

1

3,108,006

PLATING ON ALUMINUM

Peter G. Kenedi, Red Bank, and Robert T. Gore, Middletown, N.J., assignors, by mesne assignments, to M & T Chemicals Inc., New York, N.Y., a corporation of Delaware

No Drawing. Filed July 13, 1959, Ser. No. 826,497
11 Claims. (Cl. 106-1)

The present invention relates to plating on aluminum. Aluminum, which is abundant, economical, and has favorable physical and electrical properties, is used in large quantities. Its use in certain fields has been limited by its surface characteristics. Aluminum surfaces oxidize to form a tight adherent refractory film which interferes with surface-to-surface contact. Aluminum surfaces cannot be joined by soldering.

Techniques have been developed for both immersion plating and electroplating on aluminum. One of the few useful, although limited, techniques is the immersion tinning of certain aluminum alloys using alkali stannate solutions. This technique is successful only when applied to aluminum alloys containing several percent of copper. The most widely used process for plating on aluminum is that in which an immersion zinc coating replaces the oxide film. To be successfully applied, immersion zinc processes require close control of a large number of process steps and variables. This has limited its industrial utilization and applicability. A need exists for a relatively simple and widely applicable method for plating on aluminum.

It is an object of the present invention to provide a bath and a process for immersion tinning aluminum.

It is a further object of the present invention to provide a process for electroplating aluminum.

The invention also contemplates providing a bath useful without change for both immersion plating and electroplating tin on aluminum.

It is still another object of the present invention to provide a process for electroplating one or more metals on aluminum for decorative and/or industrial purposes.

The invention also contemplates a continuous method of plating aluminum wire and sheet.

We discovered that when aluminum, having a properly cleaned surface, is immersed in an aqueous stannate-cyanide bath having the following preferred composition: CuCN—about 11 g./l. (grams per liter), free KCN—about 26 g./l., KOH—about 7.5 g./l., and $K_2Sn(OH)_6$ —about 120 g./l., at a temperature of about 50° C., an adherent tin layer is chemically deposited on the aluminum surface in about 5 to 30 seconds. The aluminum may be retained in the immersion bath for as long as 2 to 3 minutes at which time further deposition practically ceases. A deposit of about 0.00025 cm. is built up, dependent somewhat upon the temperature and specific bath utilized. Thick immersion deposits of this type are somewhat porous but have sufficient continuity and stability to (i) protect the aluminum surface from oxidation; (ii) provide a surface suitable for making sliding contact; and (iii) provide an aluminum article with sufficient conductivity at the surface during its service life to enable the part to be used as an electric conductor, e.g., for screw or friction type electric contacts. The adhesion of these immersion deposits is markedly improved by reflowing the deposit at an elevated temperature.

An important feature of this process is the successful immersion tin coating formed on the aluminum surface in the stannate-cyanide solution. When the aluminum is immersed in the solution, a dark "flash" deposit takes place within about 1 to 3 seconds and continues for about 2 seconds, followed almost instantaneously by a white deposition. As the stannate-cyanide

2

solution is transparent and fairly clear, the initial dark flash followed by the deposition of a white metal is easily observed. This initial "flash" is believed to be an extremely thin layer of copper. The subsequent white deposit is tin. Analyses of thick immersion deposits (2 to 3 minutes' immersion) have shown them to have a tin content greater than 99%. The immersion deposit which is believed to contain a small amount of copper in the tin alloy is referred to herein as an immersion tin deposit.

Although thick immersion deposits obtained by long immersion have many uses, they are not suitable as an undercoat for adherent electrodeposits. To obtain sound adherent electrodeposits, the undercoat should be one obtained by immersion for not more than about 30 or 40 seconds.

We also discovered that a sound and adherent tin-copper alloy plate may be electrodeposited on aluminum surfaced with a thin immersion tin deposit prepared by immersing the aluminum in a bath of the type specified herein for between approximately 5 and not more than 40 seconds, and preferably not more than 15 seconds. The electrodeposition of the tin-copper alloy is preferably carried out in a bath of the same composition as that useful for the immersion dip. The immersion dip and the subsequent electrodeposition may be carried out in the same tank or in separate tanks. Aluminum surfaced with this tin-copper alloy is suitable for many purposes. The alloys plated from baths also useful for the immersion dip, contain between 40% and 60% of tin, the remainder copper. Aluminum surfaced as aforesaid is also useful as a basis metal for one or more subsequent electrodeposits to provide decorative and/or utilitarian finishes. Without further finishing it is useful for a wide variety of applications, including tin plated wire, tin coated sheet, fabrication of cans, electrical applications, sliding and other bearing-type applications, etc.

