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(54) **Process and composition for producing protective and colour-receptive coatings on aluminium.**

(57) This invention is for an improved process for chemically forming a protective, color receptive coating on the surface of aluminum. The aluminum may be aluminum parts or substrates coated with a layer of aluminum. Absent conventional steps such as water rinses and the like, the process comprises cleaning the aluminum surface to the extent necessary, including desmutting, and contacting the part with an aqueous alkaline solution containing a soluble nitro- or nitroso-substituted organic compound, particularly a nitrobenzoic acid or derivative thereof, for a time sufficient to form the coating. The treated aluminum part has enhanced corrosion resistance and the coating acts as a base which will accept other treatments such as dyeing or painting.

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PROTECTIVE AND COLOR RECEPTIVE COATING FOR ALUMINUM

BACKGROUND OF THE INVENTION

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Introduction

This invention relates to the formation of protective, color receptive coatings on aluminum and its alloys, and particularly to a composition and method for formation of such coatings using chemical means.

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Description of the Prior Art

15 Methods and compositions for providing integral oxide coatings on aluminum are known in the art. These coatings are corrosion resistant, may be dyed, and act as bases for various finishes such as paint. The most common method for forming such a coating is an electrochemical method known as anodizing. This method involves the formation of an oxide coating over the surface of an aluminum article by passing a current through an electrolyte where the aluminum part to be oxidized is the anode and the tank containing the solution is the cathode. A conventional electrolyte comprises a sulfuric acid solution. Following formation
20 of the oxide coating, the aluminum part may be immersed in a dye bath to impart desired coloration to the aluminum. A process for anodizing aluminum is disclosed in the Metal Finishing Guidebook Directory for 1967, Metals and Plastics Publication, Inc., Westwood, New Jersey, pages 515 to 525.

25 Though anodizing is one of the most widely used methods for oxidizing aluminum, it has drawbacks such as relatively high cost. This is due to the requirement for special equipment needed to pass a current through a solution. Thus electrodes, a rectifier and special lead lined or stainless steel tanks are required. Further, after prolonged use, the anodizing solution must be discarded due to a build up of aluminum in solution.

To overcome limitations in electrolytic anodizing, chemical methods for forming protective and color
30 receptive aluminum surfaces have been suggested. U.S. Patent No. 2,976,371, incorporated herein by reference, discloses an aqueous acidic treatment solution comprising a mixture of chromic acid and an iron (III) cyanic acid. Treatment with this solution forms a color receptive coating complex of aluminum and chromic acid on the surface of the aluminum part. This coating may be finished by treatment with dye, paint or lacquer.

35 The above process, while avoiding disadvantages inherent to anodizing, provides a soft, non-uniform coating that yields iridescent colors when dyed. Further, it is difficult to dispose of spent chromic acid solutions.

In U.S. Patent No. 3,765,952, assigned to the same assignee as the present invention and incorporated
40 herein by reference, a chemical process is disclosed that results in the formation of color receptive, corrosion resistant coatings over aluminum. The process comprises cleaning and desmutting an aluminum part and contacting the part with an aqueous alkaline solution of an iron (III) cyanide compound for a time sufficient to form a coating. If desired, the aluminum part may then be dyed or coated with any other suitable finish such as paint or lacquer. The coating formed is analogous to the coating formed by electrical anodizing.

45 The process of the above patent overcomes the disadvantages to electrical anodizing as special equipment is not required. The process also overcomes problems associated with the above described process for formation of chromium complex coatings in that the coatings are harder, more corrosion resistance, and when dyed, the color is more uniform, brighter and substantially more desirable. Further, with appropriate replenishment, the treatment solutions are useful for extended treatment times. However,
50 though providing excellent coatings, iron (III) cyanide solutions present waste disposal problems.

