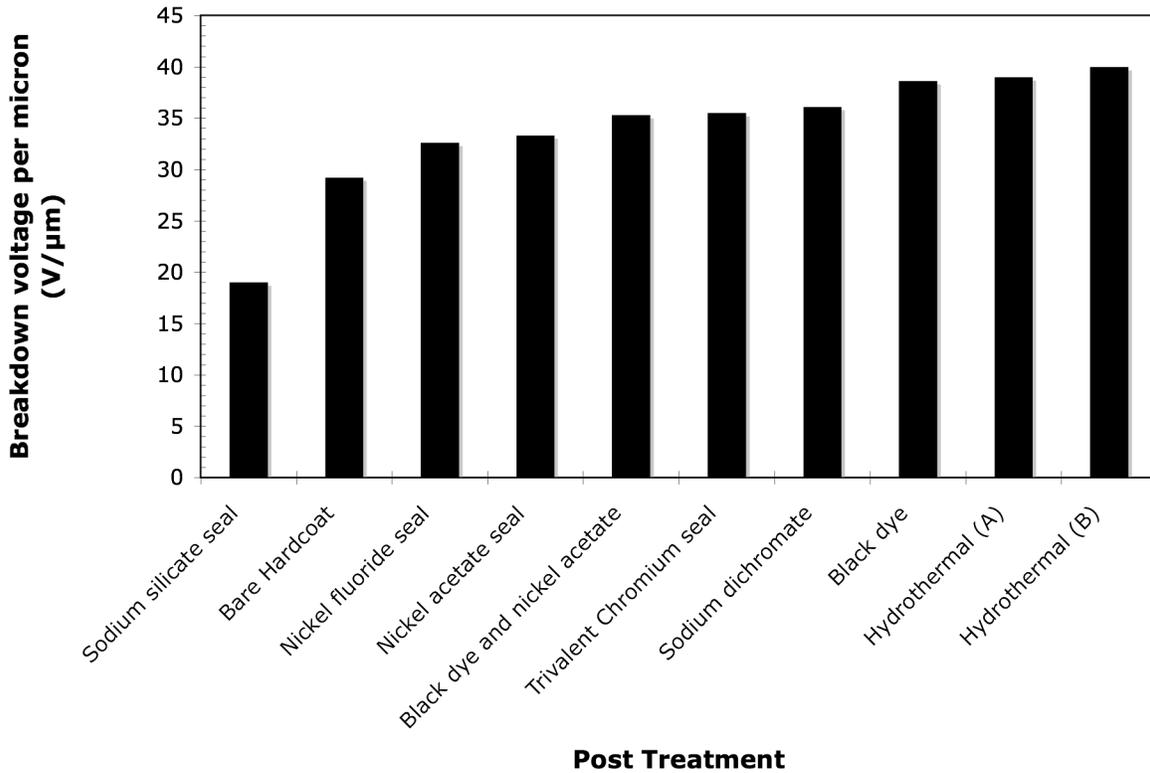


FIGURE 3 - Electrical properties of hard anodized aluminum sealed with different post treatment processes.

CONCLUSIONS

Environmentally friendly trivalent chromium based anodic seal is able to meet the requirements for the applications of Type III anodized aluminum. All post treatment processes used in this study decrease the wear resistance of hard-coated aluminum except trivalent chromium based seals. Trivalent chromium, dichromate, and silicate based seals provided the best corrosion resistance and wear index. Although silicate sealing enhances the corrosion resistance of hard anodized aluminum without significantly reducing the abrasion resistance, it is not suitable for applications where the dielectric strength of an anodic coating is an important factor. On the other hand, trivalent chromium based seal readily matches the technical, process, cost, and flexibility of dichromate based seals. Furthermore, unlike hexavalent chromium, trivalent chromium based seals are easy to operate and does not require high operating temperatures. Furthermore, OSHA PELs suggest that the use of trivalent chromium based seal is acceptable.

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