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SEALING AND INHIBITING CORROSION OF ANODIZED ALUMINUM

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This application is a continuation-in-part of my copending application Serial No. 59,509, filed September 30, 1960, now abandoned.

This invention relates to an improved method of aqueous hydration of anodically formed aluminum oxide layers on aluminum and aluminum base alloys by the application of corrosion inhibiting and sealing agents to such layers. More particularly, the invention concerns the treatment of anodically formed aluminum oxide layers of films with water soluble basic organic nitrogen compounds, alone or in combination with one or more water soluble inorganic salts of metals of Group VI of the Periodic System. Another aspect of the invention concerns the treatment of anodically formed aluminum oxide layers with combinations of said water soluble inorganic salts per se.

Aluminum oxide layers are conventionally formed by anodizing procedures involving the use of baths containing sulfuric acid, aliphatic and alicyclic water soluble carboxylic acids, chromic acid, or phosphoric acid, or mixtures or combinations of these acids to provide an electrolyte of the oxide dissolving type. The anodizing is customarily accomplished by the passage through the electrolyte in which the aluminum is the anode, of direct or alternating current, or a combination thereof. A typical anodizing bath is one containing from about 10 to 20 percent of sulfuric acid by weight, at a temperature of 68°–72° F., using direct current at a voltage of about 5 to 20 volts at a current density of 10–15 amperes per square foot. The duration of the treatment determines the thicknes of anodic film formed.

The novel method of the present invention is adapted for retarding corrosive action on aluminum oxide films of all types, including bright anodized, matte surface, and hard-coat anodic coatings, but it is especially valuable in conjunction with bright anodized surfaces.

The principal purpose of an anodic film is that of providing a mechanical and chemical protective layer to prevent general or selective corrosion or atmospheric oxidation of the underlying aluminum metal surface. The amount of possible corrosive action is determined by the environment in which the anodized article is employed. Thus for automotive bright trim and various types of domestic appliances where frequent exposure to moisture, salt, dirt, and other corrosive agents occurs, the highest possible quality of the anodic surface is required to retain the initial attractive appearance. For such applications anodic film thicknesses in the range of 0.1–0.6 mil are used. There are also employed for such anodized aluminum alloy surfaces having optical properties which entitle them to be classed as bright anodic surfaces, aluminum base alloys having a chemical and metallurgical composition promoting the formation of a relatively clear transparent anodic film upon anodizing. Such alloys are those containing a minimum quantity of elements other than aluminum with the exception of alloys containing magnesium and magnesium silicide. Commercial designations of these alloys include Aluminum Association numbers 1199 (super pure aluminum), 1188, reflectance sheet 5357, 5457, 5557, 5657, 6063, and 6463. Bright anodic coatings on all of these alloys are capable of being improved by the novel process of the present invention.

It is well known that during anodizing in commercial

electrolytes such as sulfuric acid which provides continuous solvent action on the aluminum oxide film during formation, pores are formed which provide the necessary channels for passage of current through the film during the continuing growth of the oxide layer. The resulting film structure consists of large numbers of hexagonally shaped oxide cells. The center of each hexagon contains the pore, the dimensions of which are determined by the anodizing potential between the electrolyte and the anodic aluminum article. Thus, it has been found that using a 15% sulfuric acid bath, the pore diameter is approximately 150 Angstrom units and the wall thickness of each pore is approximately 8 Angstrom units per volt. It has been found that there are approximately 400×10^9 pores per square inch of anodic surfaces. Additional measurements of the dimensions of the pores in the anodic film have indicated that the volume occupied by the pores is approximately 5–15% of the entire volume of the film.

