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PROCESS OF METAL COATING LIGHT METALS

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This invention relates to the application of metal coatings on metal surfaces and more particularly to the application of metal coatings on the surfaces of aluminum, magnesium and their alloys.

This is a continuation-in-part of my copending applications Serial No. 453,131, filed July 31, 1942 and Serial No. 461,333, filed October 8, 1942.

The light metals, aluminum, magnesium and their alloys are widely used as structural materials and have the advantage of light weight combined with adequate strength. Aluminum is fairly resistant to corrosion, but under some conditions corrosion of aluminum and its alloys occurs to an undesirable extent. This is particularly true when they are brought into contact with salt solutions such as sea water, or alkaline solutions. Magnesium is less resistant to corrosion than aluminum.

It has long been desired to protect aluminum and magnesium by application of coatings of other metals, for example, copper or tin. However, the usual methods for coating metals are not easy to apply to these metals. For example, the ordinary methods of electroplating are not satisfactory for coating these metals and satisfactory electroplated coatings can be produced only by utilization of special and expensive methods. It has been proposed heretofore to coat aluminum with copper by contacting the aluminum surface with fused copper chloride. Heretofore, this method has not proved satisfactory, chiefly because of the difficulty encountered in removing the adhering film of copper chloride without damage to the copper coating. It has also been desired to produce aluminum and magnesium having clean coatings of copper, tin or the like which can be soldered more readily by ordinary methods than can aluminum surfaces.

An object of the present invention is to provide a novel and useful method for economically coating aluminum, magnesium and their alloys with other metals. Another object is to prepare aluminum surfaces so that they can be more easily soldered. Other objects will be apparent from the following description.

In accordance with my invention the surface of an article of aluminum, magnesium or an alloy containing one or both of these metals in preponderating amount may be coated with an adherent, substantially impervious, clean copper coating by immersing the article to be coated into a bath of fused cuprous chloride for a time sufficient to form the coating and then treating the coated article in a molten bath containing dissolved alkali metal hydride to remove all adhering copper chloride. In coating aluminum by the cuprous chloride bath treatment, aluminum chloride is formed and this escapes as vapor, so that the bath does not become contaminated and may be used for an indefinite period of time. Any oxide on the surface of the aluminum or magnesium article is fluxed off by the cuprous chloride, so that extraordinary cleaning operations are unnecessary before treating the metal.

When the article is removed from the cuprous chloride bath, the copper coating therein acquired is covered with a film of cuprous chloride, which must be removed. As cuprous chloride is practically insoluble in water, it cannot be removed by the washing methods commonly employed after treating metals in fused salt baths. Heretofore, it has been proposed to remove the cuprous chloride by mechanical means, e. g., by scraping while the cuprous chloride is still molten. However, this method has not proved practicable, since it is practically impossible to thus remove the chloride without damage to the underlying thin copper coating.

I have discovered that the adhering cuprous chloride can be rapidly and completely removed by dipping in a fused bath containing a small amount of dissolved alkali metal hydride, for example, sodium hydride (NaH) dissolved in fused caustic soda. This treatment may be applied either while the cuprous chloride is still molten or at any time after the coated article has cooled. The hydride rapidly and completely converts the cuprous chloride to metallic copper without damage to the copper coating or to the aluminum or magnesium base. The reduced copper so formed is a finely divided material which can be readily recovered as pure copper.

The fused caustic can be readily removed from the coppered article by water washing. I prefer to contact the article with water by dipping or spraying while the caustic film is still molten. Most, if not all, of the reduced copper formed by the hydride treatment remains adherent to the coppered surface, together with an adhering film of caustic. This reduced copper readily separates from the coated article during this washing operation and may be separated from the washings in the form of finely divided copper of high purity.

In a preferred method for practicing my invention, aluminum articles to be coated are dipped in a bath of fused cuprous chloride at a temperature of about 450 to 460° C., then dipped in a bath of fused caustic soda containing 0.5 to

5% of sodium hydride at a temperature of about 380 to 420° C., then dipped in a bath of water and finally sprayed or otherwise washed with water to remove the last traces of caustic. Usually a treating time of a few seconds, e. g. 2 to 10 seconds in each bath is sufficient and the same time of treatment may be employed for each bath. Hence my process is well adapted for continuous operation by means of conventional conveyors for moving articles through the dipping operations or by passing a continuous aluminum or magnesium strip or wire successively through the baths. The temperatures of the cuprous chloride and caustic baths may be as desired between the respective melting points of the baths and the melting point of the base metal coated, i. e. below 660° C. for coating aluminum and below 650° C. for coating magnesium. Longer times of treatment, e. g. up to 1 to 5 minutes, or even longer, may be employed if desired. Ordinarily there is no harm in leaving the article in the baths for longer times.

