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IRON-PHOSPHORUS ELECTROPLATING

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This invention relates to electrodepositing iron-phosphorus alloys and pertains more particularly to the composition of solutions or baths for electrodepositing such alloys and the process relies in conjunction therewith.

Essentially, the present invention relates to the discovery that the addition of the hypophosphite radical to many conventional iron plating baths results in the depositing of iron-phosphorus alloys which not only possess better physical characteristics but can also be controlled in novel fashion to achieve different types of deposits for use under various circumstances.

For example, the iron-phosphorus deposit can be made extremely hard, it can be made bright, or it can be made to contain fissures as desired, dependent upon the manner in which the plating and bath conditions are controlled. Thus, a hard, smooth alloy may be deposited to build up or repair mismachined or worn parts for hard facing or coating of such parts as shafts and rolls. On the other hand, a hard, fissured alloy is desirable for the lining of the bores of internal combustion engines or other full or partially lubricated units since the fissures tend to retain lubrication and minimize dry or boundary lubrication conditions.

More particularly, the present invention is concerned with the electrodeposition of iron-phosphorus alloys from a solution consisting primarily of the ferrous ion in the form of one or more of its salts such as chloride, sulfate or fluoborate salts or mixtures thereof and which solution contains in addition thereto the hypophosphite ion which as a practical matter is introduced most economically in the form of a sodium salt, that is, preferably sodium hypophosphite monohydrate ($NaH_2PO_2.H_2O$). By varying the composition of the plating solution and the operating conditions, the properties of the deposit may be varied to meet a particular demand. In general, it has been found that lowering of the bath temperature, a lowering of the current density or the raising of the concentration of hypophosphite radical or any combination thereof results in increased hardness of the deposit. As the hardness becomes greater, the deposit tends to become less sound physically, which is manifested by fissures, lack of cohesion and extreme brittleness, at the upper extremity of the conditions.

Table I

In order to illustrate a preferred embodiment of this invention and also to illustrate physical characteristics of the present invention as compared to conventional iron-plating, a bath according to Patent 2,745,800 with and without the addition of the hypophosphite radical thereto will be considered. The approximate composition of this bath according to the above patent is as follows:

Table I

	G./l.
Ferrous fluoborate	60
Ferrous sulphate heptahydrate	400
Ammonium chloride	20
Wetting agent	0.5

The hardness of deposits obtained from this bath alone and with various concentrations of the hypophosphite radical were determined with a Tukon tester on a cross section of the deposits. Similar hardness tests were also conducted on the various deposits after subjecting them

to heat treatment at 600° F. for 2 to 3 hours and in each case a chemical analysis for phosphorus content was made, with the following results:

Table II

Concentration of Sodium hypophosphite monohydrate (g/l)	0	1	3	9	27
Knoop hardness (100 g. load) as plated	200	550	708	587	695
Knoop hardness (100 g. load) after heat treatment	225	600	818	857	960
O/O Phosphorous in deposit	0	0.4	1.1	3.1	3.2

In the above examples, the plating bath was maintained at a temperature of 140–145° F., at pH 3.0–4.0 and the plating was done at 40 amperes per square foot at the cathode.

To illustrate the effect of the temperature of the plating bath, an identical bath containing 1 gram per liter of sodium hypophosphite monohydrate was used, with all conditions as above being maintained except that the bath was held at 120° F. The results as compared to deposits obtained with the same concentration of sodium hypophosphite monohydrate at a bath temperature of 140–145° F. is as follows:

Table III

Bath Temperature, ° F.	140–145	120
Knoop hardness as plated	550	630
Knoop hardness (100 g. load) after heat treatment	600	765

To illustrate the effect of varying the plating current density, the above preferred bath was utilized with a concentration of sodium hypophosphite monohydrate of 1 g./l., the bath being maintained at a temperature of 120° F. and pH 3.0 to 4.0. The hardnesses of the resultant deposits at varying current densities were found to be as follows:

