United States Patent Office 2,926,124 Patented Feb. 23, 1960

2,926,124

TIN NICKEL ALLOY PLATING PROCESS AND COMPOSITION

Richard Taylor, Rochester, and Robert R. Phillips, Livonia, Mich., assignors to Chrysler Corporation, Highland Park, Mich., a corporation of Delaware

No Drawing. Application July 1, 1957 Serial No. 668,894

15 Claims. (Cl. 204—43)

This invention relates to an electrolytic process for tin-nickel alloy plating and to a composition and aqueous bath thereof for effectuating said plate. It especially relates to an electrolytic bath that may be employed without harmful effects upon operatives employing the same.

It has heretofore been discovered that tin-nickel alloys are excellent corrosion-resistant materials and hence of considerable value, and considerable work has been done to obtain tin-nickel alloy deposits electrolytically from an aqueous salt bath. Currently tin-nickel alloys are commercially electrolytically plated out of an aqueous bath composed of metal chloride salts and alkali fluorides, specifically an aqueous bath containing stannous chloride ($SnCl_2 \cdot 2H_2O$), nickel chloride ($NiCl_2 \cdot 6H_2O$), sodium fluoride (NaF), and ammonium fluoride ($NH_4F \cdot HF$).

Although commercially useful, such a bath has certain undesirable characteristics. For example, it contains free fluorides which fume and which upon hydrolysis form free hydrofluoric acid. Both the gas and acid are very toxic and corrosive. Hence in using electrolytes of this type it is customary to take adequate precautions to prevent the inhalation of the toxic fumes by the operatives, and to provide them with special rubber gloves and clothing to protect their skin against acid absorption. Fluoride-type electrolytes of this character also readily precipitate insoluble salts when not in use or when stored unless held above temperatures of between 100 to 115° and are therefore wasteful. Furthermore it also has been a problem with such electrolytes to obtain tin-nickel deposits that are bright as formed and that do not require substantial buffing to obtain full brightness.

The present invention aims to overcome the foregoing hazards and problems and to provide an electrolytic tin-nickel plating composition and process that will avoid the formation of hydrofluoric acid or free fluorides and that will produce a satisfactory tin-nickel plate which may by proper bath composition also be one providing a full bright finish as formed and without the use of any fluoride or substantial buffing.

Other objects and advantages of our invention will be apparent from the following description.

In accomplishing our novel results we preferably employ an essentially all-chloride tin-nickel aqueous bath conditioned for satisfactory plating by the addition of hydrochloric acid (HCl) which is the key to this satisfactory plating operation. The exact function of the hydrochloric acid in the bath is not exactly known, but without limiting ourselves to any given theory it may be explained that it is believed to bring down the potential of the nickel and raise that of the tin of the electrolyte to a plating condition and to form a complex of tin, nickel, and chloride from which the tin and nickel plate out as an alloy and not separately.

Basically the bath is made up of nickel chloride, stannous chloride, and hydrochloric acid. The amounts of these substances to be used may be varied over a substantial range to produce satisfactory alloys which it will be found will have a composition comprising essentially 65 to 75% tin and 25 to 35% nickel.

In general we prefer that the bath contain at least about 100 grams of nickel chloride per liter of aqueous solution at the start of operations to get good control such being supplemented by action of the acid on the nickel anode where used. The upper limit of nickel chloride is dictated solely by economics, about 400 grams per liter of solution being a good practical limit.

The stannous chloride should for purposes of good control be present in amount at least about 5 grams per liter of aqueous solution with an upper limit of about 50 grams per liter dictated solely by cost. The use of too much stannous chloride will have an adverse effect on the brightness of the finished plate obtained. Moreover, it increases the pH of the solution which it is desired to maintain at a high acid concentration in order to obtain best results.

