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METHOD OF COATING MASSES OF SMALL COPPER-BEARING ALUMINUM ARTICLES

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1 Claim. (Cl. 204—23)

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This invention relates to the provision of aluminum articles with a protective coating of aluminum oxide, and it is especially concerned with the anodic treatment of aluminum articles in bulk to produce thereon a coating consisting substantially of aluminum oxide. Such coatings are referred to herein as "oxide coatings," and the term does not include the very thin film of oxide formed on aluminum surfaces on exposure to the atmosphere.

The term "aluminum" as herein employed is intended to include both aluminum and aluminum base alloys.

The process of providing aluminum articles with a protective coating of aluminum oxide by anodic treatment is one well understood and widely practiced in the art. In carrying out the process, the aluminum article is made the anode in an electrolytic cell containing an electrolyte, and, under suitable conditions as to temperature, current density, and voltage, a current is passed through the article to be coated for a given length of time. When it is desired to anodically coat a large number of small aluminum parts, such as rivets or screws, and it becomes impractical to connect each part separately to the source of current, the practice is to coat the articles in bulk by placing them in a compact mass in a suitable perforated container. The container is then placed in the electrolyte and through properly placed contacts, the articles to be coated are connected to the source of current and thus made anode. Despite the fact that the articles in the container are packed together as tightly as possible to insure electrical contact and passage of current through each article during the entire time of immersion in the electrolyte, occasionally the electrical contact with one or more of the articles is broken, or may never be made. When this occurs, it is found that any copper present in solution in the electrolyte tends to deposit galvanically on the surface of the articles which are not in the electric circuit. The material in these deposits, referred to herein as "copper-containing material," may be made up either of copper or of copper-containing compounds, and usually varies in color from brick red to black.

The presence of these adhering deposits of copper-containing material on the aluminum surface is deleterious from the standpoint of the resistance of the surface to corrosion, since the surfaces exhibiting such deposition tend to pit and give other evidences of failure due to corrosion much more rapidly than would otherwise be the case. Accordingly, when coating articles which must

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exhibit good resistance to corrosion, it has been necessary to resort to a careful inspection procedure so as to eliminate those pieces upon which deposits of copper-containing material are found. This inspection procedure is, of course, tedious and expensive and it would be desirable if it could be eliminated.

The electrolyte which is generally employed in the anodic treatment of rivets and other articles treated in bulk, and with which this invention is concerned, is one consisting of an aqueous solution of sulfuric acid. The concentration of sulfuric acid may range from about 1 to 70 per cent by weight, though a concentration between about 10 and 25 per cent by weight thereof is usually preferred. While this sulfuric acid electrolyte is well adapted for anodically coating aluminum articles, it does not prevent the deposition of any copper present in solution in the electrolyte upon the surface of any aluminum article which fails to maintain proper electrical contact as an anode during the time of its immersion in the bath. Copper is not ordinarily a component of the sulfuric acid electrolyte as originally compounded, but when the electrolyte is used to anodize copper-bearing aluminum base alloy articles, copper passes into the solution. The quantity of copper which is thus present in solution in the electrolyte is in most cases very small, representing but a fraction of 1 per cent by weight of the electrolyte, since the bulk of the copper is plated out at the cathode.

It is an object of this invention to provide a method of anodically coating aluminum articles in an electrolyte comprising an aqueous solution of sulfuric acid, and having a quantity of copper present in solution therein, by which method no copper or copper-containing substance will be deposited upon the surface of the aluminum article immersed in the electrolyte even though no current passes through the article during part or all of the period of its immersion. A further object is to provide a sulfuric acid-containing electrolyte which, though copper be present in solution therein, may be employed to anodically coat aluminum articles in bulk without depositing said copper in any form upon the surface of any of said articles immersed in the electrolyte.