In order to reduce the porosity of anodic films there has long been used a sealing step carried out commercially by treatment of the anodized aluminum with hot water at a temperature between about 180° F. and the boiling point. This sealing step is essentially a chemical hydration of the anodically formed anhydrous oxide film. If the anodically formed film is subject to prolonged atmospheric exposure or to contact with a moist environment at a temperature below about 180° F. hydration gradually takes place with the formation of aluminum oxide trihydrate. This form of oxide has been found by experience to be less desirable from a protective standpoint than that obtained by sealing with hot water, whereby aluminum oxide monohydrate is formed. The mechanism of monohydration has been described in "Surface Treatment and Finishing of Aluminum and Its Alloys," by S. Ernick and R. Pinner, pages 354–369. During monohydration of the anodic oxide, a 10–20% film volume increase is achieved, and it is believed that the pores are substantially closed by this hydration step. Experience has proved, however, that simple hot water sealing fails to give adequate protection to the coating against corrosion. Accordingly, attempts have been made in the prior art to improve corrosion resistance of the anodic coatings by incorporating in the sealing bath various inorganic and organic chemicals, such as dichromates, nickel acetate, chlorinated paraffin, molybdates, and the like. Many of these chemicals are disadvantageous in that they result in imparting a dark shade to the aluminum oxide, thereby impairing its usefulness in applications where the original bright color of the aluminum is to be preserved. Thus, while the dichromates and chromates are effective anticorrosion agents, they must be applied in concentrations well above 0.1% and up to about 5% by weight to produce useful results, and these concentrations result in excessive yellow tinting of the surface of the anodic coating. On the other hand, the use of concentrations of dichromates and chromates below about 0.1% by weight, while avoiding the tinting problem, does not result in effective corrosion protection. Accordingly, it has been proposed in U.S. Patent 2,899,368, to employ molybdates of alkali metals as a sealing treatment for anodic coatings, in concentrations between 0.1% and 5%, and preferably about 2%. But the treatment with molybdates alone, while avoiding discoloration, still produces a final light grey color, takes as long as treatment with dichromate alone, and of itself produces no substantial improvement in corrosion resistance compared with dichromate.

Accordingly, it is an object of this invention to provide an improved sealing and corrosion inhibiting treatment for anodic coatings on aluminum and aluminum base alloys which will avoid discoloration of the coating,

reduce the time of treatment, and at the same time furnish virtually complete protection against all common forms of corrosive attack. It is a further object of the invention to provide sealing and corrosion inhibiting agents which will exert their action by adsorption on the anodic layers, but it is to be understood that applicant is not bound by any particular theory of the manner in which the novel agents of this invention produce their effect.

In accordance with one aspect of the present invention, it has been found that anodically formed aluminum oxide layers or films may be sealed and protected against corrosion by treatment with a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, such as, for example, a hydroxy group; or a water soluble salt thereof. Advantageously, there is employed for this purpose a basic organic nitrogen compound containing one or more nitrogen atoms in a heterocyclic ring, and which does not contain a polar substituent, such as, for example, a pyridine, quinoline, or quinazoline ring containing compound, or a water soluble salt thereof. Examples of heterocyclic nitrogen compounds which may be used include:

Nicotinamide
Ethyl qinolinium iodide
1-ethyl-2.6-dimethylquinolinium iodide
6,8-dichloro-2.4-(1H, 3H)-quinazolinedione.

There may also be employed water soluble carbocyclic compounds containing basic nitrogen in the form of a primary or unsubstituted amino group, such as, for example derivatives of aniline. Examples of such compounds include:

m-Tolylurea
Ethyl p-aminobenzoate.

These heterocyclic and carbocyclic compounds may be incorporated in the sealing baths in amounts ranging from as low as about 0.001% by weight to the limit of their solubility, but preferably in an amount ranging from about 0.1% to about 1.0%. They may be employed singly, or one or more of the compounds may be employed in conjunction. Their sealing and corrosion inhibiting action is believed to be attributable to adsorption on the anodic layer, accompanied by crosslinking effects, but applicant does not wish to be bound by any particular theory of action.

The organic nitrogen compounds will normally be applied to the coatings in aqueous solution at a temperature between about 160° F. and the boiling point, preferably between 180° F. and the boiling point, and at a pH between about 5 and about 8. They should therefore be stable at this pH range, and have a solubility in water greater than 1 millimole per liter at 25° C. Treatment time is about 15 minutes, but this may be varied according to materials and conditions.

Corrosion of anodic coatings is of two types: (1) pitting, characterized by formation of small pits bordered by whitish areas, and (2) clouding, hazing or bloom, evidenced by staining in irregular areas.

Two standard corrosion testing procedures have been used to evaluate the performance of the sealing and corrosion inhibiting compositions of this invention.

