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## ZINC PLATING PROCESS AND ELECTROLYTE

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1

The present invention relates to the art of electroplating and is particularly concerned with a new method of, and a new electrolyte for, electrolytically coating ferrous metal with zinc.

Many efforts have been made heretofore to coat ferrous metal electrolytically with bright, dense, fine, adherent zinc, but, so far as I know, none of these efforts has been entirely satisfactory, particularly as applied to long pieces of ferrous metal such as endless strip. Such a strip must be pickled before it is electroplated and such pickling is accomplished by passing the strip thru a dilute sulfuric acid bath. Then the strip is passed thru a plating bath where zinc is electrolytically deposited thereon. The moving strip carries with it into the plating bath iron salts formed during the pickling operation. In the presence of aluminum chloride the iron of those salts is precipitated as ferrous or ferric hydroxide and aluminum hydroxide is formed. When ferrous hydroxide is precipitated it is oxidized in the bath to ferric hydroxide. The ferric and aluminum hydroxides are difficult to remove by filtration or otherwise because of their flocculent nature. Zinc deposited from an electrolyte containing these hydroxides is not of the high character desired. These hydroxides may be removed by periodic shut downs and the use of settling tanks and complicated filtering equipment, but such removal is so expensive as to be uncommercial. Furthermore, ferrous iron salt can not be permitted to build up in the bath for its adversely affects the character of the deposited zinc.

The present invention is predicated on the discovery that the previous difficulties can be avoided by converting any ferrous iron salts in the electrolyte into fluoride complexes and periodically changing those complexes into crystalline compounds before the amounts of those complexes become sufficient to form a film on the anodes which interferes with the plating operation. I have found that a bright, dense, fine, adherent electrolyte coating of zinc on ferrous metal can be commercially obtained by electrolyzing an aqueous electrolyte having a pH value of from about 4.8 to about 5.4 and consisting essentially of zinc chloride, sodium chloride and an alkali salt of fluorine, and periodically adding small amounts of aluminum chloride to the electrolyte.

In carrying out the present invention ferrous metal in long, or what might be called continuous lengths is passed endwise thru a pickling bath and then thru an electrolyte of the foregoing composition and thru which an electroplating current is passing, the ferrous metal constituting

2

the cathode. Currents of 450 to 500 amperes per sq. ft. of cathode area and at 5 volts have been found to be satisfactory.

The new aqueous electrolyte of the present invention contains, per gallon thereof, from about 10 oz. to about 20 oz. of zinc chloride, from about 10 oz. to about 20 oz. of sodium chloride, and from about .15 oz. to about 1.0 oz. of fluorine preferably in the form of an alkali salt, such as alkali fluoride or bifluoride. When sodium fluoride is used from .3 oz. to 2.2 oz. will contain substantially that amount of fluorine. A small amount of aluminum chloride is added to the electrolyte from time to time. About .2 oz. per gallon of aluminum chloride is sufficient for each 600,000 sq. ft. of ferrous iron plated with zinc by this process, that is, about .2 oz. aluminum chloride may be added to the electrolyte at the beginning of the plating operation and again after about 600,000 sq. ft. have been plated. I believe that the aluminum chloride reacts with the ferrous fluoride complexes with resultant partial oxidation of some of the ferrous iron to ferric iron and precipitation of crystalline ferric fluoride, and precipitation of crystalline aluminum fluoride.

The fluorine salt, in addition to forming iron complexes, also appears to refine the grain of the deposited zinc and to increase the cathode polarization and thereby gives an even thickness of zinc plating all the way across the ferrous metal. When the amount of fluorine is less than the minimum just mentioned, the thickness of zinc deposited is less than when amounts within the specified range are used and also the thickness of the zinc varies from a maximum near the edges of the ferrous metal strip to a minimum near the center thereof. However, with quantities of fluorine within the above specified range and particularly between the range of about .15 oz. to about .40 oz. per gallon the uniformity and thickness of the deposited zinc is quite satisfactory.