As previously stated, the use of hydrochloric acid is essential to and the key to the success of the present invention. This ingredient should be used in amount to bring the pH of the bath down to about 1.0 or less, preferably 0.5 or less for best results. Above 0.5 the activity of the bath is retarded and there is a loss in brightness and above about 1.0 the tin salts will hydrolize and precipitate. As a guide to the amount of hydrochloric acid needed to obtain this pH range, we have found that in an aqueous bath containing a mixture of 20 grams per liter of stannous chloride and 300 grams of nickel chloride and having a pH of about 3.0 it takes about 5 milliliters or about 0.5% by volume per liter of commercial concentrated hydrochloric acid (38% hydrochloric acid) to prevent hydrolysis of the stannous chloride in the solution and precipitation of stannous hydroxide $Sn(OH)_2$ and obtain a pH of 1.0; 2.5 milliliters or 0.25% by volume to lower the pH from 3.0 to 1.5; 1% by volume to lower the pH to 0.5, and 10% by volume to lower the pH to 0.15. It is preferred to start with an excess of hydrochloric acid in order to provide sufficient quantity for preventing hydrolysis of the stannous chloride and so that further balancing of the bath may be controlled by merely adding stannous chloride, or preferably an equivalent amount of tin metal to the solution. From the foregoing example, it will be evident that about 1% by volume per liter of the solution of hydrochloric acid will usually produce a bath having a pH of 0.5 and, obviously, greater volumes will have the effect of correspondingly still further lowering the pH of the bath. Hydrochloric acid in amounts up to 75% by volume per liter of solution have been used with satisfactory results but it is found that an amount of hydrochloric acid in the range of 10 to 15% by volume per liter of solution will take care of most operating conditions, maintain the pH within the preferred range, and provide a smooth uniformly thick alloy plate. Dependent upon the concentration of nickel chloride, acid and the other ingredients of the bath, the plate will be semi or fully bright in the as formed condition. It is to be observed that by the present invention the pH value of the bath is necessarily less than about 1.0 whereas in aqueous fluoride baths in current use the pH value of the bath is necessarily between 2.0 and 2.5. Moreover, the pH of our bath is substantially lower than that of nickel chloride in solution which has a pH of about 2.0 or more and stannous chloride in solution which has a pH of 4.0 and more.

It is found that the amount of hydrochloric acid employed in the bath dictates to some extent the optimum temperature at which the bath should be operated for best results and vice versa. We have found, for example, that a temperature of between 100° to 150° F., preferably about 145° is adequate when the bath contains up to 50% by volume per liter of solution of hydrochloric acid,

However, when the concentration of hydrochloric acid is increased above 50% by volume for example in the range 50 to 75%, it is preferred that lower operating temperatures be employed for example between 100 to 125° as a lower temperature with increased acid concentration produces about the same result as a lesser amount of acid at a higher temperature. By preference the temperature of the bath should not be substantially in excess of 160° F. as such is apt to cause substantial fuming, a condition which is preferably avoided.

In operating a bath with the foregoing basic ingredients, any suitable anode high in nickel may be employed. However, a substantially pure, i.e., commercially pure nickel anode is preferred from the standpoint of its ability to maintain the nickel balance in the bath, the free chlorides of the bath acting upon the nickel anode to facilitate the removal of nickel. This balance is customarily obtained by the addition of nickel chloride. The current density to be employed will largely depend upon the pH of the bath. The higher the pH, the lower the current density needed for brightness. In general, densities between 5 to 120 amperes per square foot are operable with densities in the range of 20 to 40 amperes per square foot being preferred for most purposes.

Various ingredients may be added to the basic bath ingredients described above in those cases where the concentrations of acid or nickel chloride are insufficient to obtain a bright plate as formed, or where it is desired to further brightening of the plate, inhibit pitting of the plate, and serving as balancing controls on the bath. For example, ammonium chloride (NH_4Cl) may be employed as an addition to keep the bath in balance and to act on the nickel anode to replenish the nickel content of the bath. Ammonium chloride also serves to improve the solution conductivity and as an aid in obtaining a brighter plate deposit. Ammonium chloride for best results will be used in amounts between about 75 to 100 grams per liter of solution. Lesser amounts may be employed where other brightening agents are also included and larger amounts up to the limit of solubility, about 200 grams per liter, is likewise possible.

Cobalt chloride ($CoCl_2 \cdot 6H_2O$) is a preferred addition for orienting the nickel deposition of the bath and serving as a brightening agent. It is also believed to plate out with the nickel to a minor extent. Suitable amounts for use in the bath are between 0.5 and 5.0 grams per liter of solution. Zinc chloride ($ZnCl_2$) may be employed as a brightening additive agent and as an anti-pitting agent. Good results are obtained with amounts between 1 to 2 grams per liter of solution. Zinc sulfate ($ZnSo_4$) and titanium sulfate ($TiOSO_4$) may be employed for similar purposes, the former being used in amounts the same as zinc chloride and the latter in amounts between 2 to 20 grams per liter.

There are other additive agents from which some improvement in the plating deposit is obtained. For instance, potassium chloride (KCl) when used in amounts 75 to 200 grams per liter of solution aids in the bath conductivity and plate brightness. Gluconic acid

$$[CH_2OH(CHOH)_4 \cdot CO_2H]$$

when employed in amounts between 2.5 to 7.5 grams per liter serves as a brightening agent. Thiourea, also called thiocarbamide ($NH_2 \cdot CS \cdot NH_2$) when used in amounts between .01 to 5.0 grams per liter acts as a brightening and anti-pitting agent. "Nacconal NR" which is alkyl aryl sodium sulfonate made as described in Patents 2,387,572, 2,393,526, and 2,397,133 may be added to the bath in amounts between 0.1 to 0.6 gram per liter to serve as an anti-pitting agent. Fluorides such as ammonium bifluoride ($NH_4F \cdot HF$), sodium fluoride (NaF) and potassium titanium fluoride (K_2TiF_6) although not essential to the practice of the present invention, may be employed where proper controls are used in amounts between 0.5 gram to 5 grams per liter of solution as additional brightening agents.

