

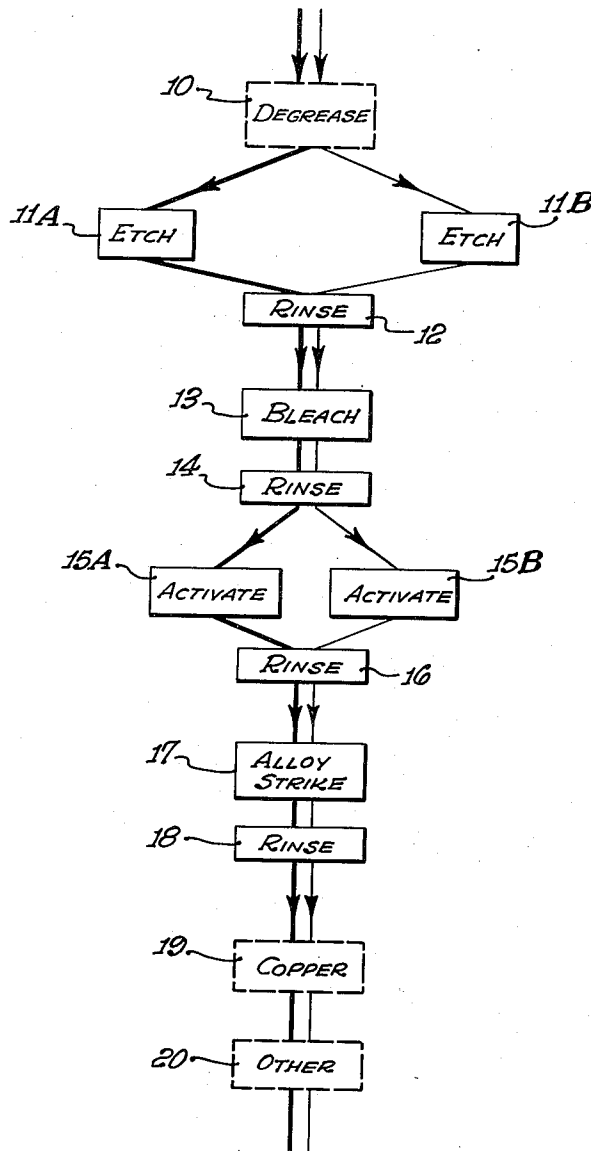
Oct. 6, 1953

E. R. CALDERON ET AL

2,654,701

PLATING ALUMINUM

Filed June 8, 1950



EDWIN R. CALDERON,
GEORGE W. SLOMIN,
INVENTORS.

BY

C. E. Wilbur

ATTORNEY.

UNITED STATES PATENT OFFICE

2,654,701

PLATING ALUMINUM

Edwin R. Calderon and George W. Slomin,
Los Angeles, Calif.

Application June 8, 1950, Serial No. 166,839

16 Claims. (Cl. 204—33)

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This invention relates to improvements in the art of plating on the surfaces of objects made of aluminum and alloys thereof and is also applicable to the treatment of castings from zinc-base alloys. The invention is particularly directed to a plating process in which the use of dangerous and poisonous acid pickles and etching solutions is eliminated, and the surfaces to be treated are provided with the uniform, adherent coating or plating which will not develop the incipient blistering which characterizes prior attempts to plate aluminum and aluminum alloys in extruded, drawn or cast form. The invention also contemplates the use of a novel strike solution which results in the formation of a tenaciously adherent, fine grained alloy plating which forms a base for subsequent electroplating with copper, nickel and other metals.

