Patented Aug. 22, 1939

2,170,375

UNITED STATES PATENT OFFICE

2,170,375

ELECTRODEPOSITION OF ALUMINUM

Frank C. Mathers, Bloomington, Ind., and Robert D. Blue, Midland, Mich.

No Drawing. Application May 10, 1937, Serial No. 141,706

3 Claims. (Cl. 204—1)

The present invention relates to the electrolytic plating with aluminum of other metals. The term "aluminum", as employed in this description and in the appended claims, includes aluminum and alloys whereof aluminum is the major constituent.

It is among the objects of the invention to provide an improved method for electrodepositing aluminum on metal articles. A further object of the invention is to provide a bath wherefrom aluminum can be electrodeposited at substantially room temperature. Another object of the invention is to provide a bath for the electrodeposition of aluminum which has a relatively high electrical conductivity, and in which high electrode efficiencies are obtained.

In our process for the electroplating with aluminum of dissimilar metals such as iron, copper, zinc, and the like, we employ a bath composed essentially of the reaction product or benzene with an alkyl halide and an aluminum halide. Certain derivatives of benzene, such as the alkyl-benzenes, halo-benzenes, and alkyl-halo-benzenes, can be substituted for, or employed in combination with, benzene in forming our plating bath; and hydrogen halides may be substituted for alkyl-halides in such procedure.

In plating aluminum upon a dissimilar metal article, we employ the article to be plated as the cathode in our bath, and a mass of aluminum is attached to or employed as the anode therein. Direct current is passed through the electrolyte whereby aluminum is dissolved off the anode into the bath and plated out on the cathode article. A supernatant liquid layer of benzene or derivative thereof is maintained over the bath to protect the same from oxidation by air and hydrolysis by the moisture normally present therein. The plating operation is carried out at room temperature, although elevated temperatures may be employed, e. g., 50° C.

In the preparation of our novel plating bath we have successfully employed benzene, and toluene, xylene, cymene, ethylbenzene, chlorobenzene, and bromobenzene, poly-methyl-benzene, and poly-ethyl-benzene, as reaction materials instead of, or in combination with, benzene. Other materials of a similar nature which can be used are isopropyl benzene, tertiary butyl benzene, normal amyl benzene and the chloro-, bromo-, and iodo-, derivatives thereof. Certain of the foregoing materials or their equivalents do not produce a bath which is sufficiently fluid at room temperatures for good operating conditions, and in such cases we admix with the material sufficient benzene to produce a final reaction product whereof the viscosity is lower than that obtained by using such materials alone. Among the alkyl halides which are entirely satisfactory for use as reactants in the preparation of the bath are ethyl bromide, ethyl chloride, methyl chloride, isopropyl chloride, isopropyl bromide, normal-butyl chloride, tertiary amyl bromide, and the like. Hydrogen chloride or hydrogen bromide may be substituted for the alkyl halide in preparing the plating bath. The third ingredient we use in the preparation of the bath is aluminum chloride, aluminum bromide, aluminum iodide, or mixtures of the foregoing. The supernatant liquid maintained above the bath may be benzene, or any of the equivalents therefor above named for use as reactants in preparing the bath.

A preferable way of combining the ingredients which we employ in making up our bath comprises dissolving or suspending an aluminum halide, in anhydrous condition, in the benzene or derivative thereof, and then mixing this product with the alkyl or hydrogen halide, preferably at a substantially uniform rate over a suitable period of time. If the alkyl halide employed is a gas, or if hydrogen chloride is used in preparing the bath, then the aluminum halide may be suspended in the benzene and such gaseous reagent bubbled thereinto. All of the reagents should be in substantially anhydrous condition prior to being combined. When a bath is being used for the first time, a small quantity of finely divided metallic aluminum may be added thereto advantageously. During the use of the bath in electrodepositing aluminum, it is sometimes necessary to add small quantities of freshly prepared electrolyte because the anode efficiency is higher than the cathode efficiency. The addition of small amounts of any of the alkyl halides herein mentioned gives equally good results, although the repeated addition thereof increases the viscosity of the electrode. Small amounts of the various components of the electrolyte may be present in the supernatant layer.

