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ELECTROPLATING PROCESS

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This invention relates to electroplating metals and more particularly to a method of producing bright, smooth coatings of electroplated tin, cadmium, zinc and their alloys.

Electroplated coatings of tin, cadmium, zinc and alloys of these metals when taken directly from the electroplating bath ordinarily have a dull finish and are very susceptible to finger-staining and to tarnishing. For most purposes a bright, non-tarnishing finish is desirable. Ordinarily such electroplated coating is brightened by buffing and polishing; this, however, does not substantially reduce the tendency to tarnish.

Coatings of these metals, having a bright appearance, also may be obtained by dipping the metal articles to be coated in a molten bath of the coating metal. In order to obtain a smooth, uniform and bright surface by this method it is usually necessary to further treat the coated articles, e. g. by rolling, wiping or other treatment to remove excess metal and smooth the coatings. While this hot dipping method of coating metals is capable of producing a bright, smooth surface, it has a number of disadvantages. In the first place, when iron or steel articles are thus coated, careful and tedious preparation of the metal surface to remove oxide and other impurities are necessary before the metal is hot dipped in order to obtain a smooth adherent coat. These preliminary steps include pickling operations and annealing. Furthermore, metals which are coated by hot dipping have a relatively thin layer of coated metal because of the fact that the molten metal has a relatively low viscosity and when the article is removed from the hot dipping bath excess metal drains off, leaving a relatively thin coating on the article. The thickness of the coating is further reduced when a wiping or rolling operation is used. Hot dipping methods are also in general not readily applicable to odd shaped or deeply recessed articles. Frequently great difficulty is encountered in hot dipping methods because the metal to be coated tends to dissolve in the coating metal so that the coating metal bath becomes rapidly contaminated.

In many cases an electroplating process is preferable for coating metals because less preparation of the metal prior to plating is required and a thicker coating may be obtained. However, heretofore no entirely satisfactory process has been proposed for producing bright electroplated coatings of soft metals such as tin, cadmium or zinc. While bright electroplated coatings may be obtained by plating under certain carefully controlled conditions or by buffing and polishing, such plates are very easily tarnished and finger-stained. While it is possible to obtain a bright surface on a plated article by buffing and polishing without undue removal of coated metal, it is difficult and usually impractical to obtain a uniform bright coat on articles of irregular shape because of the difficulty of buffing and polishing deep depressions and irregular surfaces.

An object of the present invention is to produce smooth, bright, electroplated coatings of fusible metals such as tin, zinc, cadmium or their alloys without the use of mechanical polishing operations, bath addition agents, etc. A further object is to produce such coatings on iron or steel. A still further object is to produce electroplated coatings of tin, cadmium, zinc or their alloys on iron or steel which coatings have superior adherence to the base metal and increased corrosion resistance. Other objects will appear from the following description of my invention.

The above objects are accomplished by electroplating metallic articles with metals fusible below the melting point of the base and subjecting the electroplated articles to a heat treatment under substantially non-oxidizing conditions at a temperature above the melting point of the coated metal. Preferably the coated metal is heated to a temperature slightly above its melting point for a short time, for example 10 to 30 seconds. My invention also comprises a novel method of pickling iron or steel articles prior to electroplating as hereinafter described which results in a superior electroplated coating. By these novel methods I have obtained smooth, bright coatings of zinc, cadmium, tin and their alloys which are characterized by having a low degree of porosity.

I am aware that it has been proposed to improve electroplated coatings by the application of heat. However, so far as I am aware, heretofore it has not been proposed to electroplate metals and subsequently heat the electroplated surface to a temperature above the melting point under substantially non-oxidizing conditions to obtain the smooth, bright, oxide-free coating which characterizes my invention.