In place of the caustic soda-sodium hydride bath I may utilize any solution of an alkali metal hydride in fused caustic alkali, e. g. in potassium hydroxide or mixtures of sodium and potassium hydroxide, or in any other molten material which will dissolve alkali metal hydride and which is substantially chemically inert thereto. The hydride bath may be diluted, if desired, with any fusible non-acid salts not reactive with the hydride, for example, alkali metal halides or carbonates, borax, and the like. The hydride content may vary from 0.1 to 20% by weight. I prefer to employ a bath of fused caustic soda containing 0.5 to 5% by weight of sodium hydride.

In my process, the copper coating formed in the cuprous chloride bath is protected from atmospheric oxidation at all times until it has cooled to a temperature where rapid oxidation does not occur. On removal from the molten chloride and caustic baths, I have found that the copper is always uniformly and completely coated with a thin but impervious layer of the bath which fully protects the hot copper. On cooling to room temperature, the frozen film of bath still protects the copper. When, as in my preferred method, the hot article coated with the caustic-hydride bath is contacted with cold water, no oxidation or other discoloration of the copper can be observed.

The reduced copper separated by the water treatment forms a valuable by-product. Usually I prefer to use this to prepare fresh cuprous chloride. This may be done, for example, by adding it to a bath of fused cupric chloride in amount sufficient to completely reduce the cupric chloride to the cuprous salt. Thus my process permits substantially complete recovery of the cuprous chloride removed from the coppered articles and in a relatively simple and economical manner.

The copper coating produced by my method is approximately 0.002 inch thick and is clean and bright. Since the copper coating formed in the cuprous chloride bath does not come into contact with the air or other oxidizing influence until it is cooled by the water wash, it is substantially oxide free and hence has excellent physical properties. I have found that the copper formed by the hydride reduction of the adhering cuprous chloride is substantially all removed during the water washing step. Hence, no mechanical after-treatment is ordinarily necessary to insure continuous production of uniform, bright, smooth, copper coatings. The copper coating is very tightly adherent to the base metal and resists all attempts to strip it off by mechanical means. For example, a coating thus applied to an aluminum sheet was tested by over-plating it with an extra heavy nickel electrodeposit and then flexing the sheet to cause the hard nickel layer to crack and peel. No tendency for the copper to separate from the aluminum could be observed. This copper coating also was found to be substantially non-porous and to afford excellent protection to the aluminum base, in spite of its relative thinness. This was evidenced by immersing the coated article in a bath of fused caustic soda containing sodium hydride, which rapidly attacks unprotected aluminum. The coated article suffered no damage whatsoever from the caustic soda treatment. When the copper coated aluminum is placed in a fused caustic soda bath containing a small amount of sodium hydride, any copper oxide or copper salt on the surface is cleaned off, but otherwise the article is not changed. Microscopic examination also shows that the coating is substantially non-porous.

I have found that my herein-described metal coatings are more or less alloyed with the base metal, which probably accounts for the unusual tenacity with which the coatings adhere to the base metal. This may be demonstrated, for example, by overplating the copper coated aluminum with a copper electrodeposit and observing a polished and etched cross-section under the microscope. Microphotographs of such sections show the original copper coating as a layer of aluminum-copper alloy interposed between the aluminum and the electrodeposited copper overplate. This result is obtained even when my copper coating is applied as herein described at a temperature below that at which copper dissolves in aluminum. Thus, my copper coating produced at a temperature of about 450° C. is alloyed with the aluminum, although that temperature is well below the melting points of copper-aluminum alloys.

Similar results may be obtained in utilizing my method to coat aluminum, magnesium or their alloys with lead and silver, i. e. by treating the base metal with fused lead chloride or fused silver chloride and subsequently treating in the alkali metal hydride bath to remove adhering chloride and washing, as described above. Further, my invention may be practiced with various other halides of copper, lead and silver, as well as with the chlorides. While I prefer to use the cheaper chlorides of these metals, the bromides, iodides, and fluorides or mixtures thereof, which melt below the melting point of the aluminum or magnesium base, may be used with good results. Thus, halides used for coating aluminum should melt below 660° C. and those used for coating magnesium should melt below 650° C. Generally I prefer to use halides of copper, silver or lead, or mixtures thereof, which melt below about 650° C. Alloy coatings may be produced by using appropriate mixtures of the metal halides for the coating baths, for example, a mixture of copper and silver halides.

My invention is not restricted to coating metals of pure aluminum, pure magnesium or pure aluminum-magnesium alloys but is applicable to any metal or alloy which is composed at least preponderantly of aluminum, magnesium or aluminum-magnesium alloy. It is applicable, for example, to the various known commercial aluminum and magnesium alloys which are useful

for structural purposes. Preferably, an alloy to be coated by my process should contain not more than about 30% by weight of metal other than aluminum or magnesium.