U.S. Patent No. 4,212,685, also assigned to the same assignee as the subject invention and incorporated herein by reference, provides an alternative material and method for forming a protective coating over aluminum, which coating is corrosion resistant and readily dyed. The process comprises cleaning and desmutting the aluminum part, then contacting the part with an aqueous alkaline solution of iron (III) citrate for a time sufficient to coat the surface of the part. Iron (III) citrate does not present significant waste

disposal problems. However, the coating formed using iron (III) citrate, though having properties similar to those formed using the iron (III) cyanide treatment solution, are somewhat inferior thereto.

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SUMMARY OF THE INVENTION

The subject invention provides alternative materials and processes for treatment of an aluminum part to provide corrosion resistant protective, color receptive coatings. The process comprises cleaning and desmutting an aluminum part to the extent required by methods known to those skilled in the art, and contacting the aluminum part with an alkaline solution containing a soluble nitro- or nitroso-substituted organic compound, particularly nitrobenzoic acid or a substituted derivative thereof, for a time sufficient to coat the surface of the part. If desired, the coated aluminum part may be dyed with a suitable dye to impart a desired color to the part or may be coated with another suitable finish such as paint or lacquer.

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DESCRIPTION OF THE PREFERRED EMBODIMENTS

The invention described herein relates to the treatment of aluminum parts where an aluminum part is defined as a part fabricated from aluminum or aluminum alloys and includes articles coated with aluminum such as a vacuum metalized plastic or glass. For coated articles, the thickness of the aluminum coating is not critical, though for extremely thin coatings, e.g., 2000 angstroms or less, the oxidizing solution may attack the metal to the extent that a coating will not form.

Prior to treatment in accordance with this invention, the aluminum part is preferably cleaned as necessary. For example, cleaning can be a combination of steps comprising solvent degreasing, preferably with a hydrocarbon solvent such as benzene to remove grease and oil, or by soak cleaning, then etching with a mild acid or alkaline cleaner to remove dirt, oxides and other contamination, but not so as to form visible surface irregularities. Finally, if necessary, the part may be treated with a conventional desmutter to remove any residues left on the surface of the part. The desmutter typically comprises dilute nitric acid with or without hydrofluoric acid admixed therewith. Intermediate to each of the aforesaid steps is a water rinse. The aforescribed process of cleaning and desmutting is well known in the art. The next step in the process comprises formation of a color receptive coating in accordance with the present invention using an aqueous, alkaline solution of a soluble nitro- or nitroso-substituted organic compound.

The nitro- or nitroso-substituted organic compounds useful in the treatment solution of the present invention are those which are soluble under the alkaline pH conditions employed during the treatment process and which do not contain other reactive moieties that would interfere with the desired reaction. Typical compounds which may be utilized are nitro- or nitroso-substituted benzenes, naphthalenes and lower alkanes with 1 to 6 carbons which, in addition to the nitro or nitroso group, contain one or more water solubilizing groups such as carboxylic or sulfonic acid or hydroxy. Thus, compounds which may be utilized include nitrobenzoic acid, nitrobenzene sulfonic acid, 2-amino-5-nitrobenzene sulfonic acid, nitrophenol, dinitronaphthalene sulfonic acid, nitrosophenol, nitrosonaphthol sulfonic acid, nitrosobenzoic acid, tris-(hydroxymethyl)nitromethane, and substituted derivatives thereof. Various additional substituents may be included on the organic moiety, such as halogen, amino, hydroxy, lower alkoxy, trifluoromethyl, nitro, cyano, etc., provided that such substituents do not adversely affect the solubility of the compound and are non-reactive under the treatment conditions employed.

The preferred compounds for use in the present invention are the soluble nitro aromatic compounds, preferably nitrobenzoic acid and nitrobenzene sulfonic acid, and substituted derivatives thereof. Most preferred is meta-nitrobenzoic acid.

The nitro- or nitroso-substituted organic compounds are generally used in an amount of about 0.1 to about 0.5 moles per liter, preferably about 0.15 to 0.35 moles/liter. Greater or lower amounts may be used but would likely not be economically efficient.

The treatment solution of this invention is an aqueous alkaline solution having a pH adjusted to between about 7.5 and 14.0, preferably between about 10 and 13, and most preferably about 12. To obtain the desired solution pH, a pH adjustor such as alkali hydroxides, carbonates and/or mono-, di- or tribasic phosphates is used. The preferred pH adjustors are the sodium and potassium salts of said hydroxides, carbonates and phosphates.

