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ELECTROPLATING ZINC ON BASIS METAL

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This invention relates to electroplating zinc on basis metal and has to do with the employment of an electrolyte and imposed conditions of operation resulting in the obtaining of an electrodeposited coating of zinc of high quality and desired characteristics with unprecedented efficiency. I attain a speed of deposition substantially higher than speeds heretofore attained in the production of an electroplated product of equivalent quality. Also I provide for operating the plating bath at unprecedentedly high temperatures whereby further advantages are realized.

I electroplate zinc on basis metal by passing an electroplating current from an anode to the basis metal as a cathode through an acid electrolyte containing zinc sulphate and a silicofluoride or at least one metal of the group consisting of calcium and strontium. I preferably include in the electrolyte both a silicofluoride and at least one metal of the group consisting of calcium and strontium. I preferably further include in the electrolyte lead. For optimum results the acid electrolyte should contain zinc sulphate, a silicofluoride, lead, and at least one metal of the group consisting of calcium and strontium.

While my invention is applicable to the electroplating of zinc on various basis metals its most common application is in the electroplating of zinc on ferrous metal and particularly ferrous metal in strand form, e. g., strip or wire. Desirably the basis metal is electroplated while being moved through the electrolyte. Basis metal in strand form is preferably drawn continuously through the electrolyte while being electroplated.

For many years organic addition agents have been employed in the electrolyte in an effort to obtain a uniform bright lustrous electroplated zinc coating. Organic addition agents have well-recognized disadvantages among which are difficulty of control and consequent lack of uniformity of the coating produced. It has heretofore been proposed to substitute inorganic addition agents for organic addition agents and while improvement has been realized in some respects the optimum efficiency of electroplating has not been obtained. I find that I can produce a superior electroplated product at greater efficiency and higher speed than heretofore by employing an electrolyte containing zinc sulphate and suitable small quantities of the inorganic addition agents mentioned above. My electrolyte is preferably substantially free from organic addition agents.

The zinc for electroplating may be introduced into the electrolyte in the form of zinc sulphate or by means of a zinciferous anode or both. When zinc is introduced directly into the electrolyte either a zinciferous anode or a non-zinciferous anode or both may be employed. When a non-zinciferous anode is employed it may to advantage be of carbon. When a zinciferous anode is employed it may be of commercial metallic zinc anodic material. When a zinciferous anode is employed the zinc for plating may come substantially entirely from the anode even

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though a potential source of zinc such as zinc sulphate is employed in the electrolyte. While as above indicated I may use at the same time both a zinciferous and a non-zinciferous anode I obtain excellent results using a zinciferous anode without a non-zinciferous anode.

Since one of the primary uses of my invention is the electroplating of zinc on steel strip I shall refer to such use by way of example. Heretofore in production electroplating lines for coating steel strip with zinc the usual current density has been 100 to 150 amperes per square foot with an absolute maximum to the best of my knowledge and belief of about 300 amperes per square foot, and the results attained have been considerably less than optimum. The coating has been rough, dull and of unpleasing appearance. I increase the current density far beyond the highest current density heretofore employed commercially, enabling me to greatly increase the efficiency and speed of electroplating and at the same time produce a superior product. The electrolyte which I use makes possible the employment of a current density much higher than the highest current density previously employed commercially, and I desirably maintain during electroplating a current density between 400 and 1500 amperes per square foot. For example, I have used a current density of 1000 amperes per square foot with excellent results and I have increased the current density substantially beyond 1000 amperes per square foot without substantial diminution of the quality of the product. Using a current density of 1000 amperes per square foot I have been able to electrodeposit zinc on steel strip and obtain a uniform lustrous silky finish, the zinc coating attaining a thickness of about .001 inch in fifty-three seconds.

