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(54) **IMPROVED METHOD FOR INCREASING THE CONCENTRATION OF IRON(II) IONS IN IRON SIDE PHOSPHATING SYSTEMS AND ACCORDING PHOSPHATING PLANT**

(57) The present invention refers to an improved method for increasing the concentration of iron(II) ions in iron side phosphating systems, which comprising the following steps:

- i) at least one magnet is attached onto the inside and/or outside wall of a phosphating bath container and/or hung, each one by means of at least one holder element, into the inside room of the bath container,
- ii) at least one iron-containing body is attached to the at least one magnet by means of magnetic forces, and
- iii) the phosphating bath container is filled with an acidic

aqueous phosphating composition such that the at least one iron-containing body is at least partially immersed in the phosphating composition,

as well as, subsequently, the following step:

- iv) iron(II) ions are dissolved out of the at least one iron-containing body into the phosphating composition such that the concentration of iron(II) ions in the phosphating composition is increased to a concentration of at least 0.5 g/l.

Moreover, the present invention also refers to an accordingly modified iron side phosphating plant.

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Description

[0001] The present invention refers to an improved method for increasing the concentration of iron(II) ions in iron side phosphating systems as well as to an accordingly modified iron side phosphating plant.

[0002] Above all, so-called iron side phosphating systems are used to phosphatize steel substrates, in particular steel wires or construction elements, and exhibit a content of iron(II) ions. As iron side phosphating systems, manganese phosphate systems as well as heavy zinc phosphate systems additionally containing iron(II) ions are particularly suitable. The phosphate layers being formed on the substrates usually consist of Phosphophyllite and/or Hureaulite crystals including a significant amount of iron atoms in their structure and/or of Hopeite crystals. By such phosphate layers, the corrosion resistance of the substrates as well as the adhesion of subsequent paint layers on the substrates is enhanced effectively.

[0003] It is important that iron is present as dissolved iron(II) ions in the according phosphating bath and not as iron(III) which would result in the precipitation of iron(III) phosphate, this means to the formation of so-called sludge. Thus, no air should be blown into the phosphating bath nor should an oxidizing agent such as nitrite or chlorate be added to the bath.

[0004] Before an iron side phosphating process can be started, it is necessary to increase the concentration of iron(II) ions in the phosphating system, this means in the acidic aqueous phosphating composition filled in the phosphating bath container, to a concentration of at least 0.5 g/l. With concentrations below 0.5 g/l it is not possible to form a sufficient phosphate layer on the substrates.

[0005] Due to the integration of iron(II) ions into the phosphate layer, a continuous consumption of iron(II) ions in the phosphating system takes place during the phosphating process. Thus, in order to maintain the necessary concentration, replenishment of iron(II) ions is required - especially in times of low throughput of iron-containing substrates, this means when the amount of iron(II) ions dissolved out of said substrates is correspondingly low.

[0006] For increasing the concentration of iron(II) ions, soluble steel wool is typically used which is just thrown into the phosphating bath. However, there is the danger of undissolved portions of steel wool swimming around in the bath and settling down on the surface of the substrates to be phosphatized, thereby, causing defects of the phosphate layer formed and possible subsequent layers, for example paint layers, as well.

[0007] Another common option to achieve the required concentration of iron(II) ions is to put steel-containing scrap into the phosphating bath. Due to the acidic aqueous milieu, iron(II) ions are dissolved out of the scrap into the phosphating composition. However, steel-containing scrap has an unknown content of chromium which is poisonous for the phosphating process and is dissolved out

into the phosphating composition as well. In addition, oxide layers on the surface of the scrap may prevent the iron(II) ions from being dissolved.

[0008] It is also possible to increase the concentration of iron(II) ions by adding an according amount of aqueous iron(II) phosphate solution (available for example as Gardobond® Additive H 7432 from Chemetall, Germany) to the phosphating system. Thereby, the disadvantages of steel wool and steel-containing scrap as described above are avoided. The iron(II) ions are already dissolved. However, the production of iron(II) phosphate solution is very difficult, expensive and - due to the pronounced formation of hydrogen gas during the dissolution of iron powder in phosphoric acid - dangerous:

It takes an entire day to produce only one ton of iron(II) phosphate solution. Because of the European Regulation (EG) Nr. 1907/2006, also known as REACH Regulation (REACH = Registration, Evaluation, Authorization and Restriction of Chemicals), it is not permitted to produce more than six tons per year without having conducted an expensive registration.