Table IV

Current Density (amperes per square foot)	20	40	60	80
Knoop Hardness (100 g. loading) after heat treatment	790	765	755	735

From the above, it will be apparent that the hardness of the iron-phosphorus deposit is (1) inversely proportional to the bath temperature, (2) directly proportional to the concentration of the hypophosphite radical and (3) inversely proportional to the current density. However, certain limitations are imposed upon these conditions by the physical soundness of the deposit. For example, excessive fissuring, lack of cohesion and extreme brittleness of the deposit may be normally expected to occur at bath temperatures below 100° F., at concentrations of sodium hypophosphite monohydrate above 10 grams per liter and at current densities above 100 amperes per square foot.

Therefore, the lower limit on the bath temperature may be stated to be approximately 100° F. whereas the upper limit of the concentration of sodium hypophosphite monohydrate may be stated as 10 grams per liter (equal to hypophosphite radical concentration of approximately 6 g./l.) and the upper limit on plating current density may be stated as 100 amperes per square foot. However, the addition of adjuvant substances, themselves well known in the art, which are normally used to effect stress reduction tends to alleviate excessive fissuring, lack of cohesion and extreme brittleness of the deposit and therefore serves to somewhat spread the above limits. For example, the addition of 0.5 gram per liter of saccharine to the plating bath being operated under conditions which will normally yield a mildly fissured electrodeposit will cause the deposit to form free of noticeable fissures.

With the preferred bath as specified above, where a fissured deposit is desirable, such as for the bores of cylinders of internal combustion engines, the bath may be operated at low temperatures (say 100° F.) and/or high current densities (say 80 amperes per square foot) and/or high concentrations of sodium hypophosphite monohydrate (say 9 grams per liter). On the other hand, where a hard but fissure-free deposit is desirable as in the coating of rolls and shafts, the bath may be operated at a high temperature (say 160° F.) and/or low current density (say 20 amperes per square foot) and/or low concentration of sodium hypophosphite monohydrate (say 1 gram per liter, equal to hypophosphite radical concentration of approximately 0.6 g./l.) with or without the use of adjuvant organic addition agents, as for example saccharine.

EXAMPLE II

To a conventional iron plating bath containing approximately 375 grams per liter of ferrous chloride dihydrate and 168 grams per liter of calcium chloride and operated at a temperature of 170° F., pH 4.0, was added 1 gram per liter of sodium hypophosphite monohydrate. This bath yielded without the addition of the hypophosphite radical, a semi-bright deposit up to 40 amperes per square foot current density and a light gray matte deposit in the region of 40–100 amperes per square foot current density. The addition of the stated 1 gram per liter of sodium hypophosphite monohydrate resulted in a deposit which was smoother, harder and even brighter throughout the entire current density range.

EXAMPLE III

To a conventional iron plating bath of approximately 300 grams per liter ferrous ammonium sulfate, operated at 100° F., pH 3.9, was added 1 gram per liter of sodium hypophosphite monohydrate. The bath yielded, without the addition of the hypophosphite radical a streaked and pitted deposit from the lowest current density to a current density of over 100 amperes per square foot. Upon the addition of 1 gram per liter of sodium hypophosphite monohydrate, the resultant deposit was less pitted, brighter over the whole range and showed less cracking and streaking. A total content of 3 grams per liter of the hypophosphite salt showed no further improvement.

EXAMPLE IV

The deposit obtained from the conventional iron plating bath containing approximately 240 grams per liter of ferrous sulfate heptahydrate, 36 grams per liter of ferrous chloride dihydrate and 20 grams per liter of ammonium chloride yielded a badly pitted gray deposit, the bath being operated at 120° F., pH 3.8 at current densities above and below 40 amperes per square foot. Upon the addition of 1 gram per liter of sodium hypophosphite monohydrate, the deposit obtained brightened somewhat compared with the conventional deposit but was still streaked and pitted. By increasing the concentration of sodium hypophosphite monohydrate to 3 grams per liter, the deposit obtained at current densities below 40 amperes per square foot was gray matte with no pitting or streaking and above 40 amperes per square foot current density, the deposit was also homogeneous but very bright.