I have discovered that when heavy base metals such as iron, copper or brass are electroplated with metals having a melting point lower than the base metal, such as zinc, cadmium, tin or their alloys and the electroplated article is subsequently heated under substantially non-oxi-

dizing conditions to a temperature above the melting point of the base metal, a bright smooth plate is obtained which has a low degree of porosity. Such plate is similar in appearance to that obtained by the best methods of hot dipping or hot galvanizing and may be made of a much greater thickness. I have further discovered that such base metals, especially iron or steel may be plated with improved results if prior to plating the metal is treated with a strong acid to such extent that a distinct and uniform etching corrosion of the surface is obtained, followed by an alkaline treatment. With such pretreatment, the adherence of the plated coating is improved and the porosity of the plate is materially decreased. I have further found that when such pretreated metal is plated with tin, cadmium, zinc or their alloys and the plated coating is heat treated to a temperature above its melting point as described above, the resulting plate is smoother and more uniform than is the case when the base metal is not so etched and alkali treated prior to plating.

The above-mentioned etching prior to electroplating is especially useful in obtaining adherent, non-porous coatings of tin or the rust-resisting metals on cold-rolled sheet steel. Cold-rolled steel ordinarily has a bright, smooth surface. When bright, cold-rolled steel is electroplated for example with tin, the plated metal has relatively poor adherence and corrosion resistance. However, if the steel is previously treated with acid and alkali as described above, the electroplated tin has good adherence to the base and the corrosion resistance is markedly improved, without increasing the depth of the electroplated layer. These improved results are especially marked when the electroplated coating is in the neighborhood of 0.0001 inch thick or heavier.

One method of practicing my invention will be illustrated by reference to the production of a smooth, bright coating of tin or tin alloy on steel. The surface of the steel after suitably cleaning to remove grease and dirt, is first treated by immersion in a strong acid solution preferably at an elevated temperature, e. g. 100–200° F., until the surface of the metal is distinctly etched so that a uniformly etched or corroded surface is plainly visible to the unaided eye. The steel is then treated with an alkaline solution, preferably by making the steel the anode in an alkaline cyanide bath and applying a moderate electric current for a minute or two. The treated steel is electroplated with tin or tin alloy by any suitable method to produce a tin layer of the described thickness. I prefer to electroplate from an alkaline solution, especially by the methods described in U. S. Patents 1,841,978 and 1,919,000. These or similar methods may be used for plating tin or tin alloys on the treated iron or steel.

After the desired thickness of tin or tin alloy has been placed on the steel, the article is heated under substantially non-oxidizing conditions to a temperature above the melting point of the tin or tin alloy coating. If the coating is of substantially pure tin (which melts at about 450° F.), heating may be to a temperature of about 460 to 500° F. for a period of ten to thirty seconds.

Various known means of heating under non-oxidizing conditions may be utilized in order to carry out my invention. For some work and with relatively low melting coatings I have found a bath of molten tallow to be suitable; for other pieces and especially for continuous operation, or high melting coatings, a muffle furnace having an atmosphere of a non-oxidizing gas such as hydrogen or nitrogen or a furnace having small openings for the entrance of the articles to be heated and provided with means for continuously maintaining a substantially non-oxidizing atmosphere of such non-oxidizing gas may be utilized.

My invention will be further illustrated by the following examples.

Example 1

Samples of cold rolled sheet steel (automobile body stock) were first freed from grease and dirt by cleaning in an alkaline electrolytic cleaner containing:

	Oz./gal.
Sodium cyanide	2
Caustic soda	2
Trisodium phosphate	4

Temperature of solution—160°–180° F. making it cathode and anode alternately, until entirely free from grease and dirt.

The samples then were pickled in a sulfuric acid solution containing 15% by volume of sulfuric acid (66° Bé.) at a temperature of 70°–90° C. for a period of 4 minutes. Aside from the removal of oxide or scale, the pickling was continued until the rolled surface layer was removed and a distinct etching was visible to the naked eye.

The samples then were water rinsed and further treated electrolytically in a sodium cyanide solution containing 4 oz./gal. of NaCN at 140°–160° F., by making it the anode at 100 A/SF for 1 minute. After this treatment the samples again were water rinsed and then tin plated in an alkaline tin solution containing:

	Oz./gal.
Sodium stannate	12
Caustic soda	1
Sodium acetate	2
Hydrogen peroxide (100 vol.)	⅛

Data

Anode	Straits tin
Ratio of anode to cathode area	3 to 1
Cathode current density	10 to 50 A/SF
E. M. F	4.0 to 6.0 volts
Temperature of solution	60° to 80° C.
Time of plating	3 to 20 minutes

Thicknesses of 0.00005'' to 0.0004'' of tin were produced.