The test designated as the copper accelerated acetic acid salt spray test (CASS) was used to evaluate the performance of variations in the method of sealing in terms of resistance to accelerated corrosion environment. Briefly, the test employs a conventional salt spray cabinet having an exposure chamber provided with plastic coated sample racks allowing placement of test samples between 15–30° from the vertical and parallel to the principal direction of flow of corrosive sprays. The salt solution employed is prepared by dissolving 5±.1 parts by weight of sodium chloride in 95 parts of distilled water containing not more than 200 p.p.m. of total solids. The pH of this solution is adjusted to 3.2 by addition of acetic acid following which 1 gram of cupric chloride is added for each gallon of the salt solution. The exposure chamber is maintained at a temperature of 120° F. At the conclusion of the test, the exposed side of each panel is rinsed in distilled water and allowed to dry, permitting a qualitative or semi-quantitative evaluation of corrosive attack to be made.

A second corrosion test is known as the Corrodkote test. This is carried out in a humidity cabinet maintained at 98–100° F. with a relative humidity of 99–100%. In this test a corrosive paste is applied to the surface of the sample. The paste has the composition:

$FeCl_3 \cdot 6H_2O$	g.	0.99
$Cu(NO_3)_2 \cdot 3H_2O$	g.	0.21
NH_4Cl	g.	6.00
Kaolin (Florida, air-floated)	g.	180
Water (distilled or deionized)	ml.	300

After exposure, the samples are evaluated for corrosion.

The novel method of the present invention employing organic nitrogen compounds as additions to aqueous sealing baths and the improved corrosion resistance obtained is illustrated in Examples 1 and 2, but it is to be understood that these examples are not to be regarded as limiting.

In accordance with another aspect of this invention, the aforementioned organic nitrogen compounds may be employed in conjunction with one or more water soluble salts of metals of Group VI of the Periodic System, such metals including, for example, chromium, molybdenum, and tungsten. The chromium salt is preferably one in which the chromium is hexavalent, such as the chromates or dichromates. Ordinarily the alkali metal salts, including ammonium, sodium, and potassium chromates or dichromates will be employed. The molybdenum and tungsten salts may be employed in the form of alkali metal salts, such as sodium or ammonium or potassium molybdate, or tungstate.

The organic nitrogen compounds when added to the sealing bath act to retard the hazing type of corrosion, and are superior in this respect to either the dichromates or the molybdates. The latter are effective mainly in retarding the pitting type of corrosion.

However, when an organic nitrogen compound such as nicotinamide, and, for example, a dichromate, are employed in conjunction as bath additives, it is found that whereas the nicotinamide alone in a given test time of say 24 hours produces a satisfactory degree of corrosion protection, the combination of the organic compound with the dichromate imparts complete freedom from both pitting and clouding types of corrosion in the same test time. A similar effect is obtained with combinations of organic nitrogen compound and a molybdate. These effects are illustrated in Examples 2 and 3 below.

An even more complete corrosion protection is obtained when using the combination of organic nitrogen compound, dichromate and molybdate, illustrated in Example 4.

The remarkable degree of corrosion protection thus obtained appears to represent more than the additive effect of the individual bath ingredients, and to be indicative of a potentiating or synergistic effect. Moreover, the combination of compounds makes possible a drastic reduction in treating time, ranging from as little as ½ minute up to 15 minutes, as compared with normal sealing times of about 30 minutes as employed in this industry, with resultant economies.

The pH of the treating baths with the combination of organic and inorganic chemicals may range from about 5 to 8 in value, but a pH range of 6.0 to 6.5 is preferred. Bath temperatures range from 160° F., and preferably 180° F. to the boiling point of the bath. The dichromate or chromate concentration will generally be below about

0.1% by weight, down to about 0.005% by weight, thereby avoiding danger of tinting by the chromium salt. Whereas the effective lower limit of concentration for the dichromate would ordinarily be about 0.01%, the synergistic effect of the organic nitrogen compound makes it possible to obtain an equivalent protection against pitting with the use of only 0.005% dichromate. However, the preferred concentration of chromium salt is about 0.01%. The concentration of molybdate or tungstate may range from about 0.1% upward, but 0.1% is generally preferred.

