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(54) Corrosion resistant coated aluminium articles and process for making same.

(57) Aluminium and aluminium alloy articles, and method for making same, in which a thin, adherent, chemically formed coating is provided on the article surface to preserve the uncoated article appearance and provide a combination of functional properties including resistance to chipping and flaking during elevated temperature use, resistance to corrosion from chemicals in the form of gases or aqueous acidic or alkaline solutions including salt spray, organic solvents, oils and vehicle fuels and suitability as a base for paint for parts within the engine compartment of vehicles. The coating has a chemical complex of alkali metal-chromium-silicates.

CORROSION RESISTANT COATED ALUMINUM ARTICLES AND PROCESS FOR MAKING SAME

BACKGROUND OF THE INVENTION

This invention relates to aluminum and aluminum alloy articles having integral chemically-formed surface coatings that provide an improved combination of adherence and corrosion resistant properties to such products and to a process for making same. More particularly, the articles of this invention have on their aluminum or aluminum alloy surfaces an integral, chemically-formed coating that is strongly adherent and resistant to chipping or flaking at elevated temperatures and provides to the product a unique combination of corrosion properties including commercially satisfactory resistance to oxidation during use in gases at elevated temperatures such as encountered in the engine compartments of vehicle engines, resistance to corrosion from humidity, from organic solvents such as ethylene glycol, oils and gasoline, from acidic or alkaline solutions such as salt spray to the extent that is required of a base for paint or other protective organic or water-based protective coating on parts used within the engine compartments of vehicles.

Chemical coatings on aluminum for various purposes including oxides, chromate-phosphates, chromates, and phosphates have long been known and have been commercially employed since the 1930's when the original Bauer-Vogel process of German patent 423,758 for chemically forming oxide coatings on aluminum was improved in 1937 by reducing the time required from hours to minutes but still produced only gray coatings at near boiling temperatures, see Aluminium, 1937, 19, 608-11. Colorless oxide coatings suitable for a wider range of aluminum alloys were later developed but were less desirable as a base for paint than the Bauer-Vogel products and could not be successfully dyed, see Aluminium, 1938, 20, 536-8. Chromate-phosphates were developed in the 1940's as paint base coatings and disclosed in U. S. Patent 2,438,877 and later modified as disclosed in British Patent 1,114,645 and French Patent 1,477,179. Chromate processes developed during the 1960's and 1970's have been asserted to provide improved paint bases relative to the chromate-phosphate coatings and are disclosed in a number of United States patents, including U. S. Patents, 3,009,482, 3,391,031, 3,404,043, 3,410,707, 3,447,972, 3,446,717, 3,982,951, 4,036,667, 4,146,410 and British Patent 1,409,413. Even though extensive development of chemical coatings for aluminum and its alloys has resulted from worldwide research efforts each heretofore known process and product present some problem or lack a particular set of properties needed for use in specific applications. Thus, there is a continuing need for other efficient, low cost processes for providing corrosion resistant coatings on aluminum and its alloys to satisfy specific commercial needs. For example, there are needs for uses other than bases for paints or other organic finishes, other needs for coating aluminum alloy substrates which contain alloy constituents known to hinder coating formation on alloys such as magnesium, silicon, copper, chromium and manganese. There remains a need for coating aluminum alloy sand castings which contain silicon, copper and magnesium and may contain other heavy metals such as nickel, chromium, titanium or silver to provide coatings that resist thermal and gaseous engine fume degradation and development of localized white corrosion products during long periods of use such as in commercial truck and automobile engine compartments.

The present invention provides aluminum and aluminum alloy articles that are coated with a new integral coating that satisfies specific commercial requirements for aluminum articles having a good corrosion resistance and resistance to dislodgment during use in vehicle environments. This invention also provides an economic, continuous process for producing the new aluminum coated articles of this invention, as will be described hereinafter.