Following the plating, the samples were rinsed in cold and hot water and dried. The dry samples were immersed for 10 to 20 seconds in a molten tallow bath at a temperature of 240°–260° C. This treatment produced bright, smooth coatings of tin similar in appearance and hardness to that produced by hot tinning processes.

Example 2

Samples of cold rolled sheet steel were cleaned and then treated with acid and cyanide solution as described in Example 1. The treated samples were placed in an acid tin solution made up as follows:

	Oz./gal.
Sodium stannate	6
Sulfuric acid	16
Cresylic acid	1
Glue	½

Data

Anodes	Straits tin
Ratio of anode to cathode area	3 to 1
Cathode current density	6 to 60 A/SF
E. M. F	2.0 to 4.0 volts
Temperature of solution	normal room temperature
Time of plating	3.0 to 20 minutes
Thickness of coatings	0.00005'' to 0.0004''

Following the plating, the samples were heated in a tallow bath as described in Example 1, with substantially identical results.

Example 3

Cold rolled sheet steel samples were treated, plated and heat treated as described in Example 1, except that the following acid solution was used to etch the steel:

HCl	1 part by volume
Water	1 part by volume
Temperature of solution	70° to 90° C.
Time of immersion	2 to 5 minutes

Example 4

The procedure of Example 3 was repeated except that the following acid solution was used to etch the steel:

HNO_3 (conc.)	1 part by volume
Sulfuric (conc.)	1 part by volume
Water	4 parts by volume
Temperature	normal room temperature
Time of immersion	30 seconds to 2 minutes

Example 5

Samples of hot rolled steel were first freed from grease and dirt by cleaning at 160° to 180° F. in an alkaline electrolytic cleaner containing:

	Oz./gal.
Sodium cyanide	2
Caustic soda	2
Trisodium phosphate	4

The work was made cathode and anode alternately until entirely free from grease and dirt.

The samples were then pickled in a sulfuric acid solution containing 15% by volume of sulfuric acid (66° Bé.) at a temperature of 70° to 90° for a period of 1 to 3 minutes so that all fire scale was removed and etching was plainly visible to the naked eye.

The samples were then water rinsed and further treated in a warm sodium cyanide solution containing 8 oz./gal. of NaCN at 140° to 160° F., by making them anodes at a current density of 50 to 100 A/SF for 1 minute. After this treatment, the samples were plated and heat treated as in Example 1, with substantially the same results.

Example 6

In place of the anodic cyanide treatment mentioned in the foregoing examples, sheet steel samples, after being etched in various acid solutions, were subjected to anodic treatment at about 70° C. in a solution containing:

	Oz./gal.
Sodium hydroxide	2
Sodium carbonate	4

The anodic treatment was continued for 1 to 2 minutes at a current density of 50 to 100 A/SF. The samples were then plated and heat treated as in Example 1, with the same results.

Example 7

Samples of sheet brass and copper were first cleaned by making them cathodes for 3 to 5 minutes at 160° to 180° F. in an alkaline solution containing:

	Oz./gal.
Sodium cyanide	2
Trisodium phosphate	2
Caustic soda	4

The cathode current density was 50 to 100 A/SF. After water rinsing, the samples were pickled at 140° to 160° F. for 2 to 4 minutes in a solution containing:

	Part by volume
Water	1
Muriatic acid	1

The samples then were water rinsed and immersed for 3 minutes at 140° F. in a solution containing 4 oz./gal. of sodium cyanide. The treated samples then were plated and heat treated as in Example 1.

Example 8

Samples of sheet brass and copper, cleaned as described in Example 7, were treated in the following solution:

	Cc./L
Sulfuric acid 66° Bé	530
Nitric acid 42° Bé	160
Hydrochloric acid 24° Bé	0.75
Water	320

After the acid treatment, the samples were immersed in a sodium cyanide solution containing 4 oz./gal. of sodium cyanide for 3 minutes at a temperature of 140° C. The samples then were plated and heat treated as described in Example 1, with similar results.

