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AMPHOTERIC METAL ELECTROPLATING PROCESSES

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As far as is known no method has been developed for electroplating a metal object except when the object is immersed in or is in contact with a solution of a salt of the metal which it is desired to electroplate.

This invention relates to improved methods and processes for electrodepositing certain metals without the necessity of contacting the metal object to be electroplated with an aqueous solution containing a soluble salt of the metal to be electrodeposited.

More particularly it relates to methods of electrodepositing the amphoteric metals (except aluminum, which cannot be deposited from aqueous solution) by means of an electrolyte which needs to contain no soluble salt of the amphoteric metal being deposited.

An object of this invention is to chemically react a calcareous coating on a metal structure, similar to the types produced by the methods given in my U.S. Patents No. 2,200,469 of May 14, 1940, or No. 2,534,234 of December 19, 1950, with a soluble salt of an amphoteric metal so that an insoluble salt or basic complex containing the amphoteric metal will be deposited either in or in place of the calcareous coating on the metal structure, and thereafter suitably electrolyzing the complex to give the desired amphoteric metal coatings.

An object is to chemically react a low soluble basic non-metallic coating on a metal structure with a soluble salt of an amphoteric metal in order to produce a low soluble salt or basic complex containing the amphoteric metal in or in place of the basic low soluble coating and thereafter suitably electrolyze the complex to give the desired amphoteric metal coating.

A further object is to cause a basic low soluble inorganic non-metallic coating which has been sprayed in place on a metal structure, applied as a slurry on the structure or painted on the structure to chemically react with a soluble salt of an amphoteric metal thereby producing in situ a low soluble salt or basic complex containing the amphoteric metal, and thereafter suitably electrolyzing the complex to give the desired amphoteric metal deposit.

A further object is to combine into an amphoteric coating complex type of slurry a low soluble salt of an amphoteric metal with other low soluble coating constituents and then apply this material to a metal structure by spraying, painting or dipping, and thereafter suitably electrolyzing this amphoteric metal coating complex to form a metal deposit of the amphoteric metal on the metal structure.

For simplicity the chemical reaction product containing the low soluble amphoteric metal complex, which can be produced in situ and which results from the reaction of a basic, low soluble, inorganic non-metallic coating with a soluble salt of an amphoteric metal, or which results from a mechanical mixture of a low soluble salt of an amphoteric metal with the other low soluble coating constituents in the form of a slurry, will hereafter be referred to as the "amphoteric coating complex."

The originally deposited basic, low soluble, inorganic, non-metallic coating which can be deposited on the structure to be protected by electrolytic means, when using the methods of the above-mentioned patents, or by mechanical spraying, dipping into a slurry, painting, or by other means will hereafter, for simplicity, be referred to as the initial "basic low soluble coating deposit."

A further object is to solubiiize increment after increment by electrolytic means the amphoteric coating complex at the interface between this coating complex and the metal on which it is deposited, while at the same time electrolytically depositing the desired amphoteric metal on the cathode surface to be electroplated from the solubilized product.

In other words, these processes allow an amphoteric metal: (1) to be incorporated by chemical or mechanical means in a low soluble form in place of or in a basic low soluble protective coating on a metal structure; (2) to be slowly solubilized as needed by an electric current at the cathode surface of the structure; and (3) then to be electrolytically deposited in metallic form on the cathode surface of the structure from the solubilized product.

Step (1) of the preceding paragraph can be omitted by combining a suitable low soluble amphoteric metal complex directly into a slurry which can be sprayed or painted in place on the structure, or into which the structure to be coated can be dipped. Steps (2) and (3) as listed in the preceding paragraph would then be carried out as given.

Another object is to decrease the cost of electrolytically depositing a metallic coating of an amphoteric metal which can be electrodeposited on a structure such as the inner surface of a large tank, etc. For example, when it is desired to electroplate the inside of a large tank with any one of the amphoteric metals which can be electrodeposited, a few gallons of the desired concentration of the amphoteric metal salt would be sprayed on to the initial basic coating deposit and then steps (2) and (3) as listed above would be carried out. It is evident that these steps (2) and (3) can be carried out when using a comparatively inexpensive electrolyte, such, for example, as a solution of sodium chloride or sulphate or similar potassium salts. Of course, for these latter two steps any electrolyte could be used which would liberate a strong concentration of sodium or potassium hydroxide or other strong base on the cathode surface.