The process of this invention is applicable not only to commercially pure aluminum but is also applicable to castings, die castings, wrought alloys, etc. These various aluminum alloys may contain silicon, copper, magnesium, manganese and chromium, either alone or in combination. In the past, the same solutions for etching, brightening, etc. could not be used on pure aluminum and on the wrought or cast aluminum objects containing alloying components. The so-called zinc-immersion process (Patent No. 1,627,900) has been used to some extent in the past but this process is complicated, requires separate handling for various types of alloys and is not satisfactory, plated objects exhibiting pitting and latent blistering; that is, the plated part which appears to be free of blisters when first plated begins to develop small blisters within a few weeks, these blisters continuing to grow in size and making the part useless for outdoor exposure applications or wherever perfect finish is desired. It is to be remembered that plating is not only of value in changing the color or appearance of the article, imparting higher brightness and reflectivity thereto, but is also of considerable value in increasing the resistance of the object to abrasion or wear, eliminating a tendency toward "smudging" which is common to many aluminum alloys, and is also of value in facilitating soft solder joining, improving electrical contacts or conductivity, and increasing resistance to corrosion. In some instances final coating with brass is extremely desirable in order to allow vulcanization and adherence of rubber to the plated aluminum part.

The zinc-immersion process is not only subject to a very high percentage of rejects due to

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the pitting and latent blistering mentioned hereinabove but is also troublesome in that it is difficult to obtain uniform plating on large or irregularly shaped articles. In addition, the process contemplates the use of mixed acid solutions, such as solutions of nitric and hydrofluoric acids or of mixtures of chromic acid and sulfuric acid. These pickles, etches and solutions are hazardous, toxic, poisonous and in many instances can only be successfully retained in costly carbon brick-lined and lead tanks, and in addition, require very efficient ventilating facilities in order to reduce the hazards of use.

The present invention is directed to a method of procedure with solutions to be described hereinafter in greater detail, the procedure being much more simple than any of the procedures contemplated and recommended heretofore. Substantially the same steps are employed, in accordance with the present process, on objects made from substantially pure aluminum and on objects made from aluminum alloys high in silicon, copper, manganese, etc. For example, the etching solutions employed differ but slightly in concentration and temperature of use; the remaining solutions including the strike solution are identical, some variation in temperature of utilization of the activating solution being the only difference between the treatment of objects made of virtually pure aluminum and those made from aluminum alloys. In all instances standard black iron or steel tanks may be used for the etching solutions, activating solutions and strike solutions.

The invention contemplates the control of pH and surface tension of many of the solutions employed in the process and a strike solution containing cyanides of copper, silver, gold, zinc and indium, whereby an alloy containing silver or gold is deposited upon the surface of the object, the resulting alloy film being characterized by a fine grained structure which is substantially non-porous.

An object of the present invention therefore is to disclose and provide a simple and economical process of plating objects of aluminum and aluminum alloys.

A further object of the invention is to disclose and provide an improved process of plating aluminum, said process eliminating the necessity of using dangerous or toxic mixtures of nitric and hydrofluoric acid or mixtures of chromic and sulphuric acid.

Another object of the invention is to disclose and provide a plating process, particularly appli-

cable to aluminum and its alloys, which virtually eliminates the necessity for expensive tanks and ventilation equipment.

A still further and important object of the present invention is to disclose and provide a process of plating aluminum and its alloys, said process insuring uniformity, homogeneity, fine grain structure practically free from porosity and tenacious adherence to the surface of the aluminum object.

An object is to disclose and provide a plating process whereby a ternary alloy is electrodeposited upon the surface of aluminum objects, said alloy including silver in diffused form throughout such ternary alloy.

A still further object of the invention is to disclose and provide a method of plating zinc-base die-casting alloys with a ternary alloy strike solution in order to increase the corrosion resistance of the die-casting alloys. Furthermore, it will be apparent from the following description, an object of the invention is to disclose and provide stable solutions and the use of solutions inhibited for excessive solubility of copper and silicon therein.

These and various objects, uses and advantages of the present invention will become apparent, to those familiar with the practice recommended in the art heretofore, from a contemplation of the description given hereinafter. In order to facilitate understanding reference will be held to the appended chart or diagram illustrating the sequence of operations which is preferably followed in the plating of aluminum and aluminum alloys.