The following table sets forth certain specific

compositions which are useful in carrying out our invention, which are only illustrative of the invention, and are not to be construed as limiting the same.

Benzene or equivalent	Parts by weight	Alkyl halide or hydrogen halide	Parts by weight	Aluminum halide	Parts by weight
C_6H_6	88	C_2H_5Br	57	Bromide	40
Do	88	C_2H_5Cl	37	do	40
Do	88	CH_3C_5	15	do	40
Do	88	$(CH_3)_2CHCl$	36	do	40
Do	88	HCl	5	do	40
Do	88	HBr	4.3	do	40
$C_6H_5CH_3$	87	C_2H_5Br	57	do	40
C_6H_6–57 $C_6H_4(CH_3)_2$–30	87	do	57	do	40
C_6H_5Cl–77 C_6H_6–44	121	do	57	do	40
$C_6H_5CH_3$–44 C_6H_5Br–75	119	do	57	do	40
C_6H_6–57 $C_6H_4(CH_3)_2$–30	87	do	57	Chloride–20 Bromide–20 Iodide–4	44

As a specific example illustrating the practice of our invention, we have prepared a bath consisting of 88 parts by weight of benzene, 57 parts by weight of ethyl bromide, 20 parts by weight of aluminum bromide, and 20 parts by weight of aluminum chloride, the total volume of the plating solution being 50 cubic centimeters. This bath was operated at a temperature of 20° C. with the aluminum anode and copper cathode spaced 6.45 centimeters apart. The anode surface was 38.7 square centimeters, the cathode surface 6.4 square centimeters, and the bath was operated at a current density of 1.55 amperes per square decimeter of cathode surface. In such bath the cathode efficiency was found to be 76.52 and the anode efficiency 105.22. This bath was operated from 8 to 10 hours daily for three months with excellent results. The anode losses were higher than the cathode gain, so that additions of ethyl bromide were necessary to maintain the bath. Three cubic centimeters of ethyl bromide added after each 100 hours of use were sufficient.

Aluminum alloy coatings may likewise be produced on a cathode in the baths herein set forth. The alloy is employed as the anode in the electrolysis. It is to be understood that alternate use as anode of aluminum and a dissimilar metal gives an equivalent result. We have employed the alloys of aluminum with zinc, with copper, and with cadmium, as the anode in baths hereinbefore described to produce desirable coatings upon copper cathodes. We have also employed an anode of aluminum alternately with a silver anode, a tin anode, a nickel anode, and various other metals, to produce aluminum alloy coatings possessing desirable characteristics.

This application is a continuation in part of our prior co-pending application Serial Number 756,830.

Other modes of applying the principle of our invention may be employed instead of those explained, change being made as regards the process or materials herein disclosed, provided the means or ingredients stated by any of the following claims or their equivalent be employed.

We therefore particularly point out and distinctly claim as our invention:

1. The method of electrodepositing aluminum upon dissimilar metals which comprises passing direct current between an aluminum anode and a dissimilar metal cathode in an electrolyte composed of the reaction product of: a material selected from the group consisting of benzene, and the alkyl-, halo-, and alkyl-halo-, derivatives of benzene; a halide selected from the group consisting of the alkyl and hydrogen halides; and an aluminum halide; under a layer comprising a material selected from the group consisting of benzene, the alkyl-, halo-, and alkyl-halo-, derivatives of benzene.

2. The method of electrodepositing aluminum upon dissimilar metals which comprises passing direct current between an aluminum anode and a dissimilar metal cathode in an electrolyte composed of the reaction product of benzene, an alkyl halide, and an aluminum halide, under a layer comprising benzene.

3. The method of electrodepositing aluminum upon dissimilar metals which comprises passing direct current between an aluminum anode and a dissimilar metal cathode in an electrolyte composed of the reaction product of: an alkyl-benzene, an alkyl halide, and an aluminum halide; under a layer comprising an alkyl-benzene.

FRANK C. MATHERS.
ROBERT D. BLUE.