The extent of alloying between the aluminum or magnesium base and the metal coating may be increased by heating the coated article to the melting point of the desired alloy, which in some cases may be close to the melting point of the base metal. Such treatment, if at a sufficiently high temperature and of sufficiently prolonged duration, may cause the apparent disappearance of the coating metal, which becomes dissolved into the metal base, forming an alloy layer or "case" on the surface of the coated metal. For example, I have coated aluminum with copper by treatment in a fused cuprous chloride bath at a temperature of about 460° C. to produce a coating interalloyed with the aluminum base but having the appearance of copper. After cleaning off the adhering copper chloride by treatment in a fused sodium hydroxide bath containing sodium hydride and water washing, the article was heated to a temperature above 500° C., whereupon the copper color gradually disappeared, and a layer of copper-aluminum alloy was formed.

The metal coatings produced by my method are ductile and may readily be buffed or burnished by conventional methods to produce desired surface finishes. They may be coated with further layers of protective materials by various known methods applicable to the surface of the coating metals, for example, electroplating, hot dipping, painting, varnishing, lacquering and the like. Thus it is possible to apply any desired protective coating to the aluminum articles by my process, without employing the expensive or tedious methods heretofore required.

My herein-described coatings are more adherent than those which can be produced on aluminum and magnesium articles by known electroplating methods. The coatings are substantially non-porous and afford excellent protection to the base metal. The coatings may be applied quickly and at low cost.

Another important advantage of my invention is that the coated articles may readily be joined by soldering. For example, whereas aluminum articles are very difficult to solder and can be soldered only by employing special methods and solders which are not economical for most purposes, my coated aluminum articles can be soldered by any method applicable to soldering the coating metal to make a variety of fabricated articles. For this purpose, when desired, I may coat only those portions of the article which are to be soldered, for example the edges of sheets where the solder is to be applied. My process thus enables the fabrication of aluminum and articles by soldering in an economical manner which has not been possible heretofore.

I claim:

1. A process for applying a metal coating to a metal base having a surface composed at least preponderantly of a light metal selected from the group consisting of aluminum and magnesium comprising contacting said base with a fused salt bath comprising a halide of a metal selected from the group consisting of those copper, lead, and silver halides which melt at temperatures below about 650° C. and thereafter removing residual metal halide from the coated base by immersion in a fused bath comprising a solution of alkali metal hydride in alkali metal hydroxide, followed by washing with water.

2. A process for coating an article composed at least preponderantly of aluminum, which comprises immersing said article in a fused halide of a metal selected from the group consisting of those copper, lead, and silver halides which melt at temperatures below 660° C. and thereafter removing residual metal halide from the coated article by immersing it in a fused bath comprising a solution of alkali metal hydride in alkali metal hydroxide, followed by washing with water.

3. A process for copper coating an aluminum article which comprises immersing said article in fused cuprous chloride and thereafter removing residual cuprous chloride from the coated article by immersing it in a fused bath of sodium hydroxide containing 0.5 to 5% by weight of dissolved sodium hydride and finally washing with water.

4. A process for copper coating an aluminum article which comprises immersing said article successively in fused cuprous chloride, in fused alkali metal hydroxide containing dissolved alkali metal hydride and in water, without cooling to a temperature below the melting points of the aforesaid fused materials between the successive immersions.

5. A process for copper coating an aluminum article which comprises immersing said article successively in fused cuprous chloride, in fused sodium hydroxide containing about 0.5 to 5% by weight of dissolved sodium hydride and in water, without substantial cooling between the successive immersions.

6. The process which comprises continuously passing an aluminum article of extended length, including sheet, ribbon, wire and the like, in succession through a molten cuprous chloride bath, thence through a molten sodium hydroxide bath containing about 0.5 to 5% by weight of dissolved sodium hydride and thence through an aqueous bath at a linear velocity sufficiently high to avoid substantial cooling of said article in the intervals between said baths.

7. A process for coating an article composed at least preponderantly of magnesium, which comprises immersing said article in a fused halide of a metal selected from the group consisting of those copper, lead, and silver halides which melt at temperatures below 650° C. and thereafter removing residual metal halide from the coated article by immersing it in a fused bath comprising a solution of alkali metal hydride in alkali metal hydroxide, followed by washing with water.

8. A process for copper coating a magnesium article which comprises immersing said article in fused cuprous chloride and thereafter removing residual cuprous chloride from the coated article by immersing it in a fused bath of sodium hydroxide containing 0.5 to 5% by weight of dissolved sodium hydride and finally washing with water.

9. A process for copper coating a magnesium article which comprises immersing said article successively in fused cuprous chloride, in fused sodium hydroxide containing about 0.5 to 5% by weight of dissolved sodium hydride and in water, without substantial cooling between the successive immersions.

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