Chlorides of alkaline earths such as calcium, strontium and magnesium may be used instead of aluminum chloride.

Electrolytes of the foregoing composition have a pH value ranging from about 4.8 to about 5.4. Preferably, the pH value should lie between 5.0 and 5.4, for when it is below 4.8 a film forms on the anode and necessitates an increase in anode voltage and when the pH value exceeds 5.5 the zinc precipitates as hydroxide.

Having thus described my invention so that others skilled in the art may be able to understand and practice the same, I state that what I

desire to secure by Letters Patent is defined in what is claimed.

What is claimed is:

1. An aqueous zinc plating electrolyte containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from .15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and about 0.2 ounce of chloride of a metal selected from the group consisting of alkaline earth metals and aluminum, said electrolyte having a pH value of from 4.8 to 5.4.

2. An aqueous zinc plating electrolyte containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from .15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and about 0.2 ounce of calcium chloride, said electrolyte having a pH value of from 4.8 to 5.4.

3. An aqueous zinc plating electrolyte containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from .15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and about 0.2 ounce of aluminum chloride, said electrolyte having a pH value of from 4.8 to 5.4.

4. An aqueous zinc plating electrolyte containing, per gallon thereof, 10 ounces to 20 ounces og zinc chloride, from 10 ounces to 20 ounces of sodium chloride, and from .15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and about 0.2 ounce of aluminum chloride, said electrolyte having a pH value of from 5.0 to 5.4.

5. An aqueous zinc plating electrolyte containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, and from .3 ounce to 2.2 ounces of sodium fluoride, and about 0.2 ounce of aluminum chloride, said electrolyte having a pH value of from 4.8 to 5.4.

6. The method of forming a bright, dense, fine, adherent coating of zinc on ferrous metal which comprises the steps of passing an elongated ferrous metal article through a pickling bath and then through an aqueous electrolyte having a pH value of from 4.8 to 5.4 and containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from 0.15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and an amount in excess of zero but less than about 0.2 ounce of a chloride of a metal selected from the group consisting of alkaline earth metals and aluminum, and electrolytically depositing zinc on said articles while it is passing through the electrolyte.

7. The method of forming a bright, dense, fine, adherent coating of zinc on ferrous metal which comprises the steps of passing an elongated, pickled, ferrous metal article through an aqueous electrolyte having a pH value of from 4.8 to 5.4 and containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from



0.15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and an amount in excess of zero but less than about 0.2 ounce of a chloride of a metal selected from the group consisting of alkaline earth metals and aluminum, and electrolytically depositing zinc on said article while it is passing through the electrolyte.

8. The method of forming a bright, dense, fine, adherent coating of zinc on ferrous metal which comprises the steps of passing an elongated, pickled, ferrous metal article through an aqueous electrolyte having a pH value of from 4.8 to 5.4 and containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from 0.15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and an amount of aluminum chloride in excess of zero but less than about 0.2 ounce, and electrolytically depositing zinc on said article while it is passing through the electrolyte.

9. The method of forming a bright, dense, fine, adherent coating of zinc on ferrous metal which comprises the steps of passing an elongated, pickled, ferrous metal article through an aqueous electrolyte having a pH value of from 4.8 to 5.4 and containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from 0.15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and an amount of calcium chloride in excess of zero but less than about 0.2 ounce, and electrolytically depositing zinc on said article while it is passing through the electrolyte.

10. The method of forming a bright, dense, fine, adherent coating of zinc on ferrous metal which comprises the steps of passing an elongated, pickled, ferrous metal article through an aqueous electrolyte having a pH value of from 4.8 to 5.4 and containing, per gallon thereof, from 10 ounces to 20 ounces of zinc chloride, from 10 ounces to 20 ounces of sodium chloride, from 0.15 ounce to 1.0 ounce of fluorine in the form of an alkali salt, and about 0.2 ounce of a chloride of a metal selected from the group consisting of alkaline earth metals and aluminum, and electrolytically depositing zinc on said article while it is passing through the electrolyte.

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