[0009] Moreover, the storage stability of iron(II) phosphate solution is rather limited as after a short period of time iron(III) ions are formed by oxidation leading to a precipitation of iron(III) phosphate.

[0010] Thus, it has been the problem underlying the present invention to provide an improved method for increasing the concentration of iron(II) ions in iron side phosphating systems as well as an according phosphating plant at least partially avoiding the disadvantageous of soluble steel wool or steel-containing scrap just thrown into the phosphating bath on the one hand and iron(II) phosphate solution on the other hand as set forth herein above.

[0011] This problem has been solved by a method for increasing the concentration of iron(II) ions in iron side phosphating systems according to claim 1, namely by a method which is characterized by comprising the following steps:

- i) at least one magnet is attached onto the inside and/or outside wall of a phosphating bath container and/or hung, each one by means of at least one holder element, into the inside room of the bath container,
- ii) at least one iron-containing body is attached to the at least one magnet by means of magnetic forces, and
- iii) the phosphating bath container is filled with an acidic aqueous phosphating composition such that the at least one iron-containing body is at least partially immersed in the phosphating composition,

as well as, subsequently, the following step:

- iv) iron(II) ions are dissolved out of the at least one iron-containing body into the phosphating composition such that the concentration of iron(II) ions in the phosphating composition is increased to a concentration of at least 0.5 g/l, preferably of at least 0.8 g/l and especially pref-

erably of at least 1.0 g/l - leading to an improved formation of phosphate layer.

[0012] By applying this method, the risk of undissolved portions of iron-containing body, of iron or steel powder for example, swimming around in the bath and settling down on the surface of the substrates to be phosphatized is strongly reduced as the iron-containing body/ies is/are effectively fixed by means of magnetic forces.

Definitions:

[0013] In the present invention, "comprising the following steps" is to be understood such that there may be one or more additional steps before, between and/or after the according steps listed. Moreover, the order of the steps is left open, and does not have to follow the numbering of the steps.

[0014] "Subsequent(ly)" does not exclude that there may be one or more additional steps between the steps listed before and after said phrase.

[0015] Herein, "iron-containing" means that an according body contains iron in such a way, preferably in its surface, that iron(II) ions are dissolved out of the body when the latter is immersed in an aqueous acidic medium.

[0016] The term "iron-containing body" should also encompass two or more or even a multitude of iron-containing bodies. For example, the iron-containing body may be a powder as an assembly of a multitude of particles.

[0017] In case of an iron-containing body being an assembly of two or more iron-containing bodies, "attached to the at least one magnet by magnetic forces" does not mean that every iron-containing body of the assembly needs to be attached to the according magnet directly but can rather be attached to another iron-containing body of the assembly by means of magnetic forces. Correspondingly, powder usually aligns in form of rods.

[0018] Moreover, in case of a magnet attached to the outside wall of the phosphating bath, "attached to the at least one magnet by magnetic forces" means that an according iron-containing body is not attached to the magnet directly but indirectly via the magnetized wall of the phosphating bath container.

[0019] In the present invention, "aqueous" is to be understood such that water makes up more than 50 wt.-% of the solvent/s and dispersing medium/a of an according composition.

[0020] Herein, a "composition" is preferably a solution or dispersion, more preferably a solution.

[0021] Possible orders of steps i) to iii) according to the method of the present invention are:

First step i), then step ii) and finally step iii),
First step i), then step iii) and finally step ii),
First step ii), then step i) and finally step iii),
First step ii), then step iii) and finally step i),
First step iii), then step i) and finally step ii), and

First step iii), then step ii) and finally step i).

[0022] In case the at least one magnet is hung into the inside room of the bath container, a preferred order of steps i) to iii) is: First step iii), then step ii) and finally step i).

[0023] In case the at least one magnet is attached onto the inside and/or outside wall of the bath container, a preferred order of steps i) to iii) is: First step i), then step ii) and finally step iii).

[0024] In step iv), the temperature of phosphating composition usually lies in the range of from 50 to 95 °C, preferably in the range of from 60 to 80 °C. The time required to increase the concentration of iron(II) ions to a concentration in the range of from 0.5 to 1.0 g/l usually lies in the range of from 10 to 60 minutes, preferably in the range of from 10 to 20 minutes.