When the ordinary electroplating methods are used to deposit a metallic coating on the inside walls, for example, of a large tank or tank ship compartment, the cost of the metal salt required to fill the compartment or tank with a suitable electrolyte is generally prohibitive. These processes of applicant allow large tanks or other large structures which can be placed in tanks to be electroplated with lead, zinc or tin at a comparatively low cost.

Similarly the wind-water areas of steel piling or bulkheads in sea water can be electroplated with lead, tin or zinc at comparatively low cost.

Lead, zinc or tin are the commercially economic metals which will: (*a*) form a low soluble compound with a limited amount of alkali, (*b*) with further additions of alkali become soluble, and then (*c*) can be electrolytically reduced to the metallic form and deposited on the cathode surface.

Lead coatings

When, for example, a calcareous coating of the approximate composition given in my U.S. Patent No. 2,417,064 of March 11, 1947, is sprayed, dipped or otherwise wetted with a suitable solution of lead nitrate

a reaction similar to one or more of the following will take place:

$$Pb(NO_3)_2+Ca(OH)_2\rightarrow Pb(OH)_2+Ca(NO_3)_2$$

$$Pb(NO_3)_2+Mg(OH)_2\rightarrow Pb(OH)_2+Mg(NO_3)_2$$

If a limited amount of sodium hydroxide is present then:

$$Pb(NO_3)_2+2NaOH\rightarrow Pb(OH)_2+2NaNO_3$$

Therefore, when an initial low soluble basic coating deposit is treated with a soluble lead salt such as lead nitrate some of the low soluble lead hydroxide will be chemically formed and deposited in situ in the basic coating deposit to form the resulting low soluble amphoteric coating complex. If the metal surface on which this amphoteric coating complex is deposited is then made cathode in an electrolyte containing sodium chloride, sodium sulphate or similar ionizable sodium or potassium salt and a sufficient current is passed to decompose some of the sodium salt, for example, sodium hydroxide will be discharged at the interface of the cathode and the amphoteric coating complex. As a result soluble sodium plumbite will be formed at the cathode interface somewhat as follows:

$$Pb(OH)_2+2NaOH\rightarrow Na_2PbO_2+2H_2O$$

This latter compound dissociates into lead ions only to a very slight extent. However, as these lead ions are discharged by depositing lead on the cathode a few more ions are liberated immediately. The reaction will continue, therefore, until all the plumbite has been used up. Within reasonably wide limits of cathode current density it has been found by experiment that firmly bonded electrolytic deposits of metallic lead can be formed on the cathode at the interface between the cathode and the amphoteric coating complex.

Some of the variables studied are as follows:

Mild steel test panels were coated at room temperature with an initial basic low soluble coating deposit from synthetic sea water in accordance with U.S. Patent No. 2,200,469 at 100 milliamperes per square foot. After washing these panels under running tap water various ones were put into room temperature solutions of lead nitrate having concentrations of N/1, N/2, N/10 and N/100 for varying lengths of time from 1 minute to 48 hours. Without any correction the pH values of these solutions varied from 3.8, 4.3, 4.7 up to 5.2. After 60 minutes of conversion reaction the gain in weight of one set of panels was 0.35, 0.28, 0.19 and 0.02 gram respectively. Extending the treating times up to 48 hours showed no appreciable gain in weight over a 1-hour treatment, and decreasing the treating times to 1 minute showed a rather rapid drop-off in conversion reaction rates at times of less than 10 minutes. Also solutions having concentrations of less than one normal lead nitrate showed a rather rapid drop-off in conversion rates. The result is that the study was continued with baths of not less than one normal lead nitrate for the room temperature conversion reaction tests, and with reaction periods of 1 hour. It should be emphasized that room temperature conversion reactions are highly desirable for low cost treatment of large tanks or structures but it is explicitly understood that the examples given in this application do not constitute a limitation in any way whatever on the various reaction conditions and variables involved in the herein listed amphoteric metal reactions.

After the chemical conversion treatment various panels were then subjected to an electrolytic reduction treatment in 3.5% sodium chloride solution having starting pH values of approximately 8.0 and with cathodic current densities varying in substantially geometric ratios from 12.5 milliamperes per square foot up to 12.5 amperes per square foot. Although greater ampere-hours will be required for thicker deposits, in general, reasonably good deposits of metallic lead were obtained after the expenditure of a quantity of electricity equal to 2.4 to about 4.0 ampere hours per square foot of cathodic surface. Some of the best lead deposits have been obtained in the cathodic current density ranges of 12.5 to 800 milliamperes per square foot although some metallic lead was deposited on each panel up to values of 12.5 amperes per square foot.