As will be readily seen from the contemplation of the appended diagram, the objects to be plated are first degreased, as indicated at 10, and then passed to an etching bath. Etching baths are indicated at 11A and 11B, since the temperature and concentration of these etching solutions varies somewhat as to whether relatively pure aluminum objects are being treated or objects made from alloys. The path of relatively pure aluminum objects is indicated by the heavy line whereas the path of the objects composed of aluminum alloys containing silicon, manganese, copper, etc. is indicated by the lighter line passing through 11B. After the etching operation, both types of objects are rinsed at 12, then bleached at 13, rinsed at 14 and then passed through an activating solution at 15A and 15B. Although the activating solution is the same in both instances certain differences in temperature of immersion are preferably followed as will become apparent from the subsequent description. During such activation a thin adherent film of zinc is formed on the bleached surface of the objects. The objects are then rinsed at 16 and are subjected to an alloy strike at 17, whereby an alloy characterized by fine grain and lack of porosity is formed on the surface of the objects. The objects are then rinsed, as indicated at 18, and may then pass to a relatively normal copper plating step, as indicated at 19, or if desired, to a subsequent plating indicated at 20, whereby nickel, chromium, cadmium, silver, gold, etc. may be plated upon the objects by any standard process. Steps 19 and 20 are indicated in dash lines since they do not form a part of the present invention. The degreasing operation is also indicated in dash lines at 10 for the same reason.

Although vapor degreasing with tetrachloroethylene is recommended, the use of inhibited alkaline cleaners incapable of exerting an etch-

ing effect upon the aluminum is not prohibited. Marking inks and other identification marks should be removed. Tetrachloroethylene is recommended as a solvent for degreasing aluminum since it is more stable than other chlorinated solvents. The acidity of the solvent should be checked at regular intervals and a degreaser should be thoroughly cleaned out periodically in accordance with careful plant practice.

In accordance with the present process, the etching solutions employed at 11A and 11B are relatively mild solutions containing the alkali-hydroxides and alkali-fluorides. Either sodium or potassium hydroxide and fluoride may be used. Purified grades of these chemicals are preferred and technical or commercial grades are not recommended.

It may be noted at this time that in order to insure freedom from blisters, pinholes and other defects, it is very desirable that all of the solutions, including the etching solution, bleaching solution, activating solution and strike solution be made with either distilled water or deionized water which may be obtained by treatment of ordinary tap water with base exchange resins as is well known in the art.

The following table indicates the composition of the etching solutions used at 11A and 11B. It will be noted that for commercially pure aluminum or aluminum alloys with a low content of alloying components from $\frac{3}{4}$ of an ounce to 2 ounces of sodium fluoride is used per gallon of the etching solution. The figure in parentheses indicates the preferred proportion of sodium fluoride.

	11A Commercially Pure Aluminum	11B Aluminum Alloys
Sodium Hydroxide.....	3 oz./gal.	3 oz./gal.
Sodium Fluoride.....	$\frac{3}{4}$ (1)-2 oz./gal.	2.0 (2.5)-4 oz./gal.

Although the etching solution is made of the same components the preferred temperature at which such solution is kept during immersion varies and the time of immersion of the object in such solution varies. In tank 11A the solution is preferably kept at a temperature of 130° F. and the objects are immersed 15 to 45 seconds. In etching operation 11B the etching solution is maintained at an operating temperature of about 140° F. and the objects are immersed for a period of 45 to 60 seconds. After such immersion under the conditions stated the objects are subjected to a thorough rinse, as indicated at 12.

It may be noted at this point that the etching solutions will attack the surface of the objects without attacking the underlying grain structure. A slightly mat finish is observed.

The objects then pass through a bleaching bath, indicated at 13. The primary purpose of the bleaching bath is to brighten the surface of the objects and remove any copper which may have been precipitated. During etching, alloys low in copper content will not be effected appreciably but alloys containing appreciable amounts of copper and magnesium will acquire a film which is dark and this must be fairly and completely bleached off in the nitric acid solution. The bleaching solution consists of a nitric acid solution preferably maintained at a temperature of about 110° F. or 120° F. Commercial nitric acid may be diluted with distilled or deionized water, the concentration of the nitric acid solution not being critical. One, two or even three volumes of nitric acid may be added to one part

of water. All of the objects being treated should be dipped in this solution for a period of not less than 15 seconds. Ordinarily the relatively pure aluminum objects may be dipped into the solution for a period of 15 to 45 seconds, this solution being maintained at temperatures of between about 80° F. and 90° F. Aluminum alloys high in copper or silicon may be dipped for a period of from 45 to as long as 60 seconds and the solution is preferably maintained at a temperature of between about 95° F. and 105° F. Every trace of nitric acid must be rinsed off before proceeding to the next step and such rinsing is indicated at 14.