Example 9

Pieces of cold-rolled sheet steel were first cleaned to remove grease and dirt as in Example 1. They were then plated without previous acid etching or alkali treatment in a tin solution similar to that of Example 1 to which had been added about ½ oz./gal. of cadmium oxide dissolved in sodium cyanide solution. The plated coatings had a thickness of 0.0001'' to 0.0004''. After plating, the coatings were treated in molten tallow at about 260° C. Evidence of the presence of cadmium in the coating was presented by the fact that the coatings melted below 231° C., the melting point of tin.

Bright deposits of cadmium-tin alloys were produced in all cases by the heat treatment. However, the coatings were lumpy, due to the omission of the acid etch and alkali treatment.

Example 10

Pieces of cold-rolled sheet steel were degreased as in Example 1. They were then etched for 3 to 5 minutes in a 15% solution of H_2SO_4 at a temperature of 70° to 90° C. After the acid treatment, the pieces were water rinsed and then treated anodically in a sodium cyanide solution (6 oz./gal.) at 140° to 160° F., using a current density of 50 to 100 A/SF for 1 minute. After water rinsing the pieces were then plated in the tin-cadmium bath described in Example 9. Upon heat treatment in tallow as described in Example 9, adherent, bright coatings of cadmium-tin alloy were obtained. These coatings were smooth and entirely free from lumps.

Example 11

Pieces of cold-rolled sheet steel were degreased as described in Example 1. They were then acid etched as described in Example 13. Following this the same anodic treatment as in Example 13 was used.

The pieces were then plated with tin as described in Example 1 to a thickness of 0.0001'' to 0.0003''. Following this, they were plated with cadmium from a solution containing:

	Oz./gal.
Cadmium oxide	4
Sodium cyanide	10
Sodium hydroxide	1

Data

Anodes	Cadmium
Cathode current density	20 to 30 H/SF
Temperature	Normal room temperature

Coatings of cadmium 0.0001'' to 0.0003'' thick were applied to the previously plated tin coating so that the total thickness of the coatings varied between 0.0002'' and 0.00006''. These coatings were then heat treated in tallow at 200° to 300° C.

Adherent bright coatings of tin-cadmium alloy, free from lumps or runs were obtained.

Example 12

Pieces of cold-rolled steel were prepared and plated with 0.0001'' to 0.0003'' of tin as described in Example 11. Following the tin plating, the samples were zinc plated in a solution containing:

	Oz./gal.
Zinc cyanide	5
Sodium cyanide	3
Sodium hydroxide	4

Data

Anodes	Zinc
Cathode current density	20 to 30 H/SF
Temperature	40° to 50° C.

The tin plated pieces were zinc plated with 0.0001'' to 0.0002'' of zinc.

Upon being heat treated in tallow at 200° C. to 300° C., adherent, bright coatings of tin-zinc alloy were obtained. The coatings were free from lumps and other imperfections.

Example 13

Pieces of hot-rolled sheet steel were degreased in an alkaline electrolytic cleaner and then acid-pickled to remove rust and fire scale until a clean surface was obtained. Following the pickling, the pieces were immersed in a NaCN solution (6 oz./gal.) and cleaned anodically for 1 minute using 50 to 100 A/SF.

The samples were then plated as described in Example 11 with 0.0002'' to 0.0003'' of cadmium. The cadmium plated pieces were then plated in a zinc solution as described in Example 12 with 0.0001'' to 0.0002'' of zinc. The double plated pieces were then treated in tallow at 260° to 300° C. Adherent bright coatings of cadmium-zinc alloy were obtained free from lumps and other imperfections.