As a mixture of carbonate and phosphate salts act as a buffer, they may be used in combination,

particularly since the phosphate also may serve as an inhibitor, preventing the darkening of the coating formed on the aluminum part. The amount of adjustor used is that which gives the desired pH. For example, potassium carbonate used in a concentration of 0.1 to 1.0 moles per liter of solution provides a pH somewhat below 12. Generally it has been found that a combination of potassium carbonate and sodium hydroxide in solution provides acceptable results, the sodium hydroxide being used in the minimum amount necessary relative to the potassium carbonate to reach the desired pH, which is preferably about pH 12. Optionally sodium aluminate may also be added, as well as citric acid and/or boric acid.

A preferred formulation in accordance with the invention is as follows:

m-nitrobenzoic acid	0.1 to 0.5 moles per liter
potassium carbonate	0.1 to 1.0 moles per liter
sodium hydroxide	to provide desired pH
water	to one liter

The treatment solution of this invention may be used over a wide temperature range but preferably is used below its boiling point and generally within a temperature range of from about 65° to 120°F, most preferably from about 70° to 100°F. The time of contact of an aluminum part with the oxidizing solution is likewise not critical, with periods of time ranging from 1 to 60 minutes being typical.

It should be understood that there is a relationship between concentration of ingredients in the treatment solution, pH, temperature and time, the more concentrated the solution or the higher the temperature or pH the shorter the treatment time. Also, pH and temperature are inversely related so that as pH increases, the temperature of the treatment bath is reduced and vice-versa. It should further be understood that different aluminum alloys might require different treatment conditions. Finally, it should be realized that the conditions of treatment vary with the objectives to be obtained-- that is, for more intense colors or better corrosion resistance, heavier coatings requiring longer treatment times may be needed. Consequently, routine experimentation within the guidelines set forth above may be required.

For best results in practicing the present invention, the treatment solution should be aged or conditioned by passing a certain amount of aluminum through it prior to treatment of actual parts. While not wishing to be bound by any theory, it is believed that this conditioning activates the treatment solution by converting at least some of the nitro compound to the nitroso derivative. Instead of forming the nitroso derivative in situ, it is also possible to simply start with the nitroso compound to begin with.

Following treatment with the oxidizing solution, the aluminum part is rinsed and may be coated with a finish such as those disclosed in U.S. 2,976,371, or a solution of a colorant, which may be either an organic dye or an inorganic pigment. Many of the colorants that may be used are those conventionally used in anodizing. Typical of such dyes are the following, set forth for purposes of example only:

Aluminum Orange 3A	
Antraquinone Green GNN	C.I. 61570
Alizarin Orange 2GN	C.I. 14030
Aluminum Fiery Red ML	
Wool fast Orange GA	C.I. 26520
Fast Mordant Yellow GD	C.I. 25100
Chromoxane Pure Blue BA	C.I. 43830
Chlorontine Fast Red 5 BRL	C.I. 35780

The parts treated with the alkaline solution may be colored in accordance with prior art anodizing treatment procedures. Thus, dye concentration, treatment temperature and time are conventional, temperatures of from room to 150°F being appropriate with treatment time ranging from about 0.5 to 20 minutes depending on dye concentration and temperature. It should be noted that dye concentration for coloring parts treated in accordance with this invention can be substantially reduced relative to those concentrations needed for dyeing aluminum anodized in the conventional manner.

Following dyeing and a water rinse, the part may be sealed if desired, using the conventional sealing step of immersion of the colored part in a solution such as nickel acetate or sodium dichromate or any other conventional material in accordance with art-recognized procedures.

The following examples are given for the purpose of illustrating the invention, all parts and percentages being by weight unless otherwise indicated.