Tests were also made when the lead nitrate conversion baths were corrected with dilute nitric acid to pH values down to 2.0 approximately. Improvements in the final lead deposit were obtained as the pH values of the baths were decreased to 2.0 and somewhat less treeing was obtained. However, the lead coatings made without any pH correction of the lead nitrate baths were also excellent.

Similar panel tests were run when using N/1 lead acetate solutions at room temperature. The results obtained were substantially like those obtained from the lead nitrate conversion baths, except that the conversion reaction rates were somewhat longer for the uncorrected lead acetate solutions having pH values of 5.8 approximately.

Magnesium hydroxide coatings which were electrolytically deposited on the clean steel panels from magnesium chloride baths and then subjected to a chemical conversion treatment and electrolytic reduction treatments as discussed above gave quite similar results. It is desired that this application include the use of any suitable lead salt for the formation of an amphoteric coating complex as defined in this application.

Zinc coatings

Dense well bonded metallic zinc coatings have been deposited on steel surfaces under the following conditions:

Mild steel test panels were coated with an initial basic coating deposit in accordance with the procedure outlined under lead coatings. Some panels were also coated with an initial basic coating deposit of magnesium hydroxide from a solution of magnesium chloride as previously outlined. These various panels were then washed under running tap water and put in uncorrected pH 5.5 and corrected pH 5.0 solutions of N/1 zinc chloride. These chemical conversion treatments were varied from 1 hour to 48 hours of treatment in room temperature solutions. As was found for the lead nitrate treated panels the 1-hour conversion treatments were essentially as complete as the 48-hour conversion treatments. However, when the temperature of the zinc chloride bath was increased from room temperature to 75° C. the chemical reaction time was decreased from 1 hour to approximately 5 minutes for a similar deposit of the low soluble zinc amphoteric coating complex.

The electrolytic reduction treatment of these panels was then made in 3.5% sodium chloride solutions at current densities varying from 100 milliamperes per square foot up to 2.0 amperes per square foot. Although various electrolytic reduction times have been studied, the reduction times were usually varied inversely as the cathodic current density until each panel had received a quantity of electricity at least equal to 2.4 ampere-hours. Although greater ampere-hours will be needed for thicker amphoteric coating complexes, good deposits of metallic zinc were obtained on each of the panels of this zinc series.

When zinc sulphate conversion baths were substituted for the zinc chloride conversion baths, essentially the same conditions were found to give useful metallic zinc coatings. It is desired that this application include the use of any suitable zinc salt for the formation of an amphoteric coating complex as defined in this application.

Tin coatings

The procedures set up for lead and zinc were used essentially with little modification for the formation and treatment of the amphoteric coating complex depositions formed from tin salts. The intial basic coatings were

formed by the procedures outlined under lead coatings. The chief difference in the procedure was the formation of the amphoteric coating complex depositions.

When using N/1 tin chloride solutions the low pH of approximately 1.0 resulting from hydrolysis of the tin chloride dissolved the initial basic coating in about 15 seconds. As a result conversion treatment solutions of N/10 were used. These N/10 solutions of tin chloride with pH values of approximately 2.1 gave good amphoteric coating complex reaction products in 1- and 2-minute treatments of the panels at room temperature. Good firmly bonded metallic depositions of tin were then obtained when these panels were treated at room temperature in 3.5% sodium chloride at the ampere-hours and cathodic current densities used for zinc and lead depositions. Well bonded deposits of tin were obtained in the 3.5% sodium chloride solutions at cathodic current densities of 100 to 800 milliamperes per square foot. It is desired that this application include the use of any suitable tin salt for the formation of an amphoteric coating complex as defined in this application.

General

One of the outstanding advantages of the use of an amphoteric coating complex to electrolyze into a metallic coating is the inherent fine grain deposits which have been obtained and to the exceptional uniformity of deposition. Probably one of the chief reasons why such fine grain deposits have been obtained over such a wide range of cathodic current densities is due to the fact that the metal ion concentration at all times is rather low. As these metal ions are discharged and plated out on the cathode other ions are immediately liberated but only in limited amounts. In other words these amphoteric coating complexes act in a way similar to the metal cyanides in the ordinary electroplating baths. Another possible reason for the fine grain metal deposits which are obtained by these processes is that the cathode polarization is greater than that obtained in the ordinary plating baths. This increased polarization causes a decreased crystal size of the metal deposit, greater throwing power of the bath and a decrease in treeing of the deposit.