The thoroughly clean surface of the objects being treated is then subjected to activation as indicated at 15A and 15B. Such activation is attained by treating the surface with an aqueous alkaline solution of potassium zincate. Preferably this solution contains a surface tension reducing agent or depressant of the alkaline type whereby the surface tension of the solution is reduced to below 50 dynes per square centimeter and preferably to a range of between about 40 and 45 dynes. Moreover, the activating solution preferably contains an agent adapted to suppress the solution of silicon and copper and zinc sulphate heptahydrate, potassium selenate, potassium tellurate and zinc phosphate are examples of agents which may be successfully used.

The potassium zincate contained in this solution may be prepared in various manners, for example, by the reaction of purified zinc oxide or other zinc compound with molten potassium hydroxide or potassium monoxide; by the dissolution of pure electrolytic zinc in aqueous solutions of potassium hydroxide; by the electrochemical dissolution of zinc in potassium hydroxide employing an alternating current of frequency of 50 to 60 cycles across the electrodes of electrolytic zinc, or in the following manner: in 82 ounces of potassium hydroxide, dissolved in a minimum quantity of water, there is dissolved 10 ounces of zinc oxide. Separately 6 ounces of zinc sulphate heptahydrate is dissolved in a minimum quantity of hot water to which there has been added 6 ounces of potassium hydroxide in the form of a saturated solution. The two solutions are then mixed together and diluted to one gallon with distilled water. The surface tension depressant is now added and the prepared solution is filtered before use. The mixing of the solution repressing agent in caustic potash solution with the solution of potassium zincate, followed by filtration is the preferred procedure.

Preferably, the activating solution contains 85-90 oz. of KOH and 9-11 oz. of ZnO per gallon. Caustic soda and sodium zincate is not recommended since pinholes, incomplete films and occlusions which form blisters follow the use of sodium compounds. It is believed that since sodium carbonate is readily formed and is relatively insoluble in the caustic solution, such carbonates precipitate and act as nuclei which engender blisters. Potassium carbonate, even if formed, is five times as soluble, and it has been found that the recommended solutions do not leave microscopically small particles nor bare spots on the activated surface.

It may be noted that the activating solution should be free from chlorides and nitrates since it has been found that these elements are highly detrimental. Furthermore, attention is again called to the preferred temperature ranges since the combination of optimum reaction tempera-

ture, low surface tension and presence of the solubility depressing agent insures instantaneous wetting of the article to be plated and instantaneous coverage with zinc. Not only is the coverage with zinc rapid but it is uniform and homogeneous, thereby insuring proper and uniform, blister-free adherence of the subsequently applied ternary alloy strike.

After the operations described hereinabove, the object, composed essentially of aluminum, is rinsed at 16 and subjected to the action of an alloy strike solution at 17. Heretofore, after the normal zinc-immersion in a sodium zincate solution, the object was subjected to a Rochelle type copper cyanide strike. The present process distinguishes therefrom in excluding sodium compounds from the step preceding a strike, and in employing a strike solution containing zinc, copper and a metal from the group consisting of silver, gold and indium (preferably in the form of cyanides), under conditions which insure the rapid electrodeposition of a ternary alloy on the surface of the object. The ternary alloy strike solution of the present invention is distinctive not only because of the presence of three compatible metals which form an alloy, but also by reason of the fact that the solution is stabilized, buffered, has a pH of between 9 and 10 and a low surface tension. The pH range is critical; if the pH is below 9, there is a tendency to decompose the cyanides present; if the pH is above 10, there is a decided tendency to dissolve zinc. Solutions adjusted to this desired range (by the controlled addition of tartaric acid or potassium hydroxide) are extremely stable and have changed but 0.2 pH in a year. The surface tension of the solution is preferably adjusted to below about 40 dynes per square centimeter by the use of a surface tension depressant of the alkaline type.