I have discovered that an aqueous solution of sulfuric acid containing copper dissolved therein may be employed to anodically coat aluminum alloy articles without danger of depositing copper or copper-containing material upon the surface of any of the aluminum articles immersed in the electrolyte provided a small quantity of

chromic acid be introduced into the electrolyte. Chromic acid may be added either in the form of chromium trioxide (CrO_3), or the addition may be made by using various chromate or dichromate salts, such as Na_2CrO_4 or $Na_2Cr_2O_7$, which produce chromic acid when introduced into an acid solution. The chromic acid content of the electrolyte will hereafter, and in the appended claims, be expressed in terms of chromium trioxide, and in the event the addition is made in the form of a salt, the chromium trioxide content thereof is the factor which determines the amount of the salt to be used. The amount of this component which should be added to the bath in order to accomplish the intended purpose will vary according to conditions of operation. In some cases, as little as 0.2 per cent by weight chromium trioxide is effective for the purposes of my invention, and in no instance has it been found necessary to add more than about 1 per cent by weight thereof in order to prevent the deposition of copper. Even though a lesser quantity of chromium trioxide would usually suffice, I prefer in all cases to employ about 1 per cent by weight of this component of the electrolyte in order to avoid the making of the frequent additions thereof which might otherwise be necessitated by reason of chemical action or drag-out. Larger amounts may also be employed, however, but this is not economical since such additional amounts are not needed to prevent the deposition of any copper-containing material. For example, an electrolyte having as high as 5 per cent chromium trioxide has been employed with good results. The chromic acid present in solution in the electrolyte tends to be reduced during the anodic process, and consequently it may be necessary to add further quantities of this component from time to time in order to maintain a given percentage of chromic acid in solution.

The presence of the chromic acid in the electrolyte may require slight modification of the operating conditions normally used with the sulfuric acid electrolyte. Ordinarily the chromic acid-sulfuric acid electrolyte will require a voltage approximately 10 to 20 per cent greater than would be the case were the bath to contain only sulfuric acid.

The following example will illustrate the manner in which this invention may be used. It was desired to provide a quantity of aluminum rivets fabricated of a copper-magnesium-manganese-aluminum alloy, which contains about 4 per cent copper, among other constituents, with a suitable oxide coating by anodic treatment in bulk. For comparative purposes, two electrolytes were employed in successive tests. One electrolyte had been made up of 16 per cent by weight of sulfuric acid, the balance water, while the other

contained 16 per cent by weight of surfuric acid, 1 per cent by weight chromium trioxide, the balance water. Each electrolyte was then employed to anodically coat a quantity of the rivets so that copper might be introduced into each solution. The rivets so treated were then discarded without comparative inspection. Thereafter, 12 pounds of the bare rivets, placed in a suitable container, were anodically treated in bulk in the sulfuric acid-water electrolyte. In this test the electrolyte was maintained at a temperature of about 70° F., and after the aluminum articles had been immersed in the solution, connected as anode, current of about 6 amp./sq. ft. at 25 volts was passed through the aluminum articles for a period of 40 minutes. The aluminum articles were then removed from the solution and were examined for evidences of deposition of copper-containing material. Approximately 1 per cent of the rivets were found to exhibit a reddish to black stain, indicating deposition of copper-containing material. A subsequent test under substantially the same conditions of operation was then conducted with a second batch of 12 pounds of rivets in the sulfuric acid-chromic acid-water electrolyte, the only difference being that here the voltage was increased to approximately 28 volts. An examination of this second batch of rivets after treatment showed that no copper-containing material had been deposited on the surface of any of the rivets.

I claim:

The method of oxide coating a compact mass of small copper-bearing aluminum articles which comprises making said mass of articles the anode in an aqueous electrolyte consisting essentially of about 10 to 25 percent by weight of sulfuric acid and about 0.2 to 1 percent by weight of chromium trioxide and having a fraction of 1 per cent by weight of copper introduced therein from the articles treated, said chromium trioxide preventing the deposition of copper-containing material on the surfaces of articles that are out of electrical contact as anode during the anodic treatment.

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REFERENCES CITED

The following references are of record in the file of this patent:

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