SUMMARY OF THE INVENTION

In accordance with the present invention, aluminum or aluminum alloy articles are coated with a new, thin colorless coating, which preserves the appearance of the uncoated aluminum or aluminum alloy articles. The coating contains as its essential component a chemical complex of alkali metal-chromium-silicates as defined in the claims. The amount of that essential component in the coating is sufficient to provide the coated aluminum articles with an unexpectedly unique combination of properties of aluminum appearance, adherence, resistance to chipping and flaking, corrosion resistance to acidic and alkaline gases and aqueous solutions and oils, solvents and fuels sufficient to make it suitable as a base for paint and the equivalent of paint on parts within the engine compartment of vehicles. The preferred coatings are colorless and so thin as to be invisible to the naked eye. The coating thickness varies from about 50 angstroms, or 0.0005 micron, to about 2 microns.

This invention also provides a process for the continuous, efficient production of the improved aluminum or aluminum alloy coated articles of this invention. The continuous process makes use of known production line dip or spray apparatus in which the aluminum articles or parts to be coated are mounted on racks or in rotating barrels supported on conveyor means capable of sequentially contacting the articles with aqueous solutions positioned in a plurality of in-line tanks, each tank containing an aqueous solution of selected coating-producing ingredients with intervening rinse solution-containing tanks, the in-line apparatus terminating in conventional means for drying the coated parts. The process of this invention has the advantages of using dilute aqueous solutions of inexpensive, commerically available chemicals that are maintained at low treatment bath temperatures ranging from ambient room temperatures up to about 160° F., or 71° C., and for short times of contact of the solution with the aluminum article being coated, for example, immersion contact in the range of about 20 - 180 seconds, preferably about 30 seconds, or spray contact for about 10 to 60 seconds and preferably 5 - 20 seconds. The end result is that the continuous production process provides a resultant product that is less expensive than most heretofore available corrosion resistant aluminum product.

The process of this invention is useful to form coatings on aluminum and all of its alloys that are commercially available as sand castings, plate, sheet, forgings or extrusions. Particularly good results have been obtained by using the process for coating vehicle engine manifolds made from sand cast aluminum alloys as described in Example I.

DETAILED DESCRIPTION OF THE INVENTION

The new articles of this invention include articles fabricated from aluminum or an aluminum alloy which have on their surfaces a thin, adherent coating having a thickness up to about 2 microns comprising as its essential component a chemical complex of an alkali metal-chromium-silicate having proportions of each in the range, expressed as oxides in weight percent of:

Na_20 - 9.9% - 12.1%
Cr_20_3 - 4.1% - 4.3%
$Si0_2$ - 76.8% - 91.2%

The process for making the coated new articles of this invention comprises the following sequential steps, omitting intervening water rinsing steps:

1) cleaning with an acidic cleaner to remove foreign matter, oils, greases or surface remnants from the forming of the article;

2) contacting the cleaned article from step 1 with an aqueous, strongly acidic solution capable of removing surface aluminum oxides;

3) contacting the clean, rinsed, substantially oxide-free article of step 2 with an aqueous acidic solution for forming a chromium-silicate-containing adherent surface coating;

4) elevated temperature water rinsing of the step 3 coated article;

5) contacting the rinsed coated article of step 4 with an aqueous, strongly alkaline solution capable of forming an alkali metal-chromium silicate coating containing a chemical complex having the composition, expressed as oxides in percent by weight of:

Na_20 - 9.9% - 12.1%
Cr_20_3 - 4.1% - 4.3%
$Si0_2$ - 76.8% - 91.2%

Cleaning solutions which have been found to be suitable for use in the first step of the process include a wide variety of commercially available inhibited acidic cleaners. Good results have been obtained by using an aqueous phosphoric acid solution containing phosphoric acid in an amount sufficient to give a pH in the range of about 5 to 6, and which may contain organic solvents such as tri- or diethylene glycol monobutyl ether in an amount of about 2% to 10% and may also contain any of a number of commercially available organic surfactants, for example, about 2 to 10% of a fluorocarbon surfactant such as FC 95 available under the tradename Fluorad from Minnesota Mining & Manufacturing Co. The parts to be cleaned are immersed in such a cleaning solution at a temperature of about 130° to 180° F (54 to 82° C) for 2 to 5 mins, preferably about 3 mins, followed by rinsing in water at a temperature of about 120° to 140° F (49 to 60° C), preferably about 130° F (54° C), for 30 to 90 seconds.