It will be understood that the above additive agents may be used singly or one or more in a group.

The tin-nickel plate obtained by the process and composition of this invention is very adherent, highly resistant to tarnishing, and can take the place of chromium plating for decorative uses. It is an excellent coating directly on steel and over a copper undercoating where corrosion resistance is also desired. It also provides an excellent base for chromium plating.

The following examples of baths will illustrate the nature of the invention but are not to be construed as a limitation upon the same. In each instance water is an ingredient to make up the balance of each liter.

Example 1

Nickel chloride, 100 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 75%, Ni 25%
The plate had a dull appearance

Example 2

Nickel chloride, 200 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 72%, Ni 28%
The plate had a semi-bright appearance

Example 3

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 71%, Ni 29%
The plate had a bright appearance

Example 4

Nickel chloride, 400 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 72%, Ni 28%
The plate had a bright appearance

Example 5

Nickel chloride, 300 grams per liter
Stannous chloride, 10 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 70%, Ni 30%
The plate had a bright appearance

Example 6

Nickel chloride, 300 grams per liter
Stannous chloride, 60 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 71.0%, Ni 29%
The plate had a dull appearance

Example 7

Nickel chloride, 300 grams per liter
Stannous chloride, 100 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 71%, Ni 29%
The plate had a dull appearance

Example 8

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 1.0% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 70%, Ni 30%
The plate had a dull appearance

Example 9

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 5.0% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 71%, Ni 29%
The plate had a semi-bright appearance

Example 10

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 25.0% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 66%, Ni 34%
The plate had a semi-bright appearance

Example 11

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 50.0% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 70%, Ni 30%
The plate had a bright appearance

Example 12

Nickel chloride, 300 grams per liter
Stannous chloride, 50 grams per liter
Hydrochloric acid, 50% by volume
Temperature 98° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 66.5%, Ni 33.5%
The plate had a bright appearance

Example 13

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Ammonium chloride, 50 grams per liter
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 71.0%, Ni 29%
The plate had a bright appearance

Example 14

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Ammonium chloride, 150 grams per liter
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 69%, Ni 31%
The plate had a bright appearance

Example 15

Nickel chloride, 300 grams per liter
Stannous chloride, 50 grams per liter
Ammonium chloride, 125 grams per liter
Potassium chloride, 100 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 69%, Ni 31%
The plate had a bright appearance

Example 16

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 10 amp. per sq. ft.
Coating analysis—Sn 68.0%, Ni 32%
The plate had a bright appearance

Example 17

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 40 amp. per sq. ft.
Coating analysis—Sn 68.5%, Ni 31.5%
The plate had a semi-bright appearance

Example 18

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 80 amp. per sq. ft.
Coating analysis—Sn 71%, Ni 29%
The plate had an appearance between a dull and semi-bright condition

Example 19

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Temperature 145° F., current density 120 amp. per sq. ft.
Coating analysis—Sn 70.5%, Ni 29.5%
The plate had a dull appearance

Example 20

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Ammonium chloride, 50 grams per liter
Potassium titanium fluoride, 2 grams per liter
Temperature 150° F., current density 30 amp. per sq. ft.
Coating analysis—Sn 75.0%, Ni 25.0%
The plate had a bright appearance

Example 21

The tin nickel plated product of Example No. 19 was etched with a 10% sulphuric acid dip at 150° F. for 15 to 60 seconds and then chromium plated by standard chrome plating procedures.

Example 22

The tin nickel plated product of Example 19 was dipped in a solution containing 8 oz. per gallon of "Versene" at a temperature of 160° F. for 30 to 90 seconds and then chrome plated by standard chrome plating procedures. "Versene" is a sodium salt of ethylene diamine tetra acetic acid.

Example 23

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Zinc chloride, 2 grams per liter
Temperature 140° F., current density 30 amp. per sq. ft.
The plate had a bright appearance

Example 24

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 10% by volume
Cobalt chloride, 3.0 grams per liter
Temperature 140° F., current density 30 amp. per sq. ft.
The plate had a bright appearance

Example 25

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 15% by volume
"Nacconal" NR .4 gram per liter
Temperature 140° F., current density 30 amp. per sq. ft.
The plate had a bright appearance

Example 26

Nickel chloride, 300 grams per liter
Stannous chloride, 30 grams per liter
Hydrochloric acid, 15% by volume
Cobalt chloride, 3.0 grams per liter
Ammonium chloride, 100 grams per liter
Temperature 145° F., current density 30 amp. per sq. ft.
The plate had a very bright appearance

Examples Nos. 20 and 24 and especially No. 26 gave the best plating results.

