Alternative to conventional aluminum anodize seals with an environmentally friendly seal process

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Sealing of an anodized surface is a standard practice to complete anodizing process and finish. There have been various seal processes that use hot deionized water (boiling temperatures), use of metal salts (Nickel Acetate, etc.), chromate sealing (such as Sodium Dichromate) and some other proprietary chemistry. This paper will describe a new process for sealing anodized aluminum with environmentally friendly, room temperature application and substantially less process time with outstanding results.

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Introduction

This paper will outline various sealing techniques for anodized aluminum. It will address a new environmentally friendly, cost efficient and performance oriented anodic seal with a unique and patented trivalent chromium post treatment chemistry for anodized coatings.

Sealing of Anodized Aluminum

Essentially, sealing is a process of chemical change whereby oxide coating is converted into a more chemically stable hydrated form, which will better resist the attack of the atmosphere and chemicals. Sealing produces a chemical change in the coating, converting it from aluminum oxide to bohmite, a stable aluminum hydrate. In the course of this change the coating swells and the pores are closed, although if there has been some widening of the pores as can happen under some anodizing conditions, they may not be fully closed towards the surface. As might be expected from the small dimensions involved the evidence of this pore closure is not absolutely conclusive, but the high resistance of these films to corrosion attack supports the general view. Sealing is, therefore, the most important operation of the whole process. In other words, sealing makes an anodized part completely finished with an oxide film. It determines the performance of the anodized part during its service. A study by Wood and O'Sullivan concluded that sealing occurs in three overlapping stages -(1) initial precipitation of material in the pores especially near the outer film surface (2) the formation of crystalline material at the surface and (3) further changes in the film depth involving aggregation of the oxide microcrystallites and a redistribution of porosity. Although at this stage the crystalline material could not be identified, it was later confirmed that it was largely bohmite and is the cause of the visible "smut" seen on most sealed anodic film surfaces. The smut formation is a normal part of the sealing process and it has been shown to be largely bohmite. It is visible as an uneven chalky or powdery deposit, which is most easily seen on color anodize work or bright anodized finishes. It occurs to varying extents with all normal sealing practices and its absence is often an indication of a fault in the sealing process. Smut or bohmite represents the completion of a sealing reaction at the surface of the film. This "surface sealing" is very important, as it represents the main chemical resistance of the film. If bohmite formation were intentionally prevented, performance of anodized part would be adversely affected resulting in poor corrosion resistance. Sealing of anodic surface provide better corrosion resistance, enhance adhesion capability and also help reduce color degradation of dyed anodic surfaces.

Most common sealing is hot water sealing. A wide variety of substances have been proposed for sealing anodic oxide coatings. They include solutions of various metal salts, which when absorbed into the anodic oxide coating, are hydrolyzed and precipitated into the pores as hydroxides. Probably most common is nickel acetate, sometimes also in conjunction with cobalt acetate. Chromate sealing using sodium dichromate is used mostly for military applications. Other seals include nickel fluoride, nickel sulphate, etc.



G. UNSEALED ANODIC FILM STRUCTURE

Ь. PRECIPITATION OF GEL ON PORE WALLS AND OUTSIDE OF FILM

1,0 approx. 100°C

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PSEUDO BOHMITE, CONTINUING REACTION RATE CONTROLLED BY DIFFUSION OF WATER INTO FILM AND ANIONS INTO THE LIQUID

General mechanism of water sealing of anodic oxide coatings

Hot Water Sealing

One of the most common sealing for an anodized coating is hot water, usually at boiling temperatures. Most common practice is to use deionized water at temperatures of 96° C to 100° C. A small amount of air agitation is suggested to keep homogeneous temperature through the entire height of the sealing tank. Ammonia and acetic acid are commonly used to adjust the pH of the seal bath, as these ions are not deleterious. Ammonium acetate addition can help buffer the pH and hence improves sealing quality. Phosphate ions in addition to inhibiting sealing, can also strip anodic coatings if their concentration exceeds 100 ppm. The pH range of 5.5 to 6.5 is recommended for maintaining quality of anodic seal. Bohmite formation is strongly pH dependent and therefore, pH below 4.0 forms extremely poor quality of seal while above pH of 6.5 the level of sealing smut tends to increase considerably. Sealing time is also an important factor for hot water sealing. A minimum of 20 minutes is required, however for most sealing 30 to 40 minutes are employed. As a general rule, sealing time of 2 to 2.5 minutes per micron of oxide film thickness is used for hot water sealing. Formation of sealing smut is a normal part of he sealing process and it has been shown to be largely bohmite. It occurs to varying extents with all normal sealing practices and its absence is often an indication of a weakness in sealing process. Smut represents a completion of a sealing reaction at least at the surface of anodic film.

