

UNITED STATES PATENT OFFICE

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ELECTRODEPOSITION OF ALUMINUM

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This invention relates to the electrodeposition of aluminum from a liquid mixture of a nitrogen-substituted alkyl pyridinium chloride or bromide and aluminum chloride.

In a co-pending application, Serial No. 522,375, filed February 14, 1944, Hurley has disclosed a process for the electrodeposition of aluminum on dissimilar metal cathodes from a liquid mixture of aluminum chloride or bromide and an N-alkyl pyridinium chloride or bromide or an N-alkylene dipyridinium chloride or bromide. Hurley points out the temperature of the bath must be sufficiently elevated to avoid spongy aluminum deposits and that one should generally work at a temperature above 100° C.

It is obvious that if one can successfully plate aluminum at a lower temperature, preferably about room temperature, the operation is materially simplified, the operation can be conducted more economically, and various articles which cannot be handled readily at the more elevated temperatures can be plated at the lower temperature.

It is in general the broad object of the present invention to provide a process for the electrodeposition of aluminum on dissimilar metals at room temperature.

Another object of the present invention is to provide a novel electrolyte for the electrodeposition of aluminum on dissimilar metals. We have discovered that by the addition of certain aromatic compounds to liquid mixtures of aluminum chloride or bromide and the N-alkyl mono-pyridinium mono-chlorides or mono-bromides in which the alkyl radical is unsubstituted, an improved bath is obtained, one which permits successful plating at room temperature.

In addition, by utilization of the aromatic compounds, it is possible to materially lower the cost of the plating solution.

Further, the plate which is secured is materially improved in appearance when compared to a plate on the same material which is effected at an elevated temperature without the use of the additional compound.

In addition to these advantages, there is less loss of the plating solution upon removal of the plated object from the bath. Further, it is possible to use higher current densities.

In making up the bath, we employ a liquid compound selected from the group consisting of liquid aromatic hydrocarbons such as benzene, toluene, xylene and the like, and their liquid chloro-substituted derivatives such as chloro-

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benzene. Mixtures of these liquids can also be used.

One proceeds to make up the desired mixture of aluminum chloride and the desired nitrogen-substituted alkyl mono-pyridinium mono-chloride or mono-bromide. One then adds the aromatic substance, such as benzene, preferably until an excess of the added compound floats on the top of the aluminum chloride-pyridinium compound layer. The lower layer is the plating solution. When the plating mixture is saturated with the aromatic compound in this way, the volume of electrolyte solution is approximately doubled, except in the case of chloro-benzene which appears to be miscible with the aluminum chloride-pyridinium compound mixture in all proportions. The upper layer, which consists principally of the added aromatic compound, is very useful for protecting the bath from atmospheric moisture. However, it is not necessary that completely saturated solutions be employed for the successful operation of the bath, and one need only add a small amount of the aromatic substance to the aluminum chloride-pyridinium compound mixture to secure some of the advantages of this invention.

Good plates of aluminum can be obtained when the nitrogen-substituted alkyl halide is the ethyl derivative. The proportion of aluminum chloride to ethyl pyridinium salt in the bath should be approximately two mols of aluminum chloride (taken as $AlCl_3$) to one mol of either nitrogen (taken as N) or halide in the pyridinium salt.

Such a bath is employed in plating by providing an aluminum anode, and a cathode object which may be of iron, copper, brass, bronze, lead, nickel, tin or the like. Zinc should not be used because it usually reacts with the bath. When current is passed between the electrodes, aluminum dissolves at the anode and is deposited upon the cathode.

In removing the cathode from the bath a thin film of the plating solution remains on the cathode. This should be removed immediately by rinsing with water.

As a container for the bath, a cell of glass, porcelain or other inert material may be used; or the container may be made of aluminum and can then serve as the anode. If the cell is made of other metals, any moisture which is present may result in corrosion of the metal by moist hydrogen halide. This can carry the metal halide into solution and may result in the formation of a plate consisting of an aluminum alloy.