The cleaned articles from step 1 are then contacted with a stronger aqueous acidic solution capable of removing the aluminium and/or other oxides from the surfaces of the article. Good results have been obtained by using a chromic acid-based solution containing 70 to 80% chromic acid, 20 to 30% potassium dichromate and 2 to 4% ammonium silicofluoride in a concentration of 3 to 6 oz/gal (45 g/l), preferably about 4 oz/gal (30 g/l) to form a solution having a pH in the range of about 0.5 to 1 and contacting the article with such solution for a time period in the range of $\frac{1}{2}$ to about 3 mins. The oxide free cleaned articles are then water rinsed in one of three water tanks at ambient temperatures, for about 30 seconds in each rinse solution.

The deoxidised, rinsed aluminium article is then subjected in step 3 to a coating forming step by contacting the article by dip or spray with an aqueous solution to form a silicon-chromate coating on the surface. Good results have been obtained in forming such coatings by using an aqueous solution made up by adding to water, preferably deionised water, about ½ -2 oz/gal (3.7-15 g/l) of a composition containing in weight percent about 50 to 60% chromic acid, about 20 to 30% barium nitrate and about 15 to 20% sodium silicofluoride and preferably containing a catalyst in an amount of up to about 5% such as an alkali metal ferricyanide, i.e. potassium or sodium ferricyanide to form a solution having a pH in the range of about 1.2 - 1.9 and preferably less than 1.5. Other formulations which are also satisfactory for use may omit the barium nitrate component, and may include additional coating catalysts of the molybdic acid type in the event color is desired, such as the formulations disclosed in U. S. Patent 3,009,842 and in the other patents identified therein. Other useful, but less desirable compositions that are suitable for coated articles having less stringent requirements for salt spray resistance include those set forth in U. S. Patents 3,410,707 and 3,404,043. Compositions that are satisfactory are commercially available from a wide variety of suppliers in the United States and especially good results have been obtained by using the material commercially designated Iridit 14-2 which is available from Witco Chemical Company.

It is to be further understood that the proportions of Cr_2O_3, barium nitrate and alkali metal silicofluoride in the preferred composition described above are not critical to the formation of the base chromium-silicate coating that is formed directly on the oxide free surface of the aluminum or aluminum alloy article being coated in accordance with this invention. Useful coated articles are formed when the formulation given above is varied to employ proportions within the ranges set forth in U. S. Patent 3,982,951. When the article is dipped, an immersion time of about 30 seconds is adequate when the temperature is maintained at less than 120° F., or 49° C. When the article is sprayed at a similar temperature, about 5 to 20 seconds is adequate.

It is important to insure a thorough water rinsing of the silicon-chromate coating formed in step number three. This is best done using deionized water at ambient temperature, i.e., about 60° F. - 90° F. (15.6°C - 32°C), in 1 to 3 immersions, preferably three, for about 30 seconds each, or a single power spray for about 30 seconds. Following thorough ambient temperature rinsing of the coated article from step 3, the fourth step is a final water rinse at a temperature that is higher than the ambient temperature employed in step 3. This higher temperature rinse serves to remove unwanted chromate colors, if present, and also to prepare the silicon-chromate coating to enhance its reactivity with the components in the strong alkaline solution to be next applied to form the alkali metal-chromium-silicate coating of this invention. Preferred conditions for step 4 include using deionized water at a temperature in the range of about 110° F. to 160° F., or about 43° C. to 71° C., and preferably about 130° F. or 54° - 55° C. The chromate-silicate coated article should be rinsed at the selected temperature for a time sufficient to raise the temperature of the article to about the elevated temperature of the rinse solution. Thus, the optimum time required varies for specific articles depending on the selected compositon used in step 3 and also depends on the size or bulk of the article. The optimum time may be affected by the particular alloy composition of the article being coated. For example, the time required may vary from about 30 seconds up to about 5 minutes, and the needed, or optimum, time is easily determinable by a few trials. Where the article is formed by sand casting an aluminum or an aluminum alloy material, the article may include pits or surface imperfections. When such imperfections are present it has been found that potential, undesirable white corrosion products may develop in such pit or imperfection areas during salt spray testing or use and this undesirable corrosion can be avoided by exercising care in selecting a sufficiently high temperature towards the 160°F (71°C) limit and a sufficiently long time for the selected elevated temperature rinse step.