Sealing in metal salt solutions

A wide variety of metal salts are in use as anodic seal which, when absorbed into the anodic oxide coating, are hydrolyzed and precipitated into the pores as hydroxides. Probably the most widely used metal salt is nickel acetate, sometimes also in conjunction with cobalt acetate. It is well known that nickel and cobalt can be detected in the pores of anodic oxide coatings sealed in solutions of their acetates or sulphates. Therefore, in such solutions there are two processes are proceeding simultaneously, sealing by the formation of bohmite and plugging of pores by precipitation of a metallic hydroxide.

Nickel Acetate -

The main advantage of sealing in nickel acetate is found in dyed anodic coatings as it avoids to leaching of dyes during the sealing process. Probably the greatest benefit of sealing in nickel salts is that it can make the process less sensitive to the common sealing variables, and, in some cases, it can make use of tap water rather than deionized water possible for sealing. However, nickel salt sealing has some weaknesses. For example, compared with hot water sealing, those sealed in nickel salt solutions develop a chalky surface deposit after a short period of weathering, and though it can be largely removed by cleaning with a

suitable lightly abrasive cleaner, the chalky film reappears. Nickel salt sealed films tend to break down and show numerous fine pin points of corrosion whereas hot water seal or steam seal films show few pits, which, however tend to be larger.

Chromate Sealing -

Sealing in sodium dichromate has become less common due to environmental guidelines and regulations. However, there are still users with application for chromate sealing. It provides good corrosion inhibition or resistance, particularly when used on anodized aluminum alloys with copper. It provides a characteristic yellow color to the coating. Studies show that optimum sealing with chromic salts is produced in a solution where pH is controlled between 6.32 and 6.64, with complete sealing being achieved in 10 minutes. At higher pH values sealing rate is higher, however at a pH value of 8.5 anodic films starts to dissolve. The corrosion resistance properties with chromic sealing are well known, but it apparently has less effect on the mechanical properties of anodized aluminum than hot water sealing. Chromate sealing is therefore generally recommended for aluminum in military or aeronautical use.

Other Aqueous Sealants -

A number of other aqueous sealants have been mentioned in the literature. They include sodium silicate sealing, nickel salts combined with high alkali, molybdate solutions, and water sealing followed by disodium hydrogen phosphate for double sealing effect.

Sealing Efficiency

In spite of the profound effects of sealing on properties and performance of anodic oxide coatings, there has been a need for a good infallible test to indicate when sealing has been satisfactorily performed. The most frequently employed property has been the increased resistance to chemical attack and this can be judged visually by the appearance of the coating, or to what extent it absorbs a dyestuff. It can also be assessed quantitatively by a photometric measurement of the depth of this dyeing, or finally with more certainty by measuring the loss of weight in specified acid solution.

Certain tests have been used in production control to assess the efficiency of sealing. However, it is important to note that sealing tests may give misleading results on coating that have been stored for some time. Therefore, it is imperative that these tests are performed as soon as possible following anodizing process cycle (usually 2 to 4 weeks or less). This paper is attributed to a new technology for anodize seal and hence a very brief information is included for seal tests.

Dye Stain Tests

This is a common test for checking seal application. At one time, this was accepted as only test needed to check if part has been sealed. However, now it is known that failure to absorb dye represents only the initial stages of the sealing operation, and they are therefore regarded as resistance to marking tests, which may be specified where a surface is intended for mild indoor service, but the tendency is to delete from the standards.

Acid Dissolution Tests

These tests involve number of different acids to check sealing on a part surface. They include acidified sulphite test, phosphoric acid and chromic acid test, and acetic acid and sodium acetate test.

Sulfur Dioxide Tests

These tests include sulfur dioxide in acetone and sulfur dioxide humidity test.

Other Chemical Tests

Other solutions that have been used in weight loss tests to indicate the degree of sealing include nitric acid, hydrochloric acid, sulphuric acid, caustic soda, phosphoric acid as well as mixtures of these. The nature of the sealed anodic coating is such that almost any chemical reagent, which attacks it, can be adjusted to an appropriate strength and temperature so that it will attack considerably the unsealed coating during a period in which there is no applicable attack or loss of weight on an adequately sealed surface. The main requirement is that the solution does not deposit solution products into or onto an anodized surface.

Dye Absorption Tests

There are a number of tests in current use, which depend on the extent to which the anodized surface absorbs dyestuff after it has been exposed to a suitable chemical reagent. Much work was carried out on the development of dye spot tests, and the currently used tests have evolved over a period of several years. This is a simple test, which is non-destructive and is ideal for production control, but one of the problems is the subjective nature of the evaluation. Limitations of the dye spot test method are that it can not be used with dark colored anodic finishes, that it is less sensitive to seal quality with nickel or cobalt sealed work, and that it can give misleading results when some anti-smutting additives are used in the sealing baths.

