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COATED ALUMINUM ARTICLES AND PROCESS AND MEANS FOR PRODUCING SAME.

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To all whom it may concern:

Be it known that I, ALADAR PACZ, a citizen of the United States, residing in East Cleveland, county of Cuyahoga, and State of Ohio, have invented certain new and useful Improvements in Coated Aluminum Articles and Processes and Means for Producing Same, of which the following is a full, clear, concise, and exact description, such as will enable others skilled in the art to which my invention appertains to make and use the same.

This invention relates to the coating of articles of aluminum or aluminum alloys. It is concerned not only with a novel process of coating such articles and solutions for practicing this process but is also concerned with the resulting new and improved products.

One of the objects of my invention is to provide a process for forming on aluminum articles an adherent, hard, non-metallic permanent coating, the color and nature of which may be varied at will and comprising an oxide or hydroxide of aluminum.

Another object is to provide a process of forming on an aluminum or aluminum alloy article, a coating which is hard, strongly adherent to the article, dense, impervious and capable of being painted, varnished, enameled or electroplated.

Another object is to produce an aluminum or aluminum alloy article having a hard, non-metallic, permanent, adherent surface coating or film containing aluminum in an oxidized form.

A further object is to provide a new and improved composition of matter for forming on aluminum or aluminum alloy article, an ornamental, aluminous surface coating or film which may have a variety of colors and shades.

A still further object is to provide a new and improved composition of matter capable of reacting with a metallic article containing aluminum to form on the surface thereof a controllably colored coating composed in part of aluminum in oxidized form.

Other objects will appear and be pointed out hereinafter.

I have discovered that a surface coating or film containing aluminum, probably in an oxidized form, may be formed on aluminum articles, including substantially pure aluminum, aluminum base alloys (in which the aluminum predominates) and certain other aluminum alloys in which the aluminum forms a small portion, by subjecting the articles to the action of suitable ammoniacal solutions. I have also discovered that such coatings may be obtained in a simple and inexpensive manner without recourse to complicated mixtures, or solutions difficult to prepare, and without the use of temperatures above the boiling point of water; and the coatings may be controllably varied over a wide range as regards thickness, color and properties. Articles provided with coatings having such widely varying properties are naturally capable of many different uses some of which I will hereinafter describe. I have also discovered that while an ammoniacal solution containing a large quantity of hydroxyl radicals is apparently indispensable for my process, I may advantageously add small quantities of certain substances, particularly solutions containing ammonia-soluble metallic salts and ammonium salts for producing the desired coatings.

To enable those skilled in the art better to understand and practice my invention, I hereinafter set it forth in considerable detail as regards the process of producing such coatings; the compositions of coating solutions adaptable for use with the process; and the nature, physical properties and uses of articles produced by the process and by the various solutions.

An aluminum article to be coated by my improved process should, as a preliminary step, have its surface suitably cleaned. The cleaning operation may vary somewhat depending upon the nature of the coating desired and the use to be made of the coated article. Where a matte, etched or roughened surface is satisfactory as contrasted with a polished, specularly reflecting surface, the cleaning may be effected by treatment of the article first in a caustic solution and then in a mineral acid. The strength of the caustic solution, and the length of time it should be used, may both vary somewhat but I prefer to immerse the article in a hot 5% solution for about one to five minutes. The article may be thoroughly washed with water after this cleaning step.

Obviously different acids will be suitable for the second treatment but I prefer sul-

phuric acid. The strength of the acid solution and the length of time for which it should be employed may vary depending on the acid and the condition and composition of the article being treated; in the case of sulphuric acid, a 10% solution used for up to about 15 minutes at temperatures up to about the boiling point of water has been found satisfactory even on aluminum alloys containing considerable quantities of silicon. To remove chemical salts, excess acid, and other substances which may remain on the cleaned article after the acid treatment, the surface thereof should be thoroughly washed with water.

For articles which have smooth polished or specularly reflecting surfaces and particularly where the coated article is to be used as a reflector, and also where the article to be coated is very thin, the caustic solution is preferably replaced by a solution capable of removing grease but not capable of noticeably roughening or corroding the surface. As examples of such substances, carbon tetrachloride or weak nitric acid, with or without a little hydrofluoric acid have been found satisfactory.

The article to be coated having been suitably cleaned is next subjected to the action of a solution containing ammonia, which I will hereinafter designate as a "coating" solution. This "coating" solution should contain from about two to twenty per cent by volume of concentrated aqua ammonia, and preferably is made up by adding one volume of concentrated aqua ammonia to nine volumes of water. For the most rapid and in many cases the best results the solution is heated to between about 50° C and 100° C., but preferably to about 90° C. A temperature somewhat on either side of this may be employed, but I have observed that the time required for, and thickness and quality of the resulting coating depends upon the temperature of the solution as well as upon the concentration of ammonia. A strong, hot solution acts quickly while a weaker or cooler solution may require from one to twelve hours or more to form a coating of a similar thickness, firmness and adherence.