The elevated temperature rinsed silicon-chromate coated article from step 4 is then subjected in step 5 to a second coating by step by contacting the coated article with a highly alkaline aqueous solution having a pH in the range of about 11 to 12 and containing disodium oxide and silicon dioxide components having a weight ratio of SiO_2/Na_2O in the range of about 2.4 to 3.25 and a range of densities between about 40 and 52° Baume' at 20°C. Otherwise expressed the silicate solutions may contain in weight percent, about 26.5% to about 33.2% SiO_2 and about 8.6% to about 13.9% Na_2O, at a similar range of densities. Preferred solutions are those which contain disodium oxide and silicon dioxide in a weight ratio of SiO_2/Na_2O of about 2.5 to 2.9 and a density in the range of about 42 to about 47° Baume' at 20°C. The best results have been obtained from a solution formulated by adding to water an amount of about 2 to 4% by volume of a sticky, heavy silicate having a weight ratio of SiO_2/Na_2O of 2.9 and a density of 7° Baume' at 20°C to thereby produce a coating solution having a pH of about 11.5. The articles from step 4 are then immersed for about 30 sec to 2 min in such a solution at a temperature of ambient to about 130°F (54°C), with the solution having a preferred pH between about 11.2 and 11.5. The thus coated articles are finally dried either in ambient air or in a low temperature furnace at 150° to 200° F (66 to 93° C) for 1 to 2 minutes.

The dried, coated articles are the new articles of this invention. In their preferred form, the articles have a thin, adherent coating that is substantially invisible to the naked eye but has been determined to have a thickness in the range of about 50 Å to 20 000 Å, or about 0.0005 µm to about 2 µm. The coated article has the same overall appearance as the uncoated article unless a yellowish chromate tint has been intentionally produced by varying the composition of step 5 or the temperature of step 4 as will be readily apparent to those skilled in the art of forming chromate coatings on aluminium.

Tests conducted on the coated articles from step 5 have established that the coating is sufficiently adherent and hard to resist chipping or flaking when used at elevated temperatures up to about 400° F (204° C) such as may be attained in the engine compartments of automobiles and trucks. When the articles from step 5 were vehicle intake manifolds and were tested for salt spray resistance under the conditions of ASTM B-117 test method no corrosion products were visible for 250 hours.

EXAMPLE 1

Automobile intake manifolds were sand cast from a Ford Motor material designated 319 Aluminium having a specification of 5.5-6.5 Si, 0.4-0.6 Mn, 3.0-4.0 Cu, 0.1-0,6 Mg, 0.7-1.0 Zn and 1.0 Max Fe. The articles were mounted on racks carried by a dip-type conveyor adapted to dip the racks into tanks to form coated manifold articles of this invention in the following sequence of steps:

1) A tank of aqueous acidic cleaning solution was prepared to contain, in wt%, 5% of the commercial product Niklad Alprep 230 (Available from Allied Kelite Division of Witco Chemical Co, Des Plains, Ill, containing phosphoric acid (75% strength), 2% butyl cellosolve and 2% FC 95 Fluorad surfactant or equivalent from 3M). The intake manifolds were dipped in the solution having a pH of 5-6 at approximately 130° F (54° C), for about 2 mins;

2) Water rinse at 130° F (54° C) ± 5° F (2.8° C), for about 30 secs;

3) Repeat step 2;

4) A tank of aqueous acidic coating solution was prepared by mixing about 1 oz/gal (7.5 g/l) of Iridit 14-2 (Available from Witco Chemical Co and containing in wt%, 50-60% Cr_2O_3, 20-30% barium nitrate, 15-20% sodium silicofluoride and 5% potassium ferricyanide) with water to form a solution having a pH of 1.4 - 1.5. The rinsed manifolds from step 3 were immersed in the solution for 30 secs;

