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ELECTROPLATING OF ALUMINIUM

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1 Claim. (Cl. 204—3)

This invention relates to improvements in the electro-plating of aluminium with other metals.

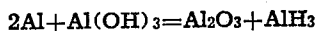
It is known that difficulty exists in obtaining by electroplating on articles of aluminium solid and durable metallic coatings. This difficulty comes from the fact that the articles of aluminium are always covered with a more or less thick layer of aluminium oxide.

Remedies for this difficulty have already been sought, either by modifying suitably the oxidized surface of the aluminium in such a manner that it permits, in spite of the presence of oxide, of the galvanic deposit of other metals, or by causing the layer of oxide to disappear, by preliminary treatment in cleaning baths or by electrical or thermal treatment, for a time at least sufficient in order that the surface of the aluminium can become covered in the plating bath with the metal intended to constitute the coating. However, it has been impossible in practice to attain this result hitherto. One has only been able to reduce the layer of oxide to very low values but the very thin layer of oxide which remains still suffices to prevent the metallic contact between the articles to be coated and the metal intended to constitute the coating.

The present invention permits on the contrary of the complete removal of the layer of oxide from the surface of the articles to be treated, for a time sufficient to allow the galvanic deposit of metal on metal. The process which forms the object of the invention consists essentially in replacing at the surface of the aluminium the layer of oxide by a film of aluminium hydride, that is to say the hydrogenated compound of aluminium which presents characteristics permitting it to be ranged in the electromotive series approximately in the same place as hydrogen.

This hydride formation is based on the following observation: aluminium in the very active state, that is to say absolutely white, is capable of reacting on the hydrate of its own oxide by removing water therefrom and by reacting with this water oxide is reformed in such a violent manner that its molecular structure is modified, the valencies thus liberated are saturated by the hydrogen produced during the reaction.

Under the conditions of the present invention, the formation of aluminium hydride is effected according to the equation:



This compound (AlH_3) is practically unknown although certain authors have admitted its existence and particularly Dutet (Comptes rendus de

l'Academie des Sciences Vol. 109 page 108—1889), Morikofer (Archives des Sciences Physiques et Naturelles) (vol. 6 page 401—1925), the Zeitschrift fur Physik (vol. 34—page 775—1925, Erikson and Hulton; vol. 35, page 519—1926 Ludloff; vol. 59, page 540—1930, Bentsown and Rydberg).

This hydride presents an appearance which recalls graphite and has a remarkable resistance to the oxygen of the atmosphere and to water; its electrical conductivity is that of a metal; its characteristics are those of an alloy, for example similar to those of the hydride of nickel. In the absence of oxygen and water its resistance is unlimited, but its resistance to water and even to strong acids is remarkable. Alkaline liquids on the contrary destroy it instantaneously with the formation of hydrate or aluminate and gaseous hydrogen. This latter fact thus forbids the employment of alkaline electrolytes for the subsequent galvanic treatment. When it is heated in an atmosphere of dry air, the aluminium hydride is sufficiently resistant up to temperatures in the neighborhood of 300° C. but at incipient redness it burns or decomposes leaving a white residue of aluminium oxide.

The position of this aluminium hydride in the electromotive series, which position is referred to above and corresponds to that of hydrogen, can be determined by its reactions towards solutions of metallic salts, in fact the hydride is indifferent to solutions of salts of metals below lead but reacts with those of metals above lead with exchange of its hydrogen for the metal.

In order to obtain on the more or less oxidized surface of the article of aluminium (to be subsequently coated with a galvanic deposit) this film of aluminium hydride in accordance with the invention, this article is heated strongly at a temperature exceeding 100° C. and it is subjected in the presence of small quantities of water to the action of violent reagents capable of attacking aluminium. As reagents of this nature can be utilized hydrochloric acid in the liquid or gaseous state, the salts of metals of a position superior to or equal to aluminium and so on.

The course of the reaction is as follows:—

When the article is heated to above 100° C. and subjected to the action of a very small quantity of water, there is produced through the numerous pores of the layer of oxide which covers the article, an attack of the subjacent surface of aluminium. But owing to the small proportion of water present, the salt of aluminium which is formed (chloride for example) instead of being diluted and eliminated remains on the article.

Under the influence of the high temperature (above 100° C.) the salt dissociates giving aluminium hydroxide with the small quantity of water present.

5 In contact with this hydroxide, the aluminium of the article, in the very active state owing to the attack of the reagent employed, reacts very violently in order to give rise according to the reaction set out above to the oxide Al_2O_3 , while
10 the hydrogen liberated gives rise to aluminium hydride of which one portion remains in the powder form mixed with the oxide Al_2O_3 on the surface of the article while the other portion forms directly at the surface of the aluminium
15 metal of the article the very adherent film of aluminium hydride desired.

What may remain of the water has been evaporated by the heat and dispersed.

20 Finally the article of aluminium is covered with a black adhering film of aluminium hydride, with a grey layer composed of a mixture of oxide Al_2O_3 , hydride AlH_3 and undissociated salt of aluminium, the whole in the state of a more or less pulverulent crust which disappears on wash-
25 ing the object.