As mentioned above, in practicing my process I prefer to treat the metal to be plated, especially iron or steel, first with a strong acid under such conditions and for such length of time that a decided visible etching corrosion of the metal is obtained and then to treat the metal with an alkaline solution. This method of pre-treatment of iron and steel markedly decreases the porosity of the electroplated coating and hence increases the corrosion resistance of the plate. This effect is not limited to the low-melting metals such as tin, zinc or cadmium; for example, I have found that the corrosion resistance of nickel plate is improved by this pre-treatment. Furthermore, when it is desired to subsequently heat treat the electroplated coating by the herein described method, this preliminary etching and alkaline treatment assists in producing a smooth coating of the final product, especially when the electroplated coating is relatively thick. If such relatively thick coatings are heat treated subsequent to plating without this preliminary treatment, the final coating sometimes has certain irregularities or lumpiness, apparently caused by an uneven flow of the molten electroplated coating during the heat treatment and/or a failure of the plated metal to adhere well to the base metal. Also, if the metal is thus etched but the alkaline treatment is omitted, the desired satisfactory results will not be obtained. I have found that when my preliminary treatment is used, such irregularities may be substantially entirely eliminated.

The herein described preliminary etching and alkaline treatment is suitable for treating various heavy metals that are to be electroplated, e. g., steel, cast iron, brass and copper. It is especially advantageous when it is desired to produce bright coatings on cold rolled steel or cast iron by electroplating followed by heat treatment, as herein described. The tendency for the plated metal to fail to adhere properly to the base metal and form an irregular or lumpy coating during the heat treatment is most marked when the base metal is cold-rolled steel. For this reason, my preliminary acid etching and alkali treatments usually are necessary in order to produce a good coating on such steel by my invention. In the case of hot-rolled steel and the non-ferrous metals, the etching and alkali treatments often may be omitted or replaced by the usual cleaning operations with more or less satisfactory results. However, it generally is preferable to use the etching and alkali treatment, since it tends to improve the quality of the plate in any case.

The extent to which the base metal should be acid etched during the preliminary treatment may vary, depending on the nature of the base metal. That is, in some cases, the minimum etching may be sufficient for the best results. The proper minimum time for treatment in the etching acid may be readily determined by simple trials, but usually the etching is carried on till a visible appearance of etching is noted.

Various acidic materials capable of corroding iron, steel or other base metals are suitable for the preliminary etching step in accordance with my invention. For example, sulfuric acid, hydrochloric acid, nitric acid or mixtures of these acids may be utilized. I prefer to use sulfuric acid in concentrations of 15 to 30% by weight. If desired, the acid may be used as electrolyte and the article to be etched made the anode in an electrolytic system. However, this electrolytic method of etching ordinarily offers little or no advantage over simple immersion in the acid solution. The time and temperature of the etching operation as well as the concentration of the acid in the solution may be varied over a wide range, provided that the operation is continued over such length of time as is necessary

to produce the required etching effect. I prefer to use a strong acid solution, that is about 2 normal to 6 normal strength and carry out the etching operation at an elevated temperature, for example 100 to 200° F.

The time required to etch the metal with acid and/or the type of acid or acid mixture required may vary, depending on the nature of the metal. The kind of acid required to corrode a given metal will be apparent to one having a knowledge of chemistry. We have found that different samples of cold-rolled steel require different acid treatments in order to obtain a satisfactory etching. These differences apparently depend partly upon the constitution of the steel and partly on the heat treatment and mechanical working to which it has been subjected. The best method of etching a given sample may easily be determined by simple trials with various acids or mixtures at various temperatures. When it is desired to produce a mirror-like plate by the herein described heat treatment after plating, the steel should not be etched too drastically. However, even when the steel is drastically etched, the heat treatment subsequent to plating produces a distinct brightening and a smooth, dense plate.

Various alkaline aqueous solutions are suitable for the alkali treatment following the above described etching operation. I have found that in general the best results are obtained when the alkaline bath contains substantial amounts of an alkali metal cyanide; if desired, a solution of alkali metal cyanide alone may be used or sodium hydroxide or other alkaline materials may be added. I prefer to use a cyanide solution containing 2 to 10 oz. per gal. of sodium cyanide as an electrolytic cleaning bath, wherein the work to be treated is preferably made the anode and using an anode current density of up to around 100 amps. per sq. ft. The best results generally are secured by keeping the bath hot, e. g. at a temperature of 140° to 160° F. and using an anode current density of 50 to 80 amps. per sq. ft. Various other alkaline solutions may be used for such electrolytic treatment. The time of treatment may be varied widely; ordinarily ½ to 3 minutes is sufficient when the electrolytic method is used. If the alkaline bath is used without the aid of the electric current, a somewhat longer time of treatment usually will be required, e. g. up to around 30 minutes.