We have also discovered that other metals such as copper, tin, bronze, nickel, etc., may be deposited directly on the thin tin immersion coating. The thin immersion tin deposit on the aluminum is susceptible to corrosive attack by the plating solution utilized for electrodepositing the subsequent layer(s). Baths and plating conditions must be selected wherein the electrodeposition process proceeds at such a rate and under such conditions that electrodeposition is preferential to the rate of corrosive attack. Generally the more neutral solutions are those from which plating is successfully accomplished; the preferred pH range being between about 4 and about 9. Such metals as copper and bronze have been plated from pyrophosphate solutions, and bright nickel from a modified Watts solution. Although it is possible and often desirable to electrodeposit metals other than the copper-tin alloy directly on the thin immersion deposit, it is generally preferred that a relatively thin tin-copper alloy be electrodeposited on the thin immersion deposit before electrodepositing the desired metal. Various metals, including bronze, tin-nickel, copper, and chromium have been successfully electrodeposited using a tin-copper electrodeposit as the undercoat.

The immersion bath specified hereinbefore is a composition which has been found particularly suitable for both immersion and electroplating. Adherent immersion tin deposits may be obtained from aqueous baths of the type:

	Broad range, g./l.	Preferred range, g./l.
Sn ⁺⁺ [added as $K_2Sn(OH)_6$]	23-59	35.6-51.5
Cu ⁺ [added as CuCN]	3.5-11.5	5.7-10.6
Free KCN	15-38	22-30
KOH	3-12	5-10

In addition to the materials noted in the table, the aqueous baths contained sufficient additional KCN to complex the copper $[\text{Cu}(\text{CN})_2]$. Thus, the solution contains about 3 mols of CN^- for each mol of Cu^+ , in addition to the free cyanide. This method of specifying the solution composition is common for cyanide copper solutions and is used herein.

It is possible to obtain immersion tin deposits from stannate solutions outside the limits specified hereinbefore. For aluminum alloys, other than the high copper alloys, deposits from sodium stannate baths are not adherent. Those deposits prepared from baths within the preferred range and those having a copper to tin ratio in the solution between 1:4.5 and 1:6.5 are the most adherent. The preferred operating range is about 48° C. to 55° C., although it is possible in the preferred bath composition range specified to operate between 32° C. and 65° C. The temperature range for obtaining adherent deposits is somewhat narrower for aluminum alloys having high silicon and/or magnesium content.

Baths prepared from the salts hereinbefore specified are preferred. It is possible to obtain adherent immersion tin deposits from baths in which the sodium salts replace in part the potassium salts. For a given bath composition more adherent deposits are obtained from the all-potassium bath. Deposits become progressively less adherent as sodium replaces potassium. Baths containing less than about 20% potassium ions (80% sodium ions) result in deposits having somewhat inferior adhesion characteristics. When replacing some of the potassium salts by the equivalent sodium salts, the weight of the salts must be modified to conform with the relative atomic weights of sodium and potassium. It is also possible to vary the salts somewhat by adding both copper and some of the tin in the form of copper stannate, if sufficient cyanide is present to form the copper complex and also to provide sufficient free cyanide within the range specified. Copper may also be added in the form of a potassium copper cyanide.

Potassium stannate is known to be normally solid as disclosed on pages 472 and 473, item No. 11, of Handbook of Chemistry and Physics, 30th edition, Chemical Rubber Publishing Co., 1947. Potassium copper cyanide and potassium cyanide are also known to be normally solids (ibid., pages 466 and 467, items Nos. 9 and 11). A composition containing the aforementioned three compounds is utilized in the solid form; it is added to the aqueous solution where it is dissolved to provide a bath suitable for producing immersion tin deposits in accordance with the process of the instant invention. Potassium stannate comprises between 90 and 130 parts of this solid composition.

The amount of dissolved copper in the solution is a

and caustic, and with low concentration of free cyanide and stannate. Low temperatures also promote copper deposition. By proper manipulation of these factors it is possible to obtain sound deposits outside the range specified hereinbefore. It is sometimes possible to obtain immersion deposits in stannate-cyanide baths of the type specified hereinbefore with a dissolved copper content as low as about 1.5 g./l., by proper manipulation of these various factors and by the addition to the solution of such materials as tartrates, citrates, gluconates, and saccharates, which are known to influence the deposition of copper from bronze electroplating baths. The use of these additives also sharply lowers the maximum amount of copper in operative baths. The operative baths contain a small critical amount of dissolved copper effective to obtain adherent immersion deposits.