During a strike, large quantities of hydrogen are evolved, and the low surface tension of the strike of this invention results in immediate liberation of such hydrogen, perfect wetting of the surface, and the formation of a continuous, homogeneous and uniform film of alloy over the entire surface, even though the object is large and has irregularly shaped surfaces. Effective surface tension reducing agents can be selected from those which are primarily aliphatic alcohols, and are stable in alkaline solutions: cyclic amines or betaines containing one non-cyclic hydrocarbon radical of 10 to 20 carbon atoms, are examples of satisfactory agents.

The use of ammonia as a brightener has been eliminated and, instead, monoethanolamine or thiethanolamine is preferably employed, these materials having a concurrent surface tension reducing effect.

A typical ternary alloy strike solution, prepared in accordance with this invention, comprises:

Potassium cuprocyanide, 4 oz. per gal.
Silver cyanide, 0.12-(0.25)-0.35 oz. per gal.
Zn cyanide (in equivalent combining quantity of KCN), 0.8-(1.5)-1.8 oz. per gal.
Monoethanolamine, 25-(38)-45 ml. per gal.
Surface tension depressant, 5-(10)-15 ml. per gal.

After the above illustrative components are dissolved in warm water, a saturated solution of tartaric acid may be slowly added to adjust the pH to the range of between 9 and 10 (preferably between 9.2 and 9.8) and the solution filtered.

pH should be determined by a glass electrode.

This ternary strike solution can be used in black iron or steel tanks; the tanks acting as the anode. The solution should be at a temperature of about 105° F. ($\pm 5^\circ$) when at work. Strike the work with current on before submerging the work. Immersion times may vary from 30 seconds to as long as 90 seconds; depending upon the morphology of the work being plated. Current densities on the order of those usually employed in a strike (say 24 amp. per sq. ft.) can be used initially and then reduced. Some circulation or agitation of the solution is desirable, and the solution should be filtered regularly in order to insure a homogeneous, non-porous plate.

Generally stated, the molecular ratios of the metals in this strike should be maintained at between about 3 to 5 Cu and 0.15-0.3 Ag to 1 of Zn. When indium is substituted for silver only 0.1-0.2 In need be used.

Attention is again called to the fact that no sodium compounds, chlorides or nitrates should be in the strike.

The film, resulting from the use of the novel strike solution above described, is perfectly bonded to the surface of the object and is of very fine grain structure, the silver, gold or indium being diffused throughout the grain boundaries.

After the strike and plating with a ternary alloy as described, the object may be plated with any other metal in accordance with known processes. For example, if it is desired to copper plate, as indicated at 13; the inventors prefer to plate with a hot, strongly alkaline high speed copper solution, using temperatures of 180° F., since no injury to the aluminum object results. Potassium cuprocyanide solutions are desirable, with the use of periodic cyclic reverse current flow, since speed, consistency, perfect covering and high corrosion resistance are attained.

As previously stated, the ternary strike solution may be used on zinc-base castings with great success because the controlled pH precludes solution or attack of the zinc and the combination of components and properties results in a highly effective protective coating of exceptional density.

By the use of the process, conditions and materials disclosed herein, objects composed essentially of aluminum (this phrase including both relatively pure aluminum and its alloys) can be plated effectively with less than 2% or 5% of rejects. Objects plated by this invention have not shown blistering with age and have successfully withstood 72 hours of an accelerated salt spray test.

All changes, adaptations, uses and modifications coming within the scope of the appended claims are embraced thereby.

We claim:

1. A method of providing objects, composed essentially of aluminum, with a tenaciously adherent, fine grained alloy plating, comprising: etching the degreased surface of objects composed essentially of aluminum with an aqueous solution of alkali hydroxide and alkali fluoride and rinsing the etched surface; then treating the surface with diluted nitric acid and rinsing the surface; then forming a thin, adherent film of zinc on such treated surface; rinsing the activated surface and electroplating the activated surface with an aqueous strike solution containing cyanides of copper, zinc and a metal from the group consisting of silver, gold and indium,

while imposing an electrical current upon the objects; said strike solution having a pH of between 9 and 10 and a surface tension below 45 dynes per square centimeter.

