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2,728,718

ALUMINUM COATING

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This invention relates to coating with aluminum. More particularly, it relates to an improved process and bath for depositing aluminum on metal or other electrically conducting surfaces and to an aluminum coating produced thereby.

The physical properties of aluminum, particularly its resistance to corrosion, tend to make it very desirable for use as a structural material. However, the low tensile strength prevents widespread usage in pure form. Accordingly, many attempts have been made to form a coating of aluminum on steel or other suitable construction materials, wherein the aluminum coating will serve to protect the surface of the base material.

This improved process for electrodepositing aluminum is also useful in electroforming articles of complex shapes. A low melting alloy can be cast or otherwise formed into the desired shape and then coated with aluminum. The base material is melted out leaving a light-weight shell. It has not been possible to make such aluminum articles by the prior-art methods of electrodepositing. The process of electroforming is particularly useful for manufacturing radar wave guides and comparable electronic equipment.

Although several processes for electrodepositing aluminum have been described in the prior art, it has not been possible to produce dense coatings thicker than about 0.002 inch, since any excess of deposited metal consisted entirely of non-adherent powder, sponge, or trees. As a result, the surfaces were not smooth and "bright" as the term is commonly used in the art.

Another difficulty encountered in prior art methods of electrodepositing aluminum is the extremely short life of the bath. After only a few days' use, the bath deteriorates, causing nonadherent deposits that are completely sponge-like.

In Patent No. 2,446,331, Hurley has disclosed an electrolyte for use in the electrodeposition of aluminum. This bath comprises an anhydrous aluminum halide and a N-alkyl pyridinium halide. Wier and Hurley, in Patent No. 2,446,349, show the addition to this electrolyte of a liquid aromatic hydrocarbon, such as benzene, toluene, xylene, and the like. Also, Wier, in Patent No. 2,446,350, discloses the further improvement of superimposing an alternating current on the direct current used in the plating bath. In the process of Patents No. 2,446,349, and No. 2,446,350, a finite amount of toluene was miscible with the aluminum halide-alkyl-pyridinium halide fusion, and any excess amount of toluene floated in a layer on top of the bath. It has now been found that if excess toluene or benzene is added and the bath is continuously agitated, so that the toluene is dispersed throughout the bath, a thicker plate can be formed without any powdering or treeing. This dispersion also improves the properties of aluminum coatings of less than 0.002 inch, being stronger, denser, and more ductile than the prior art aluminum plate. The hardness ranges from 45 to 70 Knoop as compared to 36 Knoop or less under prior art procedures.

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In addition, the life of the bath is greatly extended by the agitation.

Accordingly, it is one of the objects of this invention to provide an improved method of depositing aluminum on a metal or other electrically conducting surface.

Another object is to provide an improved, long-life electrolyte for depositing aluminum on a metal or electrically conducting surface.

In general, the bath for depositing the aluminum coating comprises a nonaqueous solution of a fusion of an aluminum halide and a quaternary salt of nitrogen. The fusion is dissolved in an excess of a liquid aromatic hydrocarbon. The excess hydrocarbon, which normally would form a layer at the top of the bath, is continuously dispersed throughout the bath.

In preparing the fusion mixture, any of the aluminum halides may be used. The aluminum halide is fused with a quaternary salt of nitrogen, preferably a pyridinium salt. Very satisfactory results have been obtained by using a N-alkyl pyridinium halide, such as methyl or ethyl pyridinium halide. Proportions of about two mols of the aluminum halide to about one mol of the nitrogen salt will form a low melting eutectic.

The solvent for the fusion mixture is a liquid aromatic hydrocarbon mixture, such as toluene or benzene. A sufficient amount of solvent is used to completely dissolve the fusion product and also form a layer of excess solvent on top of the fusion solution. Although any excess of solvent will aid in imparting desired properties to the bath, an excess of less than 23 per cent by volume of the total bath will result in a plating which is less smooth, dense, and ductile, than when a larger excess is used. If over about 45 per cent excess is used, it cannot be completely dispersed. The bath also tends to become nonconductive when more than about 45 percent of excess solvent is used. The most satisfactory plating was formed from a bath having an excess of solvent in the range of 35 to 40 per cent.

The plating cells may be constructed of glass, ceramics, plastics, or any other suitable material which will not react with the bath. It is also desirable that the cell be closed whenever possible to prevent entry of impurities into the bath.

As has been heretofore stated, it is important that the bath be agitated during the plating operation, in order to disperse the excess hydrocarbon solvent. Although any suitable means may be used for the agitation, the most satisfactory results have been obtained by bubbling an inert gas through the bath. Nitrogen, argon, or other inert gas, may be used. However, care must be taken that no oxygen is present, since this causes the bath to degenerate. It is desirable to remove any oxygen present in the gas before passing it into the bath.

The flow rate of the gas depends, to a great extent, on the surface area of the plating bath. However, best results are obtained when the rate is slightly greater than the minimum flow needed to disperse the excess solvent. A rate of 0.2 cu. ft. per hour per square inch of surface area provides satisfactory dispersion.

Dispersal of the excess hydrocarbon may also be accomplished by means of supersonic vibrations from a quartz crystal.

Articles to be coated form the cathode in the bath. Materials suitable for coating include steel, copper, silver, lead-, zinc-, and cadmium-base alloys and similar materials. The anodes are aluminum. High-purity aluminum, such as 99.9 or 99.99% forms better coatings than, for example, 2-S aluminum, and the anodes dissolve with a current efficiency nearly equal to 100 percent.

During the coating process, the bath should be maintained within a temperature range of about 80° F. to about 100° F. At temperatures appreciably lower than 80° F.,

it has been found that the resulting coating tends to be brittle and cracked. The optimum temperature for coating is from about 83° F. to about 87° F.