From the foregoing description of our invention it will be apparent that we have provided a new and novel composition and process for forming tin-nickel alloy coatings on electrical conducting surfaces, for example, ferrous, copper, and alloy metal surfaces.

It will be apparent to those skilled in the art that various changes in the composition and specific steps of processing may be made without, however, departing from the spirit or intent of our invention. All changes, modifications and equivalent compositions and processes as may come within the purview of the appended claims are therefore contemplated.

We claim:

1. A process which comprises electro depositing tin-nickel alloys from an aqueous bath consisting essentially of stannous-nickel chloride and hydrochloric acid in amount such that the acidity of said bath corresponds to a pH of no greater than about 1.0.

2. A process which comprises electro depositing tin-nickel alloys from an aqueous bath consisting essentially of stannous-nickel chloride and hydrochloric acid in amount such that the acidity of said bath corresponds to a pH of no greater than about 0.5.

3. A process which comprises electro depositing tin-nickel alloy coatings from an aqueous solution bath consisting essentially of nickel chloride, stannous chloride, hydrochloric acid and water and which bath has a pH of no greater than about 1.0.

4. A process which comprises electro depositing tin-nickel alloy coatings from an aqueous solution bath consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter of solution, nickel chloride in amount between about 100 to 400 grams per liter of solution, and hydrochloric acid in amount between about 1 to 75% per liter of solution by volume sufficient to produce a bath whose pH is no greater than about 1.0.

5. A process which comprises electro depositing tin-nickel alloy coatings from an aqueous solution bath consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter of solution, nickel chloride in amount between about 100 to 400 grams per liter of solution, and hydrochloric acid in amount between about 10 to 15% per liter of solution by volume sufficient to produce a bath whose pH is no greater than about 1.0.

6. A process for forming tin-nickel alloy coatings on a base member comprising forming an aqueous bath consisting essentially of stannous and nickel chlorides and hydrochloric acid in amount to make the acidity of the bath correspond to a pH of no greater than about 1.0, placing an anode in said bath comprising essentially nickel, immersing said base member in said bath and passing an electric current through said bath between said anode and member providing a current density between 20 to 40 amperes per square foot and sufficient to effect a bright deposition of tin-nickel from said bath upon said member.

7. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of chlorides of tin and nickel and hydrochloric acid in amount to give the bath a pH of no greater than about 1.0.

8. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of chlorides of tin and nickel and hydrochloric acid in amount to give the bath a pH of no greater than about 0.5.

9. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter, nickel chloride in amount between about 100 to 400 grams per liter and hydrochloric acid in amount between 1 to 75% per liter of solution by volume to produce a bath whose pH is no greater than about 1.0.

10. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter, nickel chloride in amount between about 100 to 400 grams per liter and hydrochloric acid in amount to produce a bath whose pH is no greater than about 0.5.

11. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter, nickel chloride in amount between 100 to 400 grams per liter and hydrochloric acid in amount between 10 to 15% per liter of solution by volume to produce a bath whose pH is no greater than 0.5.

12. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of stannous chloride, nickel chloride, a metal salt selected from the group consisting of cobalt and titanium, and hydrochloric acid in amount to give the bath a pH of no greater than about 1.0.

13. An aqueous electrolytic bath for forming tin-nickel alloy coatings consisting essentially of stannous chloride, nickel chloride, cobalt chloride, ammonium chloride, and hydrochloric acid in amount to give the bath a pH of no greater than about 1.0.

14. An aqueous electrolytic bath for forming tin-nickel alloy coatings containing between 65 to 75% tin and 25 to 35% nickel consisting essentially of stannous chloride in amount between about 5 to 50 grams per liter, nickel chloride in amount between about 100 to 400 grams per liter, cobalt chloride in amount between about 0.5 to 5.0 grams per liter and hydrochloric acid in amount between 1 to 75% per liter of solution by volume to produce a bath whose pH is no greater than about 1.0.

15. A process which comprises electro depositing tin-nickel alloy from an aqueous fluoride free bath consisting essentially of stannous chloride, nickel chloride and hydrochloric acid, said hydrochloric acid being in amount to make the pH of the bath no greater than about 1.0.

References Cited in the file of this patent

UNITED STATES PATENTS

2,658,866 Parkinson ---------- Nov. 10, 1953

OTHER REFERENCES

Tin Research Institute, "Tin-Nickel Alloy Plating," T.R.I., 492 West 6th Ave., Columbus, Ohio, March 1952.

Journal Electrodepositor's Technical Society, vol. 27 (1951), pp. 129–151.