EXAMPLE 1

An aluminum panel of No. 3003 alloy measuring 2 x 4 x 0.016 inch is degreased by soaking for five minutes in a conventional non-etching aluminum soak cleaner made up at 60 grams per liter and maintained at 150°F. The panel is then removed, water rinsed, and next immersed in a conventional mild alkaline etching cleaner consisting of 55 grams of cleaner (Strat-O-Kleen 757) dissolved in one liter of water. The cleaning bath is maintained at about 150°F. The panel is removed after about one minute treatment in the bath and rinsed in cold water. The clean panel is then immersed in a 10 percent nitric acid solution to desmut the same and provide a clean surface. A treatment time of one-half minute is used. The clean panel is rinsed with cold water and immersed in a solution comprising 20 g/l m-nitrobenzoic acid and 100 g/l potassium carbonate and water to one liter. The pH of the solution is adjusted to about 11.7 - 11.8 with sodium hydroxide as required, the temperature of the solution is held at about 75°F and immersion time is about 20 minutes. Thereafter, the panel is removed and rinsed with water. The panel having an oxide coating is then dyed by immersion for two minutes in a dye bath maintained at about 135°F consisting of 4 grams of Acid Blue #243 in one liter of water. The pH of the dye is adjusted to between 4.5 and 5.0. The dyed panel is rinsed with water and sealed in a solution containing 50 grams of sodium dichromate dissolved in one liter of water with pH maintained at about 5.9. The time of sealing is 15 minutes and the temperature of the sealing bath is maintained at about 210°F. The panel is then rinsed with water, dried in the air, and buffed by hand. It has a uniform blue to turquoise coloration and has good wear and corrosion resisting properties.

EXAMPLES 2-6

The above example is repeated except that the following treatment solutions are substituted for the one utilized therein. In each case the pH is adjusted with sodium hydroxide to about 11.8 - 12.0.

Example	Compound	Concentration	
2	m-nitrobenzene sulfonic acid	10	g/l
	potassium carbonate	10	g/l
	sodium aluminate	6	g/l
3	2-amino-5-nitrobenzene sulfonic acid	10	g/l
	potassium carbonate	10	g/l
	sodium aluminate	6	g/l
4	tris(hydroxymethyl)nitromethane	100	ml/l
	potassium carbonate	10	g/l
	sodium aluminate	6	g/l
5	m-nitrobenzoic acid	16	g/l
	citric acid	25	g/l
	boric acid	25	g/l
	sodium aluminate	6	g/l
6	m-nitrosobenzoic acid	20	g/l
	potassium carbonate	30	g/l

It will be noted that the present invention provides a process for treating and coloring aluminum which is low in cost, does not require electrical equipment or cyanide containing solutions, and can be applied to varied sized parts such as pins, bolts, and the like as well as large parts as in prior art anodizing methods. The resulting colored aluminum parts have a highly corrosion resistant, attractive finish.