The upper and lower limits of the three controlling factors, temperature, plating current density and hypophosphite radical concentration, cannot be precisely pinpointed, but the above examples serve to illustrate their trends. In establishing these limits, some consideration of economical practicality must be made. For example, in general it will be well to maintain all such factors on the low side, so long as the desired results are attained. That is to say, the higher the bath temperature, the higher the concentration of the hypophosphite radical and the higher the plating current density, the higher will be the operating cost of the bath; and the lowest value of each factor, dependent upon the specific application, will normally be utilized in order to establish an economical operation.

As far as the lower limit of the hypophosphite radical concentration is concerned, it has been found that relatively minute concentrations yield drastically beneficial results. This is best illustrated by reference to the following two tables relating to various hypophosphite radical concentrations in baths as described in Table I.

Table V

[140° F.—40 ASF—pH 3.0-4.0]

Concentration of Sodium Hypophosphite Monohydrate (gms./liter)	0	0.11	0.33	1.0	3.0	9.0
Knoop Hardness (100 gm. load)	320	394	493	600	818	857

Table VI

[120° F.—40 ASF—pH 3.0-4.0]

Concentration, etc	0	0.11	0.33	1.0
Knoop Hardness (100 gm. load)	336	451	480	800

The above tables, V and VI, clearly establish that at concentrations of sodium hypophosphite monohydrate in amounts as little as 0.11 gm./liter, the corresponding increase in Knoop hardness is appreciable. In Table V, the concentration of sodium hypophosphite monohydrate of 0.11 gm./liter represents an increase in Knoop hardness of approximately 20% over the hardness at zero concentration. Likewise, in Table VI, a concentration of 0.11 gm./liter represents an increase of approximately 35% in Knoop hardness as compared to the hardness at zero concentration.

Consequently, it will be appreciated that very small concentrations of the hypophosphite radical will produce useful results. However, for practical purposes, approximately 0.10 gm./liter of sodium hypophosphite monohydrate (equal to a hypophosphite radical concentration of approximately 0.06 gm./liter) may be considered as the lower limit, owing to the difficulty in accurately controlling the concentration in amounts less than this.

Whereas only a few specific examples of the invention have been described hereinabove it will be understood that various changes may be made therein without departing from the spirit of the invention or the scope of the appended claims.

What is claimed is:

1. The process of electrodepositing alloys of phosphorous with ferrous iron which comprises electrolyzing a solution containing ferrous iron in the form of a salt selected from the group consisting of chlorides, sulfates, fluoborates and mixtures thereof, in the presence of hypophosphite radical, in which the hypophosphite radical has been added in concentration between about 0.06 and 6.0 grams per liter of solution.

2. The process of electrodepositing alloys of phosphorous with ferrous iron which comprises electrolyzing a solution containing ferrous iron in the form of a salt selected from the group consisting of chlorides, sulfates, fluoborates and mixtures thereof, in the presence of hypophosphite radical, in which the hypophosphite radical has been added in concentration between about 0.06 and 6.0 grams per liter of solution, while maintaining the plating bath temperature between about 100° F. and about 170° F.

3. The process of electrodepositing alloys of phosphorous with ferrous iron which comprises electrolyzing a solution containing ferrous iron in the form of a salt selected from the group consisting of chlorides, sulfates, fluoborates and mixtures thereof, in the presence of hypophosphite radical, in which the hypophosphite radical has been added in concentration between about 0.06 and 6.0 grams per liter of solution while utilizing a plating

current density of from between about 20 to about 100 amperes per square foot.