I operate the plating bath at relatively high temperature and thereby obtain further advantages. I maintain the electrolyte well above room temperature, preferably between 120 and 190° F. For current densities of 800 amperes per square foot and higher I preferably maintain the bath at 170 to 190° F. while for lower current densities such as 400 to 600 amperes per square foot I preferably somewhat reduce the temperature of the bath, maintaining it at 120–160° F. While the chief reason for operating the bath at such unusually high temperatures is to produce a high quality product the elevation of the bath temperature has further important advantages. First, it results in very high efficiency, usually between 95 and 99%, that is, the amount of zinc deposited by a given electric current is 95 to 99% of the ideal maximum or theoretical amount which can be deposited by the current according to Faraday's law. Consequently the cost of electrical energy for plating is reduced to a minimum.

The second advantage incident to my high temperature plating operation is the elimination of cooling. No cooling equipment is required. Cooling a plating bath to maintain an operating temperature at or not much above room temperature is very expensive both as to the first cost of the cooling equipment and as to the operating cost and is highly objectionable to steel plant operators because of maintenance troubles. In the employment of my invention all energy transformed into heat in the plating bath is utilized to maintain the desired above-ambient temperature, while any additional heating required is very much less expensive both as to equipment cost and as to operating cost than cooling would be.

A third advantage of my high temperature operation is that the use of a high bath temperature eliminates the problem of disposal of waste plating liquor (which problem is now greatly aggravated due to the anti-stream pollution programs), permitting reclaiming of the bath, since the dilution due to the plating out of the chemicals is now

counterbalanced or even more than compensated for by evaporation of water from the plating bath, which evaporation is especially rapid at temperatures of 170° F. and above.

Because in my preferred operation no organic addition agents are used it is possible when so operating to maintain the purity of the plating bath through removal of particles which would deleteriously affect the zinc coating by filtering the solution through activated carbon which effectively removes the impurities without affecting the inorganic addition agents which I employ.

In spite of the high operating temperature no toxic fumes are evolved (as in a cyanide bath) since the inorganic chemicals in the bath do not evaporate, and what rises from the bath is substantially pure water vapor. Furthermore, even at the very high current densities employed there is remarkably little "gassing" or evolution of hydrogen.

I preferably maintain relative movement between the cathode, which is the basis metal on which the zinc coating is to be deposited, and the electrolyte. Relative movement between the cathode and the electrolyte at a rate of about 100 feet per minute produces excellent results, but the movement can be much faster.

The rate of plating according to Faraday's law is directly proportional to the current density employed in the electroplating process. High speed electroplating of zinc to form coatings of optimum quality has been impossible prior to my invention because of the relatively low current densities which could not be exceeded. Since according to my invention very much higher current densities can be employed I can produce at much higher speeds than have heretofore been attainable an unprecedented ductile uniform lustrous coating.

My invention may be employed in electroplating zinc on a wide variety of basis metals. Basis metals most commonly electroplated with zinc in addition to ferrous metal are copper and its alloys and aluminum and its alloys; my invention is applicable in the electroplating thereof.

A further advantage of my invention is that the acidity or pH value of the plating bath is not critical, although for optimum results I preferably maintain a pH value between about 2.5 and about 5.5. A still further advantage is that when a zinciferous anode is employed the anode dissolves in the electrolyte with remarkable uniformity while plating is going on, maintaining a smooth surface and avoiding the dropping off of pieces or particles; while when the bath is standing idle the corrosion of the zinciferous anodes is negligible. This is in decided contrast to a zinc chloride bath in which the corrosion of anodes on standing and even excessive corrosion while plating present difficult problems.

The zinc coating produced by my process does not exhibit the coarse crystalline grainy appearance observable in most zinc coatings; on the contrary my coating is very fine-grained as well as uniform and usually shows little "treering" at the edges of the strip.

I shall give a specific example of an electrolyte which I have employed with very successful results at current densities of the order of 800 to 1000 amperes per square foot; that electrolyte contains quantities of the order of those below indicated of the ingredients listed:

Zinc sulphate----- 16 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium ----- .004 oz. per gallon of electrolyte.
A silicofluoride----- .2 oz per gallon of electrolyte.
Lead ----- .001 oz. per gallon of electrolyte.