The combination of the organic nitrogen compound and at least one salt of chromium or molybdenum makes possible not only complete corrosion protection, but satisfactory sealing in as little as ½ to 1 minute, and excellent sealing in from 10 to 15 minutes.

In accordance with another aspect of the invention, anodically formed aluminum oxide layers are treated with sealing baths containing combinations of two or more water soluble salts of metals of Group VI of the Periodic System. Advantageously, there are employed combinations of salts of hexavalent chromium, such as the previously mentioned chromates or dichromates, together with water soluble molybdates. Here also a potentiating or synergistic action exists between the dichromate on one hand and the molybdate on the other. It is believed that action of the dichromate and molybdaate is one of deposition or of absorption-adsorption on the surface of the anodically formed aluminum oxide layer of these ions in the form of double salts. Such a mechanism of deposition would necessarily limit the amount of surface available for molecular deposition. If either the dichromate or the molybdate agents are applied individually the surface will be saturated with respect to the particular agent. Moreover, if used in conjunction, it would be expected that the total deposition would be proportionate to the concentrations of the individual agents, and that no improvement could be expected beyond the additive effect of the two components. However, in accordance with the invention, it has been found that, by reason of the aforesaid deposition mechanism, the concentration of the dichromate, when used together with the molybdate, can be safely increased well beyond the point which would result in yellowing of the coating when such concentration of dichromate is used by itself. Conversely, the molybdate-dichromate combination makes possible a reduction in the concentration of dichromate, not only below what would ordinarily be its effective lower limit for producing corrosion resistance when employed alone, namely about 0.01% by weight, but enables the dichromate to attain equivalent corrosion resistant efficacy with as little as 0.005% present. The dichromates used must be compatible in solution with the molybdates, and both must be stable at the temperature employed. The dichromate concentration employed will generally be below about 0.1% by weight, thereby avoiding the danger of tinting. The presence of the molybdate permits this upper limit to be lowered to about 0.05% while still providing equivalent results. In general, however, it is preferred to use a chromate or dichromate concentration of about 0.01%. The molybdate concentration may range from about 0.1% to about 1.0%, but 0.1% is preferred.

The treating bath containing the combinations of chromium and molybdenum salts will have a pH in the range of about 5.0 to 8.0, and preferably between about 6.0 and 6.5, and the bath temperature will range from 160° F., and preferably 180° F. to the boiling point. Satisfactory sealing can be obtained in as little as ½–1 minute treatment time, and excellent sealing in 10–15 minutes. This aspect of the invention is illustrated in Examples 5, 6, 7, and 8 below.

It is to be understood that the novel method of this invention is applicable not only to bright anodized articles. The method can also be applied to matte surfaced anodized products such as those used for building construction. The method can also be applied to the protection of anodic films such as those produced by hard coat anodizing with the electrolyte cooled to 40° C., forming an abrasion resistant coating. Coatings of this type are not usually sealed because they would soften in the hot water used for sealing. However, if a comparatively thin hard coat is applied, say 0.3 mil thickness, then this type of coating can be effectively sealed and protected against corrosion with a bath of an organic nitrogen compound and a molybdate.

The following examples illustrate the invention, but are not to be regarded as limiting.

Example 1

A series of aluminum panels of alloy 5557 (the Aluminum Association designation for a high purity magnesium-containing alloy) were prepared by mechanical buffing, chemical polishing in a phosphoric-nitric acid solution, anodizing in 10% sulfuric acid at 70° F. using a current density of 15 amps./ft.^{2} to a film thickness of 0.3 mil. The surfaces were then sealed in a solution containing 0.1% nicotinamide dissolved in distilled water with a pH of 6.5. This solution was maintained at a temperature of 208° F. and the sealing continued for 15 minutes. A group of samples of the same alloy was subjected to the entire finishing sequence with the exception of the sealing step. This group was sealed in a conventional distilled water uninhibited bath at the same operating conditions. Subsequent to the finishing, the samples were subjected to a 20 hour exposure to the Corrodkote test and evaluated for evidence of corrosion. The samples sealed in water only had developed a substantial amount of hazing or bloom accompanied by the formation of numerous pitting extending through the oxide down into the metal. The samples sealed in nicotinamide solution developed only a very slight amount of haze without any pitting.