Impedance and Admittance Tests

Measurement of impedance, or the resistance of the anodized surface to the passage of alternating current under precisely specified conditions, is the latest arrival in the catalog of test methods for measuring sealing efficiency. This method is now generally accepted and covered in ISO 2931. A limitation on admittance and impedance testing is that the values obtained are dependent on many factors other than just thickness and seal quality, and they can give misleading information with electrolytically colored finished and when sealing additives are present in the seal solution. They are also not very sensitive to the presence of silicate and phosphate contamination in the seal water. This test should not be used as the only test; it should rather be used in conjunction with the dye spot test and acid dissolution test.

Gravimetric Test

The most direct method of estimating sealing efficiency is by measuring the increase of weight that takes place, but it is only applicable in laboratory work because it is destructive, the unsealed coating must be thoroughly dried and its weight known in order to get maximum information from the test. The weight gain on sealing is expressed as a fraction of the unsealed coating weight. Gravimetric measurements are best employed when the whole procedure is completely under laboratory control.

Emissivity Measurement

The emissivity of anodized aluminum is affected by the presence of hydroxyl radicals and since these increase with sealing it should be possible to monitor the progress of sealing provided that a sensitive enough apparatus were available for detecting infrared radiation.

Body

Over the years, conventional anodic seals have been in use for sealing anodic oxide film. As mentioned earlier, it provides a complete anodization of aluminum offering corrosion resistance, hardness and durability of oxide deposit. However, each process has some weakness. Boiling water requires purity of water (generally DI water) and energy to heat up; chemical salts require energy to heat up and also proper disposal to meet regulatory guidelines.

Now there is an environmentally friendly anodic seal. It operates at ambient temperature and in most cases, would not require any expensive disposal to meet affluent guidelines due to very low concentration. This material called, trivalent chromium post-treatment can offer outstanding performance against corrosion resistance and it can save thousand of dollars in energy cost as it operates at room temperature. Tests have been performed on various aluminum alloys and they all have shown results that are beyond any practical specifications.

NAVAIR, the United States Navy had performed initial testing with their patented and unique trivalent chromium post treatment chemistry as anodic seal. Their results were very encouraging. Most aluminum alloys were able to achieve up to 2000 hours of salt spray with concentration of trivalent chromium post treatment material ranging from 10 to 20 % by volume with various time cycles that ranged from 10 to 20 minutes.

Current industry standards for anodic seal include adhesion testing per ASTM D3359, coating weight per ASTM B680, seal capabilities per ASTM B136 that includes nitric acid spot test and dye spot test. Corrosion resistance standards vary depending on the type of anodizing performed. Type I, IB, IC, II and IIB specifies 336 hours per MIL-8625F. Class II with 0.4-mil oxide thickness specifies 1000 hours of salt spray per AAMA 611-98. Class III type anodizing (hard coat) with 0.7-mil oxide thickness requires 3000 hours of salt spray.

This new chemistry has been pursued due to its tremendous success in initial testing. Its research followed industry standards such as nitric acid spot test in accordance with ASTM B136 and corrosion resistance in accordance with ASTM B117. Various aluminum alloys were tested (with sulfuric acid anodize) – Type II with and without any proprietary anodizing additive, Type II dyed, Type II bright dipped and Type II with electrolytic color. Type III included standard Type III anodize and also with dye. Trivalent chromium post treatment chemistry concentrations ranged from 5% by volume to 25% by volume. Immersion time of anodized samples in trivalent chromium post treatment is from 2 to 10 minutes. Test samples with only 2 minutes of immersion time showed definite corrosion protection. Neutral salt spray results were very encouraging as 3000 hours salt spray resistance has been observed with both 5% and 25% concentration. All test samples were removed between 2700 and 3120 hours due to availability issue of salt spray chamber. There was no failure suggesting that the capability may be higher since we could not run test samples to the failure in salt spray chamber.

One of the biggest advantages of using trivalent chromium post treatment as anodic seal is the temperature. Test samples were run at room temperature (65° – 75° F.) and also at elevated temperature of 120° F. Test panels processed with both temperatures went 3120 hours without any sign of failure. This experiment suggested that apparently there are no advantages of elevated temperature.

As mentioned above, there were various test parameters with processes and the type of anodizing. Type II sulfuric acid anodizing with a proprietary

additive in anodizing bath was used on alloys 2024-T3, 6061-T6 and 7075-T6. Immersion time ranged from 2 to 10 minutes, ambient temperature and trivalent chromium post treatment chemistry's concentration range of 5% to 25% by volume. Salt spray testing was terminated after 2765 hours. No pitting was observed.