4. The process of electrodepositing alloys of phosphorous with ferrous iron which comprises electrolyzing a solution containing ferrous iron in the form of a salt selected from the group consisting of chlorides, sulfates, fluoborates and mixtures thereof, in the presence of hypophosphite radical, in which the hypophosphite radical has been added in concentration between about 0.06 and 6.0 grams per liter of solution while maintaining the plating bath temperature between about 100° F. and 170° F. and while using a plating current density of from between about 20 to about 100 amperes per square foot.

5. The process according to claim 1 in which the solution consists of approximately 60 grams per liter of ferrous fluoborate, 400 grams per liter of ferrous sulphate heptahydrate and 20 grams per liter of ammonium chloride.

6. The process according to claim 2 in which the solution consists of approximately 60 grams per liter of ferrous fluoborate, 400 grams per liter of ferrous sulphate heptahydrate and 20 grams per liter of ammonium chloride.

7. The process according to claim 3 in which the solution consists of approximately 60 grams per liter of ferrous fluoborate, 400 grams per liter of ferrous sulphate heptahydrate and 20 grams per liter of ammonium chloride.

8. The process according to claim 4 in which the solution consists of approximately 60 grams per liter of ferrous fluoborate, 400 grams per liter of ferrous sulphate heptahydrate and 20 grams per liter of ammonium chloride.

9. The process of electrodepositing iron-phosphorous alloys which comprises adding sodium hypophosphite monohydrate to an iron plating bath in concentration between about 1 to 10 grams per liter, electrolyzing such bath while maintaining the same at a temperature of about 100° F. to about 170° F., with a plating current density of from between 20 and 100 amperes per square foot.

10. The process of electrodepositing iron-phosphorous alloys suitable for plating lubricant retentive surfaces such as the cylinders of internal combustion engines, which comprises electrolyzing an acidic aqueous solution consisting essentially of ferrous iron, a radical selected from the group consisting of chloride radical, sulphate radical, fluoborate radical, and combinations of chloride, sulphate and fluoborate radicals, and hypophosphite radical, while maintaining the solution at a temperature not less than about 100° F. with a plating current density not greater than about 80 amperes per square foot, and in which solution the concentration of hypophosphite radical is not greater than about 6.0 grams per liter of solution.

11. The process of electrodepositing iron-phosphorous alloys suitable for plating shafts and rolls, which comprises electrolyzing an acidic aqueous solution consisting essentially of ferrous iron, acid radical selected from the group consisting of chloride radical, sulphate radical, fluoborate radical, and combinations of chloride, sulphate and fluoborate radicals, and hypophosphite radicals while maintaining the solution at a temperature not greater than about 170° F. with a plating current density of not less than about 20 amperes per square foot, and in which solution the concentration of hypophosphite radical is not less than about 0.06 gram per liter of solution.

12. The process of electrodepositing iron-phosphorous alloys suitable for plating lubricant retentive surfaces such as the cylinders of internal combustion engines, which comprises electrolyzing an acidic aqueous solution consisting essentially of ferrous iron, a radical selected from the group consisting of chloride radical, sulphate radical, fluoborate radical and combinations of chloride and sulphate radicals, fluoborate radical and hypophosphite radical, while maintaining the solution at a temperature not less than about 100° F. with a plating current density not greater than about 80 amperes per square foot, and in which solution the concentration of hypophosphite radical is not greater than about 6.0 grams per liter of solution.

13. The process of electrodepositing iron-phosphorous alloys suitable for plating shafts and rolls, which comprises electrolyzing an acidic aqueous solution consisting essentially of ferrous iron, acid radical selected from the group consisting of chloride radical, sulphate radical and combinations of chloride and sulphate radicals, fluoborate radical and hypophosphite radical while maintaining the solution at a temperature not greater than about 170° F. with a plating current density of not less than about 20 amperes per square foot, and in which solution the concentration of hypophosphite radical is not less than about 0.06 gram per liter of solution.

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