5) Water rinse at ambient room temperature of about 60 - 90° F (15.6 - 32° C) for 30 secs;

6) Repeat step 5;

7) A tank of deoxidising strongly acidic cleaner was prepared by mixing 4 oz/gal (30 g/l) of Deoxidizer No 2 (Available from Amchem Products Inc, Ambler, Pa, and containing, in wt% 70-80% Cr_2O_3, 20-30% potassium dichromate and 2-4% ammonium silicofluoride) with water to form a solution having a pH of 0.5 - 1.0. The rinsed manifolds of step 6 were immersed in the solution for 90 secs;

8) Water rinse at ambient temperature;

9) Repeat step 8;

10) Repeat step 8;

11) Repeat immersion for 3 mins in the same solution as in step 4;

12) Water rinse at ambient temperature;

13) Repeat step 12;

14) Repeat step 12;

15) Water rinse, deionised water, at approximately 140-150° F (60-66° C) for about 30-50 secs;

16) A tank of strongly alkaline coating solution was prepared by mixing 4% by volume of Ultraseal (Available from MacDermid Inc, Waterbury, CT and containing by weight, 31.6% SiO_2, 11% Na_2O, trace amounts of Lithium and Molybdenum and a density of 47° Baume' at 20° C) to form a solution having a pH of about 11.5. The manifolds from step 15 were immersed at a temperature of about 130° F (54° C) for about 30 secs;

17) The coated manifolds from step 16 were drained and dried at ambient temperature.

Coated articles from step 17 were analyzed using Electron Spectroscopy for Chemical Analysis (ESCA) to establish coating thickness and the elemental composition of the surface coating. The coating thickness of the dried articles from step 17 was greater than 50 angstroms and less than 2 microns.

An ARL SEMQ electron microprobe analysis using 10 KeV accelerating voltage and wave length dispersive spectrometry (WDX) established that the elemental surface coating on the rinsed article from step 6 contained 4.2% silicon, 0.6% chromium and 2.0% oxygen, and it was concluded to be majorly a silicon-chromate coating. The rinsed coating from step 14, which resulted from the second application of the same solution which produced the article from step 6, included increased quantities of silicon and chromium in the coating to 7.4% silicon, 1.1% chromium and 2.0% oxygen. After the rinsed and elevated temperature silicon-chromate coating of step 15 was contacted with the strongly alkaline solution in step 16 the final, dried coating was analyzed. The above identified electron microprobe and accelerating voltage was used. The coating composition, in weight percent, expressed as oxides of the detected elements and taking into account the applicable accuracy level of the use conditions of the analyzing equipment, the coating contained:

9.9 - 12.1% Na_2O

4.1 - 4.3% Cr_2O_3

76.8 - 91.2% SiO_2

Articles were tested for salt spray resistance using ASTM B-117 test conditions and no corrosion products were visible after 250 hours. Other articles were tested under Engineering material Specification Number ESE-M2P128-A of Ford Motor Co. which is the specification of a superior quality of paint required on the engine, engine accessories and/or parts within the engine compartments of automobiles and trucks. Coated articles from step 17 of the above described process qualified as passing all of the requirements of a superior quality paint including adhesion, hardness, water resistance, gasoline resistance, hot oil resistance, glycol resistance, heat resistance and 96 hours salt spray resistance using the conditions of ASTM B-117.

The process was also used to coat other manifolds sand cast from the materials designated alloy 355.0 - T6, UNS Number A03550, and a die cast aluminum alloy designated BS 1490-LM20 having a specification of 13.0 Si, 1.0 Iron, 0.5 Mn, 0.4 Cu, 0.2 Mg, 0.2 Zn, 0.1 Ti, 0.1 Ni, 0.1 Pb and 0.1 Sn.

EXAMPLE II

Diode plates for automobile alternators that were stamped into the desired configuration using extruded aluminum alloy 6061-T6, AMS 4150G were coated using the process of this invention. The diode plates were approximately 5" (13 cm) long, 5/8" (1.6 cm) wide and 1/8" (3.2 mm) thick and in the shape of an arcuate segment of a circle having a radius of about 5" (13 cm), and provided with a plurality of openings for receiving and supporting diodes.

