

# UNITED STATES PATENT OFFICE

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## ELECTRODEPOSITION OF ALUMINUM

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1 Claim. (Cl. 204—14)

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This invention relates to a process for the electrodeposition of aluminum on dissimilar metals.

In a co-pending application Serial No. 522,375 filed February 14, 1944, Hurley has disclosed that aluminum can be advantageously deposited from an electrolyte comprising (1) an aluminum halide such as aluminum chloride or aluminum bromide and (2) various lower aliphatic pyridinium halides such as N-ethyl pyridinium chloride at temperatures generally above 100° C. In another co-pending application of Wier and Hurley, Serial No. 524,486, filed February 29, 1944, it has been disclosed that aluminum can also be deposited on dissimilar metals at room temperature by utilizing a bath including certain aromatic compounds in addition to the aluminum chloride and the mono-pyridinium mono-halides. The plates secured by utilizing these baths with direct current are brittle and tend to crack, break or flake away from the base, particularly if the article is repeatedly flexed. When using the above mentioned baths, I have discovered that by superimposing a suitable alternating current on the direct current, adherence of the plate to the base metal is increased with the result that the articles can thereafter be worked and bent to shape. Further, the plate secured is more uniform and, in addition, its thickness can be increased. Also, by superimposing a suitable alternating current on the direct current, at the same direct current density the voltage required is lowered somewhat. In addition, higher cathode direct current densities can be used to obtain plates of the same general type as with direct current only. These advantages are obtained without any decrease in cathode current efficiency.

In the experiments whose results are described herein, the magnitude of the alternating current was an approximately sinusoidal function of time and the frequency was about sixty cycles per second. A current of this character is usually most conveniently obtained. However, higher or lower frequencies or other alternating current wave shapes can be used.

From my observations on actual operations, I have found that the best results are obtained when the root-mean-square value of the alternating current is 2 to 3 times the value of the direct current. At lower ratios, the improvement in adherence diminishes until, at a ratio of about 1 to 1, the effect is very small. If, however, the ratio is too high, the plates become burned. The most desirable ratio of alternating current to direct current depends somewhat on the design of the cell, the direct current density employed,

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and the type of plate desired. When it is desired to employ high direct current densities, the ratio of alternating current to direct current should be increased. Likewise, when thick, non-brittle deposits are to be obtained, the ratio should be increased. The exact value of the ratio is usually not highly critical and can readily be determined for a given set of conditions. The direct current and alternating current voltages employed are usually low (of the order of a few volts, usually less than ten volts) and depend upon the several factors mentioned above.

X-ray examination of plates made in accordance with the present invention shows that when direct current alone is employed, the plates consist of partly oriented, small crystals, whereas when the alternating current is imposed in addition, the plate is composed of larger crystals which are not oriented. It is believed that the improved adherence and other properties of the plates are accounted for in this way.

The following example is set forth by way of further illustration of the practice of the present invention, and not by way of limitation:

A plating mixture was prepared by mixing 2 mols of aluminum chloride (taken as  $AlCl_3$ ) and 1 mol of fused ethyl pyridinium bromide. After cooling the mixture it was saturated with benzene. About 50 cc. of this solution together with sufficient excess benzene to provide a protective benzene layer about 0.5 cm. in depth was then placed in a cylindrical glass electrolysis cell. This cell was 4.5 cm. in diameter and about 10 cm. high. It was fitted with a cover designed to exclude moisture. The anode was a circular sheet of aluminum fitting against the wall of the cell. The cathodes consisted of suitably cleaned strips of brass 1.34 cm. wide and about 15 cm. long; these were immersed to a depth of 3.55 cm. in the bath. The source of direct current was connected across the electrodes and the source of alternating current was connected in parallel with the direct current. The circuits were so arranged as to permit separate variation of the alternating current and of the direct current. The magnitude of the current passing through the cell was an approximately sinusoidal function of time and was symmetrical about a value represented by the direct current. The frequency of the alternating current was approximately 60 cycles per second.

In a series of plating tests, varying amounts of alternating current were superimposed on a constant amount of direct current. The density of direct current at the cathode was 1.20 amps./dm.<sup>2</sup>.



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The direct current voltage was between 0.7 and 0.8 volt. The time of electrolysis was 10 minutes in each instance. The effect of variation in the root-mean-square value of the alternating current with respect to the direct current on the types of plate is shown in the following table:

A. C. (R. M. S.)/D. C.	Type of Plate
0.....	Uniform, shiny plate with small brown patches.
1.0.....	Almost the same as plate secured when using only direct current.
1.5.....	Principally shiny, partly white. Not much apparent physical change, but no brown coloration.
2.0.....	Uniform white, somewhat satiny finish.
3.0.....	Uniform white deposit, not much change from 2.0 type.

Satisfactory plates on other metals such as iron and copper were also made, using this process.

I claim:

In a process of electroplating with aluminum, the step of subjecting an article of a metal from the group consisting of brass, copper and iron, serving as a cathode, simultaneously to an alternating current and a direct current, passed between said cathode and an aluminum anode and through a fused, anhydrous bath consisting of

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(1) about two mols of aluminum chloride and (2) about one mol of ethyl pyridinium chloride, to plate aluminum onto said article; the root mean square value of the alternating current being about two to three times the value of the direct current.

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