As mentioned above, my process is suitable for coating metals with alloys of tin, cadmium, or zinc as well as the pure metals. Various other relatively fusible metals or alloys, e. g. lead or lead alloys, may be utilized in my invention. The alloy coatings may be obtained by electroplating the alloy from electrolytes containing salts of alloy constituents. An alloy coating also may be obtained in accordance with my invention by plating out the metals to be alloyed in two or more separate layers and then subjecting the electroplated article to the above described heat treatment under non-oxidizing conditions. For example, an article may be plated with a layer of tin and then with a layer of cadmium or the tin may be deposited on the cadmium plate and the article thus double plated subjected to a heat treatment under non-oxidizing conditions at a temperature slightly above the melting point of the resulting tin-cadmium alloy. Likewise, other metals may be alloyed by this method with tin, cadmium or zinc; for example, a tin-copper alloy may be made by first plating the article with tin and then with a light copper plate and subjecting the electroplated articles to the above described heat treatment. In this case, in order to produce a tin-copper alloy at the surface, it is essential that the copper be plated over the tin. If the tin is plated over the copper, I have found that complete alloying of the copper and tin cannot be obtained without the use of a heat treatment at a temperature far above the melting point of tin. Such high temperatures are in many cases impracticable to use because of the effect they may have on the base metal. Hence, in general when it is desired to produce an alloy of tin, cadmium, or zinc with another metal such as copper or silver, which has a markedly higher melting point, by means of the multiple plating method, I prefer to plate the higher melting metal as the exterior coat prior to heat treating.

Various known methods of heat treating under non-oxidizing atmosphere may be used; I prefer to use a bath of hot tallow, or other high boiling liquids, fused salts or the like; or a furnace which is continuously provided with an atmosphere of oxygen-free hydrogen. Obviously these preferred methods may be modified by using other suitable non-oxidizing liquid or gaseous media.

An advantage of my herein described invention is that it results in a smooth, bright plated coating which has superior corrosion resistant properties. The coating has the density, hardness, low degree of porosity and bright appearance which are characteristic of hot dipped coatings and furthermore, my coatings may be made of greater thickness than by hot dipping methods. Also, the step of heat treating subsequent to plating in accordance with my invention simplifies the electroplating operation, since it eliminates the need of originally obtaining plates having the best color and general appearance. The heat treatment brightens the dullest plates substantially as well as the brighter ones. Hence it is necessary only to regulate the electroplating bath to obtain plating suitable for heat treatment.

Furthermore, my improved method of treating metal prior to plating is advantageous not only in producing superior coatings by heat treating subsequent to plating, but also improves the electroplate itself as regards adherence and corrosion resistance. Hence, improved results may be obtained by this method without heat treating subsequent to plating.

I claim:

1. A process for producing an alloy coating on a ferrous metal comprising treating said ferrous metal with an acid until the surface thereof is visibly etched, then treating said metal with an alkaline solution for a period of at least 3 minutes, electroplating the treated metal with a plurality of different metals applied in successive layers and finally heating the electroplated surface under substantially non-oxidizing conditions to a temperature sufficiently high to cause the said electroplated layers to substantially completely fuse together to form an alloy coating.

2. A process for producing an alloy coating on a ferrous metal comprising treating said ferrous metal with an acid until the surface thereof is visibly etched, then subjecting said metal to anodic treatment in an alkaline solution, electroplating the treated metal with a plurality of different metals applied in successive layers and finally heating the electroplated surface under substantially non-oxidizing conditions to a temperature sufficiently high to cause the said electroplated layers to substantially completely fuse together to form an alloy coating.

3. A process for producing an alloy coating on a ferrous metal comprising treating said ferrous metal with an acid until the surface thereof is visibly etched, then subjecting said metal to anodic treatment in an alkaline solution, electroplating the treated metal first with a layer of tin and then with a relatively thin layer of copper and finally heating the electroplated surface to a sufficiently elevated temperature to cause said copper layer to substantially completely alloy with said tin layer, whereby a tin-copper alloy surface is obtained.

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