2. A method of the character stated in claim 1 wherein the strike solution is virtually free from sodium compounds, chlorides and nitrates.

3. A method of the character stated in claim 1 wherein the strike solution is at a temperature of between about 100° F. and 110° F.

4. A method of the character stated in claim 1 wherein the strike solution is virtually free from sodium compounds, chlorides and nitrates and is at a temperature of between about 100° F. and 110° F.

5. A method of providing objects, composed essentially of aluminum, with a tenaciously adherent, fine grained alloy plating, comprising: etching the degreased surface of objects composed essentially of aluminum with an aqueous solution of alkali hydroxide and alkali fluoride at a temperature of between about 125° F. and 145° F., said solution containing from about 0.75 oz. to 4 oz. of sodium fluoride per gallon, and rinsing the etched surface; then treating the surface with diluted nitric acid and rinsing the surface; then forming a thin, adherent film of zinc on such treated surface by immersion in an aqueous, alkaline solution of potassium zincate containing a solution depressant for silicon and copper, and a surface tension depressant, at a temperature of about 80° F. and 105° F.; rinsing the activated surface and electroplating the activated surface in an aqueous strike solution containing cyanides of copper, zinc and a metal from the group consisting of silver, gold and indium, said strike solution having a pH of between 9 and 10 and a surface tension below 45 dynes per square centimeter.

6. A method of the character stated in claim 5 wherein the strike solution is virtually free from sodium compounds, chlorides and nitrates.

7. A method of the character stated in claim 5 wherein the strike solution is at a temperature of between about 100° F. and 110° F.

8. A method of the character stated in claim 5 wherein the strike solution is virtually free from sodium compounds, chlorides and nitrates and is at a temperature of between about 100° F. and 110° F.

9. A method of the character stated in claim 5 wherein the solution depressant for silicon and copper is zinc sulphate.

10. A method of the character stated in claim 5 wherein the aqueous, alkaline solution of potassium zincate is virtually free from sodium compounds, chlorides and nitrates, and has a surface tension below 50 dynes per square centimeter.

11. In the plating of objects consisting essentially of aluminum provided with a zinc surface film and zinc-base castings, the formation of an alloy strike deposit upon the surfaces of such objects and castings from an aqueous strike solution having a pH of between 9 and 10 and a surface tension of below 45 dynes per square centimeter, while imposing an electrical current upon the objects, said solution containing cyanides of copper, zinc and a metal from the group consisting of silver, gold and indium.

12. A process of the character stated in claim 11, wherein the strike solution contains potassium cyanide and potassium hydroxide and is virtually free from sodium compounds, chlorides and nitrates.

13. A process of the character stated in claim

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11 wherein the strike solution is maintained at a temperature of between about 100° F. and 110° F.

14. A process of the character stated in claim 11 wherein the solution contains monoethanolamine as a brightener. 5

15. A method of providing objects, composed essentially of aluminum, with a tenaciously adherent, fine grained alloy plating, comprising: etching the degreased surface of objects composed essentially of aluminum with an aqueous solution of alkali and alkali fluoride and rinsing the etched surface; then treating the surface with diluted nitric acid and rinsing the surface; then forming a thin adherent film of zinc on such 10 treated surface by immersion in an aqueous potassium zincate bath virtually free from sodium compounds; rinsing the activated surface and electroplating the activated surface in an aqueous strike solution containing cyanides of copper, zinc and a metal from the group consisting of 20 silver, gold and indium, said strike solution having a pH of between 9 and 10 and being virtually free from sodium compounds, chlorides and nitrates.

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16. A method of the character stated in claim 1 wherein the etch solution contains sodium hydroxide and from about .75 oz. to 4.0 oz. sodium fluoride per gallon.

EDWIN R. CALDERON.
GEORGE W. SLOMIN.

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