A quantity of the stamped diode plates were positioned in rotatable barrels, as opposed to the racks described in Example I, and the barrels were sequentially processed through the same coating solutions used in Example I except that steps 4-6 were omitted and certain of the times of immersion in some of the other solutions were changed. In step 1 the immersion was for 3 mins. In step 7, the immersion was for 2-3 mins. In step 11, the silicon-chromate coating forming tank, the immersion time was 12 mins and immersion time in the rinses in steps 12 -15 was for a total of 5 mins.

The coated diode plates retained the aluminium appearance of the stamped parts and were coated with an adherent, scratch and chip resistance coating having a thickness of approximately 2 µm.

The coated diode plates from step 17 were tested for their ability to continue to pass current when assembled into an automobile alternator that was positioned in a salt spray cabinet using the slat spray test conditions of ASTM B-117. The diode plates were found to resist salt spray corrosion and to continue to pass the test current without failure for 1000 hours.

Claims

1. An aluminium or aluminum alloy article having on its surfaces an adherent, clear, thin, corrosion resistant coating, said coating containing as its essential component a chemical complex of alkali metal-chromium-silicates having the composition expressed as oxides in percent by weight of about:-

9.9% - 12.1% Na_2O

4.1% - 4.3% Cr_2O_3

76.8% - 91.2% SiO_2

said complex being present in said coating in an amount sufficient to give said article the combination of properties including resistance to degradation from air, acidic and alkaline gases at elevated temperatures up to about 400° F (204° C) for extended time periods, resistance to water, organic solvents, oils and combustion engine fuels at temperatures encountered in the engine compartments of vehicles, and resistance to salt spray under the conditions of ASTM B-117 test method up to about 250 hours.

2. An aluminium article as claimed in claim 1, wherein said coating has a thickness in the range of about 50 Å to about 2 µm.

3. An aluminium article as claimed in claim 1 or 2, wherein said coating is colourless.

4. An aluminium article as claimed in any one of claims 1 to 3, wherein said coating covers the surfaces of an aluminium alloy similar to that designated 6061-T6 or 355.0-T6.

5. A method for forming a clear, thin, adherent coating on the surfaces of aluminium or aluminium alloy articles which comprises the steps of:-

1) cleaning said aluminium article in an aqueous acidic solution;

2) removing oxides from the surfaces of the article from step 1 by contact for up to about 3 minutes with an aqueous solution having a pH in the range of about 0.5 to 1.0 and made from a composition containing by weight:-

70% - 80% Cr_2O_3
20% - 30% potassium dichromate
2% - 4% ammonium silicofluoride;

3) coating the surfaces of the article from step 2 with a silicon-chromate coating by contacting said surfaces with an aqueous solution having a pH in the range of about 1.2 to about 1.9 at about ambient temperature for a time up to about 12 minutes;

4) rinsing the coated article in a water bath at a temperature in the range of about 110° F (43° C) to about 160° F (71° C) for a time sufficient to raise the temperature of said article to about the temperature of said rinse solution;

5) contacting the rinsed coated article from step 4 with an aqueous alkaline solution having a pH of about 11-12 at a temperature of about ambient to about 130° F (54° C) for about $\frac{1}{2}$ to about 2 minutes, said solution made up from a composition containing SiO_2 and Na_2O in a weight rate of SiO_2/Na_2O of 2.4 to 3.25 and a density in the range of 40 to 42° Baume' at 20° C.

6. A method as claimed in claim 5, wherein the solution in step 3 has a pH less than 1.5 and the time of contact is less than 2 minutes.

7. A method as claimed in claim 5 or 6, wherein the solution in step 5 has a pH in the range of 11.2 - 11.5 and is made up from a composition containing in weight percent SiO_2 in the range of about 27.7% to about 31.7% and Na_2O in the range of about 8.6% to about 11% at densities in the range of about 40 to 47° Baume' at 20° C.

8. A method as claimed in claim 5 or 6, wherein the solution in step 5 has a pH of about 11.5 and is made up from a composition containing a weight ratio of SiO_2/Na_2O of about 2.9 and a density of 47° Baume' at 20° C.