It may be remarked that in the course of the reaction the temperature spontaneously increases as also does the violence of the reaction which increases progressively.

30 Instead of producing the whole quantity of the aluminium hydroxide necessary for the reaction from the article of aluminium itself it is also possible to provide this hydroxide directly in the form of basic or easily dissociated salts of aluminium; the manner in which the reaction takes
35 place remains the same.

The film of aluminium hydride formed on the surface of the article protects this latter for a sufficiently long time from the reformation of
40 hydroxide.

By reason of the metallic character of this coating of aluminium hydride any object thus coated can be metallized directly in any neutral or acid plating bath. In view of the already
45 stated position of the hydride in the electromotive series the coatings by means of metals lower than hydrogen can be effected directly without difficulty while the production of coatings of metals above hydrogen requires the known pre-
50 cautions at present employed in the art for plating in cases of this type that is to say, high initial intensity or strong simultaneous evolution of hydrogen. The metals of the coating which are distinguished by a particularly firm connection
55 with the metal of the base are chiefly those having a strong tendency to displace hydrogen such as nickel, iron and chromium and also brass and platinum. It appears probable that the metal of the coating removes the hydrogen of the alu-
60 minium hydride and itself occupies the place thus liberated in the molecular structure. This is the more probable since these metals are of the same type as aluminium from the point of view of structure.

65 It may be observed that the reaction must be carried out as indicated above in the presence of small quantities of water, sufficiently small in order not to permit of the dilution of all the salt formed at the time of the attack on the alumin-
70 ium by the reagent employed.

The idea has already been conceived to attack aluminium articles by reagents of this type which acted through the pores of the superficial coating of oxide with the object of subsequently eliminat-
75 ing this coating by washing or cleaning of the

surface. But owing to the large quantity of water in the presence of which the reaction always took place, the salts of aluminium formed were diluted and disappeared and one never arrived at an aluminium surface absolutely free from oxide. 5

The characteristic of the present invention resides in the formation of this adherent film of aluminium hydride directly on the surface of the metal, which film is formed at the expense of the hydroxide produced by the dissociation, under the effect of the heat, of the salts of aluminium
10 formed under the action of reagents and remaining on the surface of the article.

As regards the treatment of alloys of aluminium in accordance with the present process, the es-
15 sential reaction, that is to say the formation of hydride always takes place when the aluminium constitutes the major portion of the alloy. Even when the alloy contains copper the aluminium hydride is formed with certainty but the forma-
20 tion of hydride only lasts for a short time on account of the catalytic carrying of oxygen. On account of this fact alloys of this type, for example duralumin, must as rapidly as possible af-
25 ter the hydrogenation, be introduced into the plating bath. For the same reason direct chroming in baths containing chromic acid is difficult when the alloy contains copper whereas alloys free from copper and also pure aluminium can be
30 chromed directly and without difficulty in baths of this type.

The mode of execution of the present process can be in accordance with one of the three modifications described below by way of non-limiting
35 examples;

1. The article to be prepared is heated to a temperature above 100° C., plunged into a concentrated bath of basic aluminium chloride brought to the same temperature, then with-
40 drawn from the bath when the violent reaction with attack of the metal is produced, the formation of hydride then takes place, a large increase of temperature and with rapid consumption of the small quantities of water.

2. The article brought to a temperature above
45 100° C. is covered with a thin layer of dilute hydrochloric acid distributed for example if desired by means of an atomizing pistol; there is immediately formed a superficial film of aluminium hydride.

3. The articles strongly heated to above 100° C. are placed in a humidified atmosphere of gaseous HCl for example which is heated or super-
50 heated; there is formed immediately a superficial film of aluminium hydride.

The selection of which of these modifications to employ in practice will depend on the dimen-
55 sions of the articles. Articles with thin walls are preferably treated in a liquid bath on account of their low heat capacity while thicker articles can, by reason of their better conservation of heat, be treated by atomization or in a gaseous atmo-
60 sphere.

A very interesting application of this process consists in producing at the surface of an article
65 of aluminium coated with a galvanic deposit of another metal, a superficial alloy of this metal and aluminium without risk of deformation or injury of the article.

One has already succeeded in producing on ar-
70 ticles of aluminium coated with another metal alloys of this type between the aluminium and the metal of the coating, but it was hitherto always necessary in order to obtain this result to heat the object very strongly above the point of
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fusion of the aluminium or of the metal of the coating which always led to deformation and injury of the object.

5 If care is taken to treat the article of aluminium by a preliminary process according to the present invention with the superficial production of hydride before covering it with an electrolytic deposit of another metal it will suffice to heat the article to a temperature much lower than the
10 point of fusion of the aluminium (or of the metal of the coating) in order to obtain without deformation of the article an alloy of aluminium and

of the metal of the coating at the surface of the article.

I claim:

In the electro-plating of articles of aluminium and its alloys the preliminary treatment which
5 comprises heating the article to a temperature above 100° C., plunging it into a concentrated bath of basic aluminium chloride brought to the same temperature and then withdrawing from the bath when a violent reaction with attack of
10 the metal is produced.

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