For best results in coating, an alternating current should be imposed on the direct current passed through the bath. Successful results have been obtained with cathode densities of 5 to 25 amp. per sq. ft. D. C. and 2.5 to 50 amp. per sq. ft. A. C. Preferred current densities are in the range of 8 to 12 amp. per sq. ft. D. C. and 10 to 20 amp. per sq. ft. A. C. Less than 6 volts are needed.

The following example will serve to illustrate the invention with greater particularity:

44 grams of aluminum chloride and 31 grams of ethyl pyridinium bromide were fused together at 400° F. for 15 minutes. This fusion product was dissolved in 165 cc. of toluene. About 99 cc. of the toluene was used to dissolve the fusion product, leaving an excess of 75 cc. of toluene.

The bath was placed in a glass plating tank. A current was passed through the bath between a copper-base material as the cathode and an aluminum anode, using a source of direct current connected across from the anode to the cathode and a source of 60 cycle alternating current connected in series with the direct current. The cathode density was 10 amp. per square foot for both D. C. and A. C. current, and the anode density was 5 amp. per square foot for both A. C. and D. C. current. During the plating, the bath was maintained at a temperature of 100° F. The excess toluene was dispersed by bubbling high purity nitrogen through the bath at a rate of 1.5 cubic feet per hour. The cathode efficiency was about 95 per cent. After 23 hours, an electroplate about 0.015 inch in thickness was formed on the cathode. This coating was ductile, homogeneous, dense, and uniform in thickness.

The high finish on both surfaces of the aluminum coating also makes it desirable for use in forming hollow articles of complex shapes, such as wave guides. A low melting alloy can be cast in the shape desired for the finished hollow article. This mandrel is surface-finished, and preferably coated with a copper plate to facilitate deposition of a smooth aluminum plate. Aluminum is then electrodeposited, utilizing the process and bath heretofore disclosed. The mandrel is melted out and the copper plate dissolved from the inner surfaces of the hollow article. The resulting article has a uniform thickness, is light in weight, and compares favorably in physical properties to a heavy metal electroform.

Alternatively, a nonmetallic solid such as a plastic, can be used in cast or machined form by surfacing it with silver by any one of the well-known chemical reduction methods and then electrodepositing the aluminum thereon. The plastic is dissolved by means of a suitable solvent. If desired, the silver liner can be left on the inner surfaces of the electroformed aluminum article.

In summary, by utilizing the process and bath of this invention, it is possible to form aluminum coatings in thicknesses greater than 0.002 inch without treeing or forming nonadherent powders or sponge. The improved coatings have superior properties of hardness and ductility. Hollow articles of complex shapes can be formed by applying this coating to a low-melting metal base, and subsequently melting out the base. The bath used in this coating process has been used as long as 44 days without appreciable change in the quality of coatings produced, and the use could apparently be extended indefinitely.

What is claimed is:

1. The method of electrodepositing an aluminum coating on an electrically conductive surface which comprises the steps of forming a fusion of an aluminum halide and

a quaternary salt of nitrogen, making a solution by dissolving said fusion in a liquid aromatic hydrocarbon solvent, said solvent being present in sufficient quantity to form a layer of excess solvent separate from said solution, continuously dispersing said excess solvent throughout the solution, and passing an electric current through the solution between an aluminum anode and an electrically conductive surface serving as a cathode.

2. The method according to claim 1 wherein the nitrogen salt is a N-alkyl pyridinium halide.

3. The method of electrodepositing an aluminum coating on an electrically conductive surface which comprises the steps of forming a fusion of about 2 mols of aluminum chloride and about 1 mol of ethyl pyridinium bromide, making a solution by dissolving said fusion in toluene, said toluene being present in an amount sufficient to provide an excess layer in volume equal to about 23 to about 45 per cent of the total volume, bubbling an inert gas through said solution whereby the excess solvent is continuously dispersed throughout said solution, and simultaneously passing an electric current through the solution between an aluminum anode and the electrically conductive surface serving as a cathode.

4. In the method of electrodepositing aluminum on an electrically conductive surface in a bath comprising a solution of a liquid aromatic hydrocarbon solvent in which has been dissolved a fusion of an aluminum halide and a quaternary salt of nitrogen, the steps of adding an excess of said solvent sufficient in amount to form a layer of solvent on top of said solution and continuously dispersing said excess solvent throughout the solution during the deposition.

5. The method of electroforming an aluminum article which comprises the steps of forming an electrically conductive base in a desired configuration, immersing said article in a bath, said bath comprising a solution of a liquid aromatic hydrocarbon solvent in which is dissolved a fusion of an aluminum halide and a quaternary salt of nitrogen, said solvent being present in sufficient quantity to form a layer of excess solvent, continuously dispersing said excess solvent throughout the bath, passing an electric current between an aluminum anode and said conductive base as a cathode until an aluminum coating is deposited thereon, removing said coated base from the bath, and separating said conductive base from said aluminum coating.

6. The method of electroforming an aluminum article which comprises the steps of forming a solid nonmetallic base in a desired configuration, making the surface of said solid base conductive, immersing said surface in a bath, said bath comprising a solution of a liquid aromatic hydrocarbon solvent in which is dissolved a fusion of an aluminum halide and a quaternary salt of nitrogen, said solvent being present in sufficient quantity to form a layer of excess solvent, continuously dispersing said excess solvent throughout the bath, passing an electric current between an aluminum anode and said conductive base as a cathode until an aluminum coating is deposited thereon, removing said coated base from the bath, and separating said conductive base from said aluminum coating.

References Cited in the file of this patent

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