In regard to the two latter advantages the use of these lead, zinc or tin amphoteric coating complexes has greatly increased the throwing power and decreased the treeing of the resulting electrodeposits when they are compared to the electroplating baths and deposits produced by the ordinary aqueous processes. However, at the higher current densities tested a slight amount of treeing has been observed. This is probably due to an excessive formation of the soluble amphoteric metal salt at the cathode interface and its blowing out through the amphoteric coating to the electrolyte interface where it is electrolytically reduced, thereby forming a conducting chain of metallic crystal trees. That the above comments on the formation of crystal trees are probably correct is indicated by a microscopic examination of a partially electrolyzed amphoteric coating complex on a panel. At the higher current densities tested up to 12.5 amperes per square foot small volcanoes indicating a blow-out action have been found in the vicinity of crystal trees. In regard to the electrolytes suitable for the reduction operations it is intended that these electrolytes be one or more of the soluble salts of the alkali metals. In regard to the current densities used for the reduction operations these current densities should be within the following limits: (*a*) the minimum current density should be a cathodic current density of sufficient magnitude in an electrolyte which will liberate a hydroxide of the alkali metals at a cathode thereby solubilizing the amphoteric metal component of the amphoteric coating complex at the cathode interface, and (*b*) the maximum current density should be one below which the electrodeposited metal is deposited essentially as a spongy arboreal or burnt deposit.

It is intended that this application cover the use of any of the amphoteric metal salts which can be used to produce a low soluble amphoteric coating complex by any of the methods herein disclosed and which can then be cathodically reduced to a useful metallic electroplated deposit.

While preferred embodiments of the invention are herein disclosed by way of example, it is understood that the invention is not limited with respect to the precise mode of applying the initial basic coating deposit as an amphoteric coating complex or as an initial basic coating deposit which can be treated with a soluble salt of an amphoteric metal to form an amphoteric coating complex, but it is broadly inclusive of any and all equivalents, both of procedure and constituent substances such as fall within the scope of the appended claims.

Related plating methods are disclosed in my copending application Serial No. 842,021.

I claim:

1. The process of electrolytically depositing an amphoteric metal, selected from the group consisting of lead, tin and zinc, on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing the metal to be deposited, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte containing a soluble alkali metal salt which will liberate a hydroxide of the alkali metal at the cathode thereby solubilizing the amphoteric metal component of the amphoteric coating complex at the cathode interface while at the same time electrodepositing on the cathode the selected amphoteric metal from the solubilized product.

2. The process of electrolytically depositing lead on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing lead, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte containing a soluble alkali metal salt which will liberate a hydroxide of the alkali metal at the cathode thereby solubilizing the lead content of the amphoteric coating complex at the cathode interface while at the same time electrodepositing lead on the cathode from the solubilized product.

3. The process of electrolytically depositing zinc on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing zinc, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte cintaining a soluble alkali metal salts which will liberate a hydroxide of the alkali metal at the cathode thereby solubilizing the zinc content of the amphoteric coating complex at the cathode interface while at the same time electrodepositing zinc on the cathode from the solubilized product.

4. The process of electrolytically depositing tin on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing tin, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte containing a soluble alkali metal salt which will liberate a hydroxide of the alkali metal at the cathode thereby solubilizing the tin content of the amphoteric coating complex at the cathode interface while at the same time electrodepositing tin on the cathode from the solubilized product.

5. The process of electrolytically depositing an amphoteric metal, selected from the group consisting of lead, tin and zinc, on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing the metal to be deposited, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte containing a soluble sodium salt which will liberate sodium hydroxide at the cathode

thereby solubilizing the amphoteric metal component of the amphoteric coating complex at the cathode interface while at the same time electrolytically depositing on the cathode surface the selected amphoteric metal from the solubilized product.

6. The process of electrolytically depositing an amphoteri metal, selected from the group consisting of lead, tin and zinc, on a ferrous metal structure which comprises coating said structure with a firmly adherent amphoteric coating complex of low solubility containing the metal to be deposited, and then subjecting said coated structure to a cathodic current density of sufficient magnitude in an electrolyte containing a soluble potassium salt which will liberate potassium hydroxide at the cathode

thereby solubilizing the amphoteric metal component of the amphoteric coating complex at the cathode interface while at the same time electrolytically depositing on the cathode surface the selected amphoteric metal from the solubilized product.

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