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Under certain conditions these alloy plates may not be disadvantageous and accordingly the term aluminum as used here and in the claims is to be considered as including such alloys in which aluminum forms the major constituent.

To obtain the proper conditions of current density and voltage, a suitably designed cell must be employed. In general, the anode should be as large as or larger than the cathode object, and the electrodes should be so arranged in the cell that the resistance of the cell is not too high and the cathode current distribution is uniform.

In electroplating with this type of bath, cathode current densities between 0.5 and 1.0 amp./dm.² were found to be most useful. At the lower cathode densities (about 0.5 amp./dm.²) white plates of aluminum were obtained, while at the higher current densities (about 1.0 amp./dm.²), the plates were very bright and shiny. At still higher current densities brown streaks appeared on the shiny deposits and with excessive current densities, black, non-adherent deposits were obtained. These appeared to contain some occluded aluminum chloride. In some cells we have successfully used cathode current densities as high as 2.0 amps./dm.² and obtained bright and shiny plates. The white plates mentioned above may be polished if desired.

The cathode current efficiencies are very high, being about 85% at 0.5 amp./dm.² to 92% at 1.0 amp./dm.².

In addition, the voltage requirements of this plating solution are very low, of the order of one volt. However, this depends on the cell size and the current density.

To obtain the best results with this bath, it should be used in a dry atmosphere, free of oxygen and other oxidizing gases. The behaviour of the bath in the presence of moist air shows that it is subject to oxidation which can lead to deterioration of its plating properties. The oxidation is indicated by the appearance of a red color in the bath. A nitrogen atmosphere or an atmosphere of a non-oxidizing gas should be maintained over the bath.

The following example is given as illustrative of a practice within the present invention.

A mixture of ethyl pyridinium bromide and aluminum chloride in the ratio of 66.7 mol per cent aluminum chloride (taken as AlCl₃) and 33.3 mol per cent ethyl pyridinium bromide was prepared and toluene was added until the mixture was saturated. This mixture was used in a cylindrical glass cell, 5.2 cm. in diameter and filled the cell to a depth of about 5 cm. The mixture was covered with a layer of toluene about

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1 cm. deep, which served as a protection against moisture. The anode was a circular aluminum sheet, 5 cm. high and 15 cm. in circumference. Thin sheets of iron or other metal 2.5 to 3.8 cm. wide, were used as cathode objects and were immersed from 3 to 5 cm. in the plating liquid. These were suitably cleaned before use. The whole apparatus was fitted with a suitably designed top arranged so that dry gases could be passed through the cell. This apparatus was used for tests of several sorts, especially those showing the effect of varying the current density. It was found that very bright and shiny plates were obtained at current densities between 0.5 and 1.0 amp./dm.².

We claim:

1. A process of electroplating that comprises electrodepositing aluminum as a bright, adherent deposit on a metal from the group consisting of iron, copper, brass, bronze, lead, and nickel and tin from a cell containing a liquid nonaqueous electrolyte consisting essentially of a mixture of (1) about 2 mols of aluminum chloride, (2) about 1 mol of ethyl pyridinium chloride, and (3) a sufficient amount of toluene to saturate the mixture.

2. A nonaqueous electrolyte for use in the electrodeposition of aluminum as a bright, adherent deposit that consists essentially of a mixture of (1) about 2 mols of aluminum chloride, (2) 1 mol of ethyl pyridinium chloride and (3) a sufficient amount of toluene to saturate the mixture.

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REFERENCES CITED

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

UNITED STATES PATENTS

Number	Name	Date
1,911,122	Keyes et al.	May 23, 1933
1,939,397	Keyes et al.	Dec. 12, 1933
1,960,334	Ernst et al.	May 29, 1934

OTHER REFERENCES

Journal of Physical Chemistry, vol. 35 (1931), p. 2289.

Chemical Abstracts, vol. 32, No. 18 (Sept. 20, 1938), col. 6956.

Elektrochemie Nichtwässriger Lösungen by Paul Walden, pp. 194, 200, 239.

Journal of American Chemical Society, vol. 19 (1897), p. 563.