Claims

1. A process for forming a corrosion resistant, color receptive coating on an aluminum part wherein said part is comprised of aluminum, an aluminum alloy or a substrate having an aluminum or aluminum alloy surface, said process comprising the step of contacting the surface of said aluminum part with an aqueous, alkaline solution containing a soluble nitro- or nitroso-substituted organic compound.
2. The process of claim 1 wherein the nitro- or nitroso-substituted organic compound is present in an amount of from about 0.1 to about 0.5 moles per liter of said solution.
3. The process of claim 2 wherein the pH of the solution is between about 10 to about 13.
4. The process of claim 3 wherein said nitro- or nitroso-substituted organic compound is a nitro- or nitroso-substituted benzene, naphthalene or lower alkane, or substituted derivative thereof, which in addition to the nitro or nitroso group, contains one or more water solubilizing groups selected from carboxylic acid, sulfonic acid and hydroxy.
5. The process of claim 3 wherein said nitro- or nitroso-substituted organic compound is selected from nitrobenzoic acid, nitrobenzene sulfonic acid, 2-amino-5-nitrobenzene sulfonic acid, nitrophenol, dinitronaphthalene sulfonic acid, nitrosophenol, nitrosonaphthol sulfonic acid, nitrosobenzoic acid, tris(hydroxymethyl)-nitromethane, and substituted derivatives thereof.
6. The process of claim 3 wherein said nitro- or nitroso-substituted organic compound is a nitro-substituted benzene or naphthalene, or substituted derivative thereof, containing one or more water solubilizing groups selected from carboxylic acid, sulfonic acid and hydroxy.
7. The process of claim 3 wherein said nitro- or nitroso-substituted organic compound is nitrobenzoic acid or nitrobenzene sulfonic acid or a substituted derivative thereof.
8. The process of claim 3 wherein said nitro- or nitroso-substituted organic compound is meta-nitrobenzoic acid.
9. The process of claim 6 wherein the temperature of the solution is between about 70°F and about 100°F.
10. The process of claim 9 wherein the aqueous, alkaline solution contains a pH adjustor in an amount sufficient to provide the desired pH, which pH adjustor is selected from alkali carbonates, hydroxides, mono-, di and tribasic phosphates, and mixtures thereof.
11. In a process for coloring an aluminum part including the steps of cleaning the aluminum part to the extent necessary, forming a color receptive coating over the aluminum part, and contacting the aluminum part with a colorant, the improvement comprising formation of said coating by contacting the surface of said aluminum part with an aqueous, alkaline solution of a soluble nitro- or nitroso-substituted organic compound.
12. The process of claim 11 wherein said solution comprises about 0.1 to about 0.5 moles per liter of said nitro- or nitroso-substituted organic compound, and has a pH of about 10 to about 13.
13. The process of claim 12 wherein said nitro- or nitroso-substituted organic compound is a nitro- or nitroso-substituted benzene, naphthalene or lower alkane, or substituted derivative thereof, which in addition to the nitro or nitroso group, contains one or more water solubilizing groups selected from carboxylic acid, sulfonic acid and hydroxy.
14. The process of claim 12 wherein said nitro- or nitroso-substituted organic compound is selected from nitrobenzoic acid, nitrobenzene sulfonic acid, 2-amino-5-nitrobenzene sulfonic acid, nitrophenol, dinitronaphthalene sulfonic acid, nitrosophenol, nitrosonaphthol sulfonic acid, nitrosobenzoic acid, tris(hydroxymethyl)nitromethane, and substituted derivatives thereof.
15. The process of claim 12 wherein said nitro- or nitroso-substituted organic compound is a nitro-substituted benzene or naphthalene, or substituted derivative thereof, containing one or more water solubilizing groups selected from carboxylic acid, sulfonic acid and hydroxy.
16. The process of claim 12 wherein said nitro- or nitroso-substituted organic compound is nitrobenzoic acid or nitrobenzene sulfonic acid or a substituted derivative thereof.
17. The process of claim 12 wherein said nitro- or nitroso-substituted organic compound is meta-nitrobenzoic acid.
18. An aqueous solution for coating aluminum and its alloys comprising at least about 0.1 moles per liter of a soluble nitro- or nitroso-substituted organic compound adjusted to a pH of about 10 to 13.
19. The solution of claim 18 wherein the pH is adjusted with alkali carbonates, hydroxides, mono-, di-, or tribasic phosphates, or mixtures thereof.
20. The solution of claim 19 comprising 0.1 to 0.5 moles per liter of m-nitrobenzoic acid, 0.1 to 1.0 moles per liter of potassium carbonate, and sodium hydroxide as necessary to provide a pH of about 12.



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl. 4)
X	FR-A-2 461 764 (F. POPESCU) * Claims 1-3,7; page 2, lines 13-36; examples 1-3 *	1-20	C 23 C 22/66
X	FR-A- 840 367 (R.M. BERTHIER) * Abstract; page 2, lines 84-88 *	1-4,11-13	
			TECHNICAL FIELDS SEARCHED (Int. Cl.4)
			C 23 C C 23 F
The present search report has been drawn up for all claims			
Place of search THE HAGUE		Date of completion of the search 09-08-1989	Examiner DE ANNA P. L.
CATEGORY OF CITED DOCUMENTS			
X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document			
T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			