The electrodeposition of tin-copper alloy is preferably carried out from baths of the same composition as those used for the immersion dip. As noted, the tin-copper alloy is electrodeposited on a thin immersion tin deposit. The electrodeposition is carried out between 32° C. and 65° C.; preferably between 48° C. and 55° C. Current densities conventional for copper-tin alloy plating are suitable. These generally vary from 1 amp./sq. dm. to 15 amp./sq. dm. for conventional batch plating and may be as high as 150 amp./sq. dm., or higher, for continuous wire and strip plating. The tin-copper alloy may be electrodeposited to any desired thickness. Its appearance is best at a thickness of 0.0025 to 0.00025 cm. It is preferable that the electrodeposited coating be at least 0.001 cm. thick if it is to serve as the undercoat for electrodeposition of other metals deposited from highly caustic solutions, or if it is to be used in applications requiring soldering to produce joints with good physical properties. The deposit may be brightened by the addition of a lead-containing brightener to the plating solution. A multi-layered deposit with alternate tin and tin-copper layers is obtained by interruption of the current during electrodeposition using a bath specified herein.

For the purpose of giving those skilled in the art a better understanding of the invention, the following illustrative examples are given:

A commercially pure sheet aluminum, 1100 (2S) alloy, was used for comparative purposes. Before immersion in the specified solution it was cleaned by dipping in a caustic solution containing 30 g./l. of trisodium phosphate and 22 g./l. of caustic soda, between 35° C. and 55° C. It was then rinsed in cold water, dipped in a concentrated nitric acid solution and again rinsed. The solutions tested and the conditions specified in the following table resulted in sound adherent deposits. All the electrodeposits were made on thin immersion deposits.

Example number	CuCN, g./l.	Free KCN, g./l.	KOH, g./l.	$\text{K}_2\text{Sn}(\text{OH})_6$, g./l.	Type of deposition	Temp., ° C.	Additive (citric acid), g./l.
1-----	16	22.5	7.5	60	Immersion..	58	-----
2-----	16	22.5	7.5	60	Electro.....	54	-----
3-----	10.5	22.5	7.5	120	Immersion..	55	-----
4-----	10.5	22.5	7.5	120	Electro.....	58	-----
5-----	16	22.5	7.5	120	Immersion..	58	-----
6-----	16	22.5	7.5	120	Electro.....	58	-----
7-----	16	22.5	7.5	90	Immersion..	55	-----
8-----	16	22.5	7.5	90	Electro.....	60	-----
9-----	4.8	22.5	7.5	120	Immersion..	49	0.4
10-----	7.5	22.5	7.5	120	Electro.....	55	0.2

critical factor involved in obtaining sound immersion deposits. Although it is generally impossible to obtain sound deposits with a copper concentration outside the limits specified herein, it is sometimes possible to do so by careful selection of the other bath components and by the use of special addition agents which affect the relative propensity of copper and tin to deposit from solution. The relative propensity of copper to deposit from solution is increased with high concentrations of copper cyanide.

In addition to the deposition from the stannate-cyanide type baths used in the preceding examples, aluminum was also plated by electrodepositing nickel directly on the thin immersion tin deposit from a standard Watts nickel solution under standard conditions. In a similar manner, copper was electrodeposited from a pyrophosphate copper solution.

Industrially useful and/or decorative finishes of a composite nature have also been successfully electrodeposited

on aluminum. The surface was first coated with a thin adherent immersion deposit, followed by an electrodeposit from the same bath. On this base, (i) bronze has been electrodeposited from a cyanide bath, (ii) copper from a pyrophosphate copper bath, and (iii) copper-nickel-chromium from conventional baths.

Aluminum wire was surfaced with the tin-copper electrodeposit from the same bath used to obtain the immersion tin undercoat. An extremely high current density was used. This process is particularly suitable to the electro-coating of wire and sheet in continuous high speed mills.

The process has been successfully applied to a wide range of aluminum alloys. These include 1100 (2S), 3003 (3S), 2017 (17S), 2024 (24S), 5052 (52S), 6061 (61S), 7075 (75S), EC grade wire, and Al-356 (sand-cast). Before applying immersion deposits the aluminum surface must be cleaned. Cleaning steps usually involve initial solvent cleaning, followed by an alkaline dip, a water rinse, and an acid dip. The best procedure varies for different alloys. These are conventional and specified in ASTM B253-53, as well as Metal Finishing Guidebook Directory (1959).

As many embodiments of this invention may be made without departing from the spirit and scope thereof, it is to be understood that the invention includes all such modifications and variations as come within the scope of the appended claims.

We claim:

1. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution containing about 23 g./l. to 59 g./l. of Sn^{+4} , 15 g./l. to 38 g./l. of free alkali metal cyanide, 3 g./l. to 12 g./l. of alkali metal hydroxide, at least 20% of said alkali metal in the solution being potassium and the remainder sodium, and sufficient Cu^{+} selected from the range of 1.5 g./l. to 11.5 g./l. to form an adherent immersion tin deposit.

2. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution, at a temperature between about 32° C. and 65° C., containing about 23 g./l. to 59 g./l. of Sn^{+4} , 15 g./l. to 38 g./l. of free alkali metal cyanide, 3 g./l. to 12 g./l. of alkali metal hydroxide, at least 20% of said alkali metal in the solution being potassium and the remainder sodium, and sufficient Cu^{+} selected from the range of 3.5 g./l. to 11.5 g./l. to form an adherent immersion tin deposit.

3. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution, at a temperature between about 48° C. and 55° C., and containing about 23 g./l. to 59 g./l. of Sn^{+4} , 15 g./l. to 38 g./l. of free alkali metal cyanide, 3 g./l. to 12 g./l. of alkali metal hydroxide, at least 20% of said alkali metal solution being potassium and the remainder sodium, and about 3.5 g./l. to 11.5 g./l. of Cu^{+} , the ratio of copper to tin being between 1:4.5 and 1:6.5, to form an adherent immersion tin deposit.

4. The process of claim 3 in which the aluminum is immersed in the solution for between 5 seconds and 40 seconds.

5. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution, at a temperature between about 32° C. and 65° C., containing about 35.6 g./l. to 51.5 g./l. of Sn^{+4} , 22 g./l. to 30 g./l. of free potassium cyanide, 5 g./l. to 10 g./l. of potassium hydroxide, and about 5.7

g./l. to 10.6 g./l. of Cu^{+} , to form an adherent immersion deposit.

6. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution, at a temperature between about 48° C. and 55° C., containing about 35.6 g./l. to 51.5 g./l. of Sn^{+4} , 22 g./l. to 30 g./l. of free alkali metal cyanide, 5 g./l. to 10 g./l. of alkali metal hydroxide, at least 20% of said alkali metal solution being potassium and the remainder sodium, and about 5.7 g./l. to 10.6 g./l. of Cu^{+} , to form an adherent immersion deposit.

7. The process of claim 6 in which the aluminum is immersed in the solution for between 5 seconds and 15 seconds.

8. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution at a temperature about 50° C., containing about 120 g./l. of potassium stannate, 26 g./l. of free potassium cyanide, 7.5 g./l. of potassium hydroxide, and 11 g./l. of copper cyanide, to form an adherent immersion tin coating.

9. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution, at a temperature between about 32° C. and 65° C., containing about 90 g./l. to 130 g./l. of potassium stannate, 22 g./l. to 30 g./l. of free potassium cyanide, 5 g./l. to 10 g./l. of potassium hydroxide, and 8 g./l. to 16 g./l. of copper cyanide, to form an adherent immersion tin deposit.

10. A process for producing an immersion tin coating on aluminum comprising immersing cleaned aluminum in an aqueous solution containing about 23 g./l. to 59 g./l. of Sn^{+4} , 15 g./l. to 38 g./l. of free alkali metal cyanide, 3 g./l. to 12 g./l. of alkali metal hydroxide, said alkali metal in the solution being selected from the class consisting of potassium and sodium, and sufficient Cu^{+} selected from the range of 1.5 g./l. to 11.5 g./l. to form an adherent immersion tin deposit.

11. A solid composition of matter for making up an aqueous bath for producing an immersion tin deposit on aluminum comprising 90 to 130 parts of potassium stannate, and copper in the form of potassium copper cyanide, the weight ratio of copper to tin being between 1:4.5 and 1:6.5, and sufficient potassium cyanide so that when the composition is dissolved in water containing between 3 g./l. and 12 g./l. of potassium hydroxide, the solution contains between 23 g./l. and 59 g./l. of Sn^{+4} , between 5.7 g./l. and 10.6 g./l. of Cu^{+} , and between 15 g./l. and 38 g./l. of free potassium cyanide.

References Cited in the file of this patent

UNITED STATES PATENTS

1,945,718	Marino	Nov. 26, 1912
2,511,395	Baier et al.	June 13, 1950
2,600,699	Shockley	June 12, 1952
2,662,054	Passel	Dec. 8, 1953
2,758,075	Swalheim	Aug. 7, 1956
2,791,553	Connor et al.	May 7, 1957
2,793,990	Heymann et al.	May 28, 1957
2,854,388	Safranek et al.	Sept. 30, 1958
2,879,210	Howard	Mar. 24, 1959
2,891,871	Ceresa et al.	June 23, 1959
2,916,423	Passel	Dec. 8, 1959
2,947,639	Bolden	Aug. 2, 1960

FOREIGN PATENTS

626,693	Great Britain	July 20, 1949
---------	---------------	---------------