Example 2

Two groups of 5657 alloy samples (Aluminum Association designation for an aluminum alloy containing magnesium but of higher purity than the 5557) were prepared by the finishing technique of Example 1 with one group sealed in water. The other group was sealed in a solution containing 0.1% ethyl p-aminobenzoate. The additions of this compound to the sealing bath provided an increase in corrosion resistance at least comparable to that obtained on the nicotinamide additions only as evidenced by both Corrodkote and CASS accelerated exposure data.

Example 3

Two additional groups of sample panels were prepared as indicated under Example 1 using the same alloy. In this series of tests, again one group was sealed in distilled water only and the group to be tested sealed in a solution containing 0.01% sodium dichromate and 1% nicotinamide at the previously mentioned operating conditions. This group was again subjected to the aforementioned Corrodkote test and evaluated. The water sealed samples reproduced the previously described degree haze of the film accompanied by pitting type corrosion. The panels sealed in nicotinamide-dichromate were free of pits and did not develop any clouding of the film.

Example 4

Two groups of samples of the previously mentioned alloy were prepared as outlined in Example 1. One of the groups again served as a reference by consisting of water sealed samples. The test group consisted of panels sealed in a solution containing 1% nicotinamide, .01% sodium dichromate, 0.1% sodium molybdate at the previously mentioned operating conditions. At the conclusion of a 20 hour Corrodkote test, the sample sealed

in the organic-inorganic inhibited solution had sustained no evidence of corrosion.

Example 5

A series of aluminum panels, .04" gauge, was prepared using the Aluminum Association alloy designated 5557. This alloy contains 99.8% pure aluminum with approximately .6% magnesium, .25% manganese and .06% copper added. To maintain a statistically reproducibility exceeding 95%, each group of samples was prepared in numbers of 11 each. All of the test panels were finished by a commercially practiced sequence consisting of mechanical buffing, chemical polishing in a phosphoric-nitric acid type solution followed by anodizing in sulfuric acid using a current density of 12 amps./sq. ft. to an oxide film thickness of 0.3 mil. At this point, one group of 11 samples was sealed by the conventional water sealing technique involving a 15-minute immersion in a distilled water bath maintained between 210–212° F. The second group of 11 samples was sealed in a distilled water bath containing additions of 0.01% sodium dichromate and 0.1% sodium molybdate at a temperature of 210–212° F. Both baths had an electrometric pH of 6.0–6.5. The total group of 22 test panels were subjected to the CASS test by randomizing the panels in the exposure cabinet. In periods of two hours each, the samples were removed and visually examined for corrosive action. In this test, corrosive action constituting a failure consisted of the initial appearance of pitting type corrosion or clouding of the anodic film. In each case, the time to the nearest two hours was noted for initiation of this type of failure. The entire group of panels sealed in distilled water only had sustained an initiation of corrosion after 6–8 hours exposure. Of the other group of panels, those sealed in dichromate-molybdate, nine of the panels had not yet developed corrosion after 16 hours, with several of the panels requiring up to 24 hours exposure before failing. From this test, it is apparent that the additions of dichromate-molybdate enhance the corrosion resistance of anodized aluminum by a factor of two.

Example 6

A second test consisting of preparing samples as outlined under Example 5 and exposing the entire randomized group to 20 continuous hours in CASS. At the conclusion of the test, the samples were examined for corrosion. The group of panels sealed in distilled water only had developed a substantial amount of surface hazing and cloudy areas. The dichromate-molybdate group had sustained only slight hazing.

Example 7

In order to study the comparative effect of individual additions of sodium dichromate and sodium molybdate to the water sealing bath, a series of tests was carried out, in which the samples were exposed for 20 continuous hours in the CASS test, and then the piting rating range was measured in accordance with ASTM procedure, employing a scale in which 10 indicates no corrosive attack and 0 rating is given when the entire surface is corroded. The general procedure outline in Examples 4 and 5 was used. A 0.3 mil anodic coating was first applied as indicated in Example 1.

(a) Water seal only: a group of samples sealed in distilled water only and exposed for 20 continuous hours in the CASS test showed a pitting rating range of 1–3.