Since the ammonia is rapidly driven out of the "coating" solution at high temperatures, it is often advisable to add a little concentrated ammonia to the solution just before the article is introduced so as to insure the presence of sufficient ammonia to form the desired coating. Also I find it advantageous to add to the "coating" soultion a small amount, say about one percent or more of an ammonium salt, for example ammonium chloride, sulphate or nitrate, with or without small amounts of salts of alkali metals.

During the early stages of this treatment hydrogen is freely liberated, but this gas evolution decreases and finally ceases after a time which is determined by the strength and temperature of the solution. The formation of the coating is generally substantially completed when the gas evolution ceases

The coating formed by this solution on an aluminum surface is hard, non-metallic relatively resistant to abrasion, adherent under ordinary treatment but removable by the use of sharp instruments or abrasives, dense and substantially impervious to penetration by solutions, smooth, of a low coefficient of friction as compared with metallic aluminum, and comprises a base upon which paints, varnishes, enamels or the like may be readily applied and satisfactorily retained.

Such a coating when formed on articles composed of certain aluminum alloys is a sufficiently good electrical conductor to act as an electrode upon which metals may be electroplated. When, however, such a coating is formed on commercially pure aluminum, especially when the "coating" solution contains only ammonia, the coating acts as an efficient electrical insulator and two or more of such coated articles may advantageously be employed, for some purposes, as an electrical condenser.

Apparently this coating process has no harmful effect on the physical properties of the article being coated.

I am able at will to color coatings formed by my invention and to do so during and without interrupting the coating formation. Certain colors may be obtained by adding relatively small amounts of metallic salts to the "coating" solution and substantially the same colors as well as others may be obtained by having the corresponding metals present either as such or as constituents of the aluminum alloy forming the article to be coated. However regardless of what other coloring metal or metals are employed, I prefer to have silver also present in suitable form in the solution. Other colors or variations thereof may be obtained by using various other salts in the "coating" solution.

For example, if a commercially pure aluminum article is treated with a "coating" solution and to which has been added from about ½% to 2½% by weight of borax or the equivalent amount of boric acid in other form, the coating becomes a clear white; if from about ½% to 2½% by weight of sodium fluorid be added instead of borax, the coating becomes gray in color.

If small amounts, (say from about 5 to 50 milligrams or more per liter of solution) of one or more metallic salts be added to the "coating" solution, I can produce a color, ranging from silver white through all shades of yellow, brown and gray to black, including the various tints of red, blue and green

and iridescent effects. All these tints and colors appear to be about equally permanent; they will stand all ordinary heating, washing or handling and are more resistant to discoloration or corrosion than the aluminum or alloys upon which they are formed. When the coating is to be colored in this manner only such metallic salts should be used as are soluble in ammonia, as for example, copper, silver, nickel, zinc, cadmium, cobalt, tungsten, molybdenum, vanadium, etc. Combinations of two or more of such metallic salts often give better results than when only one is used.

If an aluminum alloy is treated with the "coating" solution, the resulting coating obtained corresponds to that on pure aluminum as regards most physical properties but differs in color depending on the color modifying metal or metals in the alloy.

If an alloy containing a substantial amount of silicon is coated, the coating is usually dark colored or even black and possesses a surface appearance resembling finely divided silicon. If an alloy of aluminum with from 1% to 4% of nickel is so treated the resulting color may range from a brass yellow to a dark brown depending on the increasing content of nickel. If the alloy be of aluminum and tungsten (e. g. aluminum 95 to 99%, tungsten 5 to 1%) the coating varies from a silver white at 1% of tungsten to a light brass yellow color at the higher tungsten content. If the alloy be of aluminum and silver, the color verges on yellow though with a golden cast with about $\frac{1}{10}$% of silver, and becomes darker and more prominent up to a very strong and bright red, as the silver content is increased. If the alloy be of aluminum and iron the color obtained is a light gray with about 1% of iron which progressively darkens up to 4% or 5% although never becoming very dark. Other aluminum base alloys similarly treated afford characteristic coatings, for example, those containing copper, cobalt, manganese, chromium, molybdenum, uranium, zirconium, thorium, cerium, zinc. If an alloy containing about 88% zinc, 2% copper and 10% aluminum be treated with the "coating" solution, the resulting coating is nearly black.

If commercially pure aluminum is subjected to the "coating" solution in the presence of a metallic article such as a piece of silver or nickel, the resulting coating differs somewhat from the coating formed when the same metal is absent.