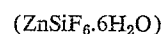
When operating at current densities of the order of 400 to 600 amperes per square foot I preferably reduce the concentrations of all four of the above listed components

to approximately 70% of the figures given. Under such circumstances the electrolyte may contain quantities of the order of those below indicated of the ingredients listed:

5 Zinc sulphate ----- 11 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium ----- .0027 oz. per gallon of electrolyte.
A silicofluoride ----- .13 oz. per gallon of electrolyte.
Lead ----- .0007 oz. per gallon of electrolyte.

The calcium or strontium may be introduced as a soluble salt, such, for example, as a chloride or tartrate. The figure given above represents the weight of calcium or strontium as metal (as distinguished from the weight of the salt) introduced into the electrolyte. The calcium or strontium produces a bright coating at high current density. The silicofluoride is employed primarily for grain refinement and ductility of the coating. However, the calcium or strontium and the silicofluoride overlap somewhat in function so that, while I prefer to utilize strontium or calcium and a silicofluoride together I can obtain good results by using either (1) calcium or strontium or both or (2) a silicofluoride without the other. The silicofluoride may be introduced as zinc silicofluoride



30 or as sodium silicofluoride ($\text{Na}_2\text{SiF}_6 \cdot 6\text{H}_2\text{O}$).

The lead is to impart lustre to the coating. It may be dispensed with but is of importance when high lustre is desired. I have found that when high lustre is of importance a minimum of about .0005 oz. of lead as metal per gallon of electrolyte should be utilized. If a less bright coating should be desired the quantity of lead may be reduced or the lead may be omitted. In any event a maximum of .002 oz. of lead as metal per gallon of electrolyte should not be exceeded.

40 In order to bring out the full lustre of the zinc coating I preferably dip the electroplated metal in acid following the plating. For the dip I may employ dilute nitric acid or a mixture of dilute nitric and phosphoric acids. A composition of the dipping solution which I have found to give excellent results with a very short time of immersion comprises 3 to 4% nitric acid and 2 to 3% phosphoric acid in aqueous solution. Using such a solution at 80° F. five to ten seconds dipping time gave good results. Higher concentrations of the acids are undesirable. When a longer dipping time is allowable thirty seconds in 1% nitric acid at room temperature gives good results.

While I have described a present preferred method of practicing the invention it is to be distinctly understood that the invention is not limited thereto but may be otherwise variously practiced within the scope of the following claims.

I claim:

1. A method of electroplating zinc on basis metal comprising passing an electroplating current from an anode to the basis metal as a cathode through an acid electrolyte consisting essentially of about the quantities below indicated of the ingredients listed:

65 Zinc sulphate----- 16 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium----- .004 oz. per gallon of electrolyte.
70 A silicofluoride----- .2 oz. per gallon of electrolyte.

2. A method of electroplating zinc on basis metal comprising passing an electroplating current from an anode to the basis metal as a cathode through an acid electrolyte

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consisting essentially of about the quantities below indicated of the ingredients listed:

Zinc sulphate..... 16 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium..... .004 oz. per gallon of electrolyte.

A silicofluoride..... .2 oz. per gallon of electrolyte.

Lead..... .001 oz. per gallon of electrolyte.

3. A method of electroplating zinc on basis metal comprising passing an electroplating current from an anode to the basis metal as a cathode through an acid electrolyte consisting essentially of about the quantities below indicated of the ingredients listed:

Zinc sulphate..... 16 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium..... .004 oz. per gallon of electrolyte.

A silicofluoride..... .2 oz. per gallon of electrolyte.

while maintaining the electrolyte at a temperature of at least 120° F.

4. A method of electroplating zinc on basis metal comprising passing an electroplating current from an anode to the basis metal as a cathode through an acid

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electrolyte consisting essentially of about the quantities below indicated of the ingredients listed:

Zinc sulphate..... 16 oz. of zinc as metal per gallon of electrolyte.

At least one metal of the group consisting of calcium and strontium..... .004 oz. per gallon of electrolyte.

A silicofluoride..... .2 oz. per gallon of electrolyte.

Lead..... .001 oz. per gallon of electrolyte.

while maintaining the electrolyte at a temperature of at least 120° F.

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