(b) A sample group sealed with an aqueous 0.01% sodium dichromate dihydrate solution, after 20 hours exposure showed a pitting rating range of 2–5.

(c) A sample group sealed with an aqueous 0.1% sodium molybdate dihydrate solution for 20 hours, showed a pitting rating range of 2–5.

(d) A sample group sealed with an aqueous solution of 0.01% sodium dichromate dihydrate and 0.1% sodium molybdate dihydrate, for 20 hours, showed a pitting rating range of 5–9. From these performances, it is clearly demonstrated that the combination of dichromate and molybdate produced a synergistic corrosion inhibiting effect beyond that of these compounds taken individually.

Example 8

In order to evaluate the optimum concentration of the sodium dichromate without rendering excessive yellow tinting to the surface, four series of samples in multiples of 11 were prepared as described in Example 5. Successively larger sodium dichromate concentrations were employed in the sealing bath for each group ranging from 0.001, 0.01, 0.10 and 1.0. All panels were exposed in the CASS test for 24 hours and examined every two hours. A concentration of 0.001% resulted in failure in 4–6 hours as evidenced by the presence of a limited number of pits accompanied by clouding of the film. The .01% concentration failed in the 13–16 hours which was also the case for the 1%. The 1% concentration rendered a slight yellow color to the anodic film which would make it commercially unacceptable for decorative applications. The test described under Example 8 illustrates what constitutes one of the main problems in obtaining increased corrosion resistance of bright anodized aluminum. This consists of retarding the formation of a clouding or hazing of the aluminum surface traceable to attack or deposit in or on the surface of the anodic oxide film. In this respect, the apparent optimum concentration for sodium dichromate consists of 0.01%. Another aspect of corrosive action consists of the development of pits in the anodic film principally caused by galvanic type corrosion. In this respect, increased concentrations thus provide improved resistance with 0.01% giving for its concentration level highest equivalent resistance.

Example 9

The following results using the Corrodkote testing technique were obtained on samples prepared in accordance with the sequence outlined in Example 1 with one group sealed in a conventional water seal and the other in the dichromate-molybdate version of the sealing bath. The group sealed in water only exhibited a very small amount of pitting but the surface was completely covered with a light diffusing appearing haze or bloom. In contrast, the group sealed in dichromate-molybdate showed no evidence of pitting with the haze being noticeably reduced. As a practical form of evaluating these surfaces, representative samples from each of these groups were subjected to a wax cleaning step using automotive type commercial compounds. The water sealed samples showed virtually no improvement resulting from this treatment. In contrast, those sealed in dichromate-molybdate exhibited as a result of the treatment a surface closely resembling the initial appearance.

While it is ordinarily advantageous to accomplish sealing of the anodic coating in the solution used for corrosion protection treatment, as previously described, the solution also may be applied at a lower temperature than that required for sealing purposes, provided the solution temperature is above its freezing point; and sealing of the solution-treated coating may be accomplished subsequently in any convenient manner. In addition, relatively thick hard-coat anodized aluminum is preferably treated at a solution temperature low enough to avoid crazing or cracking of the anodic coating. An example of the latter practice is the following:

Example 10

Panels of aluminum alloy 5052 were prepared by degreasing, alkaline etching and nitric acid desmutting, using water rinses where necessary and conventional treating solutions. The panels were subsequently hard anodized in a 20% by volume sulfuric acid electrolyte at 30–32° F.

using a current density of 24 amps./ft.^{2}. An oxide film of 1–1.2 mils was produced.

Half of the panels were left untreated after anodizing, rinsing and drying. The others were immersed in a solution of

	Percent by weight
Sodium molybdate	0.1
Sodium dichromate	0.01
Nicotinamide	0.1

at pH 6.5 and temperature of 120–125° F. for 15 minutes, rinsed and allowed to dry.

The panels treated in the dichromate-molybdate-nicotinamide solution at 120–125° F. did not show the crazing or appearance of numerous fine cracks usually evident in hard anodic films when treated in hot aqueous solutions.