For specular reflection, such as is desired in reflectors for search lights and automobile headlights, for example, it is desirable instead of pickling to first polish by the ordinary means and then clean the aluminum articles with a substance such as carbon tetrachloride which will not destroy the polished surface thereof. Such articles when coated in accordance with my invention will be found to reflect light substantially without diffusing the same.

Although in the foregoing description I have disclosed the composition of several solutions which may be used for carrying out my improved process and producing on aluminum or aluminum alloy articles the new and improved coatings, I do not wish to be understood as having included all of the various compositions which could be so employed. The presence of considerable amounts of ammonia is essential regardless of the color, thickness or physical properties of the coating desired.

This application is a continuation in part of my two prior applications which are identified as follows:—Serial No. 559,465, filed May 8, 1922; Serial No. 549,204, filed April 3, 1922. It will be understood that my invention in any of its aspects is not to be limited to what has been described since various alterations or modifications may be made by those skilled in the art without involving invention or departing from the scope of my invention.

It will be seen that my invention may be practiced by "dipping" or immersing the article to be coated in a suitable solution without the application of electrical energy from an external source, or the subsequent employment of high temperatures.

In the appended claims the term "aluminum article" is intended to include also aluminum alloy articles as herein described.

Having thus disclosed my improved process of coating aluminum or aluminum alloy articles in considerable detail together with various compositions of matter or solutions which may be employed in carrying out my process and certain of the products resulting from the process together with their properties and uses, what I desire to secure by Letters Patent is defined in what is claimed.

What is claimed:—

1. The process of producing an adherent, non-metallic, controllably colored coating upon an aluminum article which comprises the step of immersing the said article, without the application of external electrical energy, in a hot ammonia solution containing an ammonium salt and small amounts of one or more metallic salts in solution.

2. The process of coating an aluminum article which comprises cleaning the surface of the said article, and immersing the article in an ammonia solution containing a small proportion of an ammonium salt and a color modifying substance including silver without the application of external electrical energy.

3. The process of coating an aluminum article which comprises cleaning the surface of the said article, and immersing the

article in a hot ammonia solution containing a small proportion of an ammonium salt and a color modifying substance including silver until a colored coating has been formed thereon.

4. The process of coating an aluminum article which comprises cleaning the surface of the said article, and immersing the article in an ammonia solution containing a small proportion of an ammonium salt and a small amount of color modifying ammonia soluble salt including silver until a colored coating has been formed.

5. As a new composition of matter, a solution for coating aluminum articles which comprises a substantial proportion of ammonia, a small proportion of an ammonium salt, and a small amount of an ammonia soluble silver salt.

6. The process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water and from about one to three parts by weight of an ammonium salt, heating the solution, adding thereto a small amount of an ammoniacal solution of a metallic salt, and immersing therein the said article until a colored coating is formed thereon.

7. The process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water and from about one to three parts by weight of an ammonium salt, heating the solution, and immersing therein the said article until a colored coating is formed thereon.

8. The process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water, and from about one to three parts by weight of an ammonium salt, heating the solution, adding thereto a small amount of an ammoniacal solution of a metallic salt, and immersing therein the said article until a colored coating is formed thereon.

9. The process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water, and from about one to three parts by weight of an ammonium salt, heating the solution up to about the boiling point of water, adding thereto a small amount of an ammoniacal solution of a metallic salt, and immersing therein the said article until a colored coating is formed thereon.

10. As a new composition of matter, a solution for use in coating an aluminum article which comprises ammonia containing an appreciable amount of an ammonium salt and a small amount of an ammonia-soluble silver salt.

11. As a new composition of matter a solution for coating an aluminum article comprising ammonia containnig an appreciable amount of a fluoride of an alkali metal.

12. As a new composition of matter, a solution for coating aluminum articles which comprises a substantial proportion of ammonia, a small proportion of an ammonium salt, and a small amount of one or more ammonia-soluble metallic salts, including silver.

13. As a new composition of matter, a solution for coating aluminum articles which comprises a substantial proportion of ammonia, a small proportion of an ammonium salt, a small amount of an ammonia-soluble silver salt, and a small amount of an ammonia-soluble, color modifying salt.

14. A process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water, and about one part by weight of an ammonium salt, adding thereto a small amount of an ammoniacal solution of a silver salt, and immersing therein the said article until a colored coating is formed thereon.

15. The process of producing a colored non-metallic coating on an aluminum article which comprises cleaning the surface of the said article, forming a solution of approximately one part of concentrated aqua-ammonia, nine parts of water, and from about one to three parts by weight of an ammonium salt, adding thereto a small amount of an ammoniacal solution of salts of silver and one or more other colored modifying metals, and immersing therein the said article until a colored coating is formed thereon.

In witness whereof, I have hereunto signed my name this 6th day of March, A. D. 1923.

ALADAR PACZ.