Type II sulfuric acid anodizing without any additive was tested on alloy 6061-T6. Immersion time ranged between 2 and 10 minutes with the same trivalent chromium post treatment concentration of 5% to 25% by volume. Temperature varied between ambient at 65° F. to 120° F. All test panels went 3120 hours in neutral salt spray without any failure or pitting.

Next experiment involved Type II sulfuric acid anodize panels that were bright dipped. Alloy selected was 6061-T6. Process cycle included 5 minutes immersion time, ambient temperature and 5% of trivalent chromium post treatment by volume. Anodize bath had proprietary additive present. No failure was observed above 2208 hours in neutral salt spray.

Type II sulfuric acid anodized test panels were processed in a dye application for test of trivalent chromium post treatment chemistry as anodic seal. Process parameters had process cycle time of 2 to 5 minutes, concentration of 5% by volume of trivalent chromium post treatment, and ambient temperature without proprietary anodizing additive. There were no failures or pitting in salt spray after 3000 hours.

A similar test was performed for electrolytically colored test panels. Again the process was 5 minutes of immersion time in this unique chemistry bath that had 5% concentration by volume with ambient temperature. Results were identical as there were no salt spray failures after 3000 hours.

Another test was performed for Type III sulfuric acid anodized test panels. These panels were not dyed. Alloy selected was 6061-T6. Process application was 5 minutes of immersion in trivalent chromium post treatment bath @ 5% to 25% range of concentration by volume and ambient temperature. These panels were placed in neutral salt spray test per ASTM B117 and were taken out of the salt spray chamber due to availability issue after 2756 hours. There were no failures.

Type III sulfuric acid anodized test panels were followed with a black dye application. This time three different alloys were selected. They were 2024-T3, 6061-T6 and 7075-T6. Immersion time in trivalent chemistry bath was reduced to only 2 minutes. Bath temperature was ambient at 65^o F. and the concentration of trivalent chromium post treatment was also limited to 5% by volume. Salt spray

test was terminated at 2756 hours. There was no color degradation of dyed panels and no failures.

Advantages of using trivalent chromium post treatment

Our test data showed outstanding results with various experiments with usage of trivalent chromium post treatment as anodic seal for anodized aluminum alloys. First, since this process operates at ambient temperatures, there is no energy involved to heat up the bath. This alone offers a tremendous advantage over some of the common anodic seals such as hot water seal that operates at ~ 200° F. or nickel acetate seal that requires $\sim 190^{\circ}$ F. This offers a substantial cost savings in energy cost. Unlike other anodic seals, this unique trivalent chromium post treatment chemistry has a short immersion time that can vary from 2 to 10 minutes. This allows more production volume. However, the biggest advantage of using this trivalent chromium post treatment as anodic seal is that it is environmentally friendly. This process does not require any ventilation. As the concentration of trivalent chromium post treatment is rather low and does not contain any hexavalent chromium or any other hazardous or controlled substances, waste disposal is relatively a non-issue. Though it is suggested that you may check with your local, State and Federal agencies for proper disposal guidelines for this proprietary trivalent chromium post treatment as anodic seal.

<u>Summary</u>

Anodic seal is an integral and important part of anodizing process. It actually provides a complete finish of aluminum anodizing. There have been some very common seals over the years such as hot water seal, nickel acetate seal and other seals with chemical salts. However, either energy cost is involved and/or hazardous chemicals and its disposal were the issues. At the same time, any such anodic seal had rather a shorter bath life and required to drain and recharge the bath on a regular basis to maintain the performance.

Recent technological development of using this patented trivalent chromium post treatment offers quite a few benefits over conventional anodic seals. Corrosion resistance tests showed that it outperformed any conventional seals as an average salt spray hours were from 2700 to 3160. There is no advantage to operate anodic seal bath of this chemistry at an elevated temperature as tests showed that there is no significant difference in salt spray hours. Therefore, it is operated at ambient or room temperature thus offering tremendous cost savings of energy cost. This new anodic seal also has advantage for high production volume job shops since the immersion time is rather very short as compared to current conventional anodic seals. It is also possible to consolidate two baths of conversion coating and anodic seal (using the same trivalent chemistry) since it can operate within required parameters for both applications.

It is suffice to say that the most important aspect of using this newly developed, patented trivalent chromium post treatment, as anodic seal is it is environmentally friendly. There is no need for ventilation or exhaust for this new seal bath and since it does not contain hexavalent chromium or any other regulatory controlled restricted substances, it can be under "Green Technology" category.

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