The two groups of samples were subjected to exposure for 16 hours in copper chloride-acetic acid salt spray (CASS). The panels left untreated after anodizing showed considerable corrosion, pitting and staining and were rated 1–2 on a scale where 0 denotes complete coverage of corrosion and 10 denotes no corroded areas. The panels treated in the aforementioned solution had substantially less corrosion and were rated 6–7.

What is claimed is:

1. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for sealing and inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, at a temperature between about 160° F. and the boiling point of said solution, and at a pH between about 5 and about 8.

2. The method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for sealing and inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, and at least one water soluble salt of a metal of Group VI of the Periodic System, at a temperature between about 160° F. and the boiling point of said solution, and at a pH between about 5 and about 8.

3. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for sealing and inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, a water soluble hexavalent chromium salt, and a water soluble molybdate, at a temperature between about 160° F. and the boiling point of said solution, and at a pH between about 5 and about 8.

4. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for sealing and inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution containing about 1% by weight of nicotinamide, about 0.01% by weight of sodium dichromate, and about 0.1% by weight of sodium molybdate.

5. Aluminum and aluminum base alloys having an anodically formed coating thereon sealed and inhibited against corrosion by adsorption of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof.

6. Aluminum and aluminum base alloys having an anodically formed coating thereon sealed and inhibited against corrosion by adsorption of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, and a hexavalent chromium salt.

7. Aluminum and aluminum base alloys having an anodically formed coating thereon sealed and inhibited against corrosion by adsorption of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, a hexavalent chromium salt, and a molybdate.

8. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, at a pH between about 5 and about 8.

9. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salt of a metal of Group VI of the Periodic System, at a pH between about 5 and about 8.

10. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water solu-

ble salts thereof, a water soluble hexavalent chromium salt, a water soluble molybdate, at a pH between about 5 and about 8.

11. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, at a pH between about 5 and about 8, and thereafter sealing said coating in an aqueous medium at a temperature of at least about 160° F. to effect hydration of the coating.

12. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, and at least one water soluble salt of a metal of Group VI of the Periodic System, at a pH between about 5 and about 8, and thereafter sealing said coating in an aqueous medium at a temperature of at least about 160° F. to affect hydration of the coating.

13. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent, selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, a water soluble hexavalent chromium salt, and a water soluble molybdate, at a pH between about 5 and about 8, and thereafter sealing said coating in an aqueous medium at a temperature of at least about 160° F. to affect hydration of the coating.

14. Method for the treatment of an anodically formed coating on aluminum and aluminum base alloys, which comprises applying to said coating a dilute aqueous solution containing about 1% by weight of nicotinamide, about 0.01% by weight of sodium dichromate, and about 0.1% by weight of sodium molybdate, and thereafter sealing said coating in an aqueous medium at a temperature of at least about 160° F. to affect hydration of the coating.

15. Method for the treatment of hard-coat anodized aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, at a solution temperature above ambient temperature but below the temperature at which crazing of said coating may occur, and at a pH between about 5 and about 8.

16. Method for the treatment of hard-coat anodized aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, and at least one water soluble salt of a metal of Group VI of the Periodic System, at a solution temperature above ambient temperature but below the temperature at which crazing of said coating may occur, and at a pH between about 5 and about 8.

17. Method for the treatment of hard-coat anodized aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution of a water soluble basic organic nitrogen compound which does not contain a polar substituent selected from the group consisting of heterocyclic nitrogen compounds containing at least one basic nitrogen in a heterocyclic ring selected from the group consisting of pyridine, quinoline and quinazoline rings, mononuclear carbocyclic nitrogen compounds containing an unsubstituted amino group, and the water soluble salts thereof, a water soluble hexavalent chromium salt, and a water soluble molybdate, at a solution temperature above ambient temperature but below the temperature at which crazing of said coating may occur, and at a pH between about 5 and about 8.

18. Method for the treatment of hard-coat anodized aluminum and aluminum base alloys for inhibiting corrosion thereof, which comprises applying to said coating a dilute aqueous solution containing about 1% by weight of nicotinamide, about 0.01% by weight of sodium dichromate, and about 0.1% by weight of sodium molybdate, at a solution temperature above ambient temperature but below the temperature at which crazing of said coating may occur, and at a pH between about 5 and about 8.

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