[0025] Subsequent to step iv), the present method preferably comprises the following additional step:

v) At least one optionally pickled and/or cleaned metal substrate is immersed into the phosphating composition and phosphatized by an iron side phosphating process, wherein a concentration of iron(II) ions in the phosphating composition of up to 5 g/l or even up to 7 g/l is obtained.

[0026] The coating weights and the grain sizes of the phosphate layers formed in step v) are comparable to or even better than those of phosphate layers formed when using soluble steel wool just thrown into the phosphating bath, steel-containing scrap or iron(II) phosphate solution as described herein above.

[0027] In step v), the temperature of phosphating composition usually lies in the range of from 50 to 95 °C, preferably in the range of from 60 to 80 °C. The time required to phosphatize an according metal substrate usually lies in the range of from 3 to 20 minutes, preferably in the range of from 5 to 10 minutes.

[0028] The at least one metal substrate is preferably at least one iron-containing substrate, more preferably at least one steel-containing substrate, even more preferably at least one substrate made of steel, in particular at least one wire or construction element made of steel. According construction elements may be used in the construction of aircrafts for example.

[0029] The aqueous acidic phosphating composition preferably comprises, beside phosphate ions, manganese and/or zinc ions. Especially preferred are manganese phosphate systems comprising manganese, iron(II) and nickel ions, as well as heavy zinc phosphate systems comprising zinc, iron(II) and nickel ions or zinc, manganese, nickel and iron(II) ions.

[0030] Preferably, no air is blown into the phosphating composition nor is an oxidizing agent such as nitrite or chlorate added as this may cause precipitation of iron(III) phosphate, this means formation of so-called sludge.

[0031] For the present invention, permanent magnets as well as electromagnets may be used, wherein permanent magnets are preferred due to the dangers linked to the use of electrical current.

[0032] It is possible to attach at least one magnet onto

the inside wall of the phosphating bath container, in particular by means of screwing or clamping as the bath container is commonly made of stainless steel being non-magnetic. In this case, a strength of the magnet/s is required which is high enough to effectively attach the at least one iron-containing body on the inside wall of the bath container. In this regard, neodymium magnets, i.e. so-called super magnets, are especially preferred.

[0033] Alternatively, or even additionally, at least one magnet may be attached onto the inside wall of the bath container, in particular by means of screwing or clamping. Due to the contact with the phosphating composition, the magnet/s need/s to have sufficient heat as well as acid resistance. The same applies to the following case:

Alternatively, or even additionally, it is possible to hang at least one magnet, for example at least one spherical magnet, each one by means of at least one holder element, into the inside room of the bath container.

[0034] According to a preferred embodiment, the at least one magnet is attached onto the outside wall of the phosphating bath container, wherein the at least one magnet is more preferably at least two magnets and even more preferably exactly two magnets.

[0035] According to another preferred embodiment, the at least one magnet is hung, each one by means of at least one holder element, into the inside room of the bath container, wherein the at least one magnet is more preferably one magnet, for example one spherical magnet, which is more preferably hung into the inside room of the bath container by means of exactly one holder element.

[0036] In the method according to the present invention, the at least one iron-containing body is preferably selected from the group consisting of iron powder, iron wool, steel powder and steel wool, more preferably from the group consisting of iron powder and iron wool. Most preferably, the at least one iron-containing body is iron powder.

[0037] Iron powder and iron wool have the advantage that they are free or at least essentially free of toxic chromium. In comparison with iron/steel wool, iron/steel powder is advantageous because it can more effectively be attached to the at least one magnet such that the risk of undissolved portions of iron-containing body swimming around in the bath and settling down on the surface of the substrates to be phosphatized is even more reduced.

[0038] Iron powder having an average particle size of less than 90 μm is especially preferred as the iron(II) ions are more effectively dissolved out into the acidic aqueous phosphating composition.

[0039] It is sufficient that the iron-containing body/ies is/are at least partially immersed in the phosphating composition. However, complete immersion is preferred as the iron(II) ions can be dissolved out more effectively then.

[0040] The present invention also refers to a modified iron side phosphating plant according to claim 10, namely a phosphating plant which is characterized by comprising

a) a phosphating bath container, and

b) at least one magnet which is attached to the inside and/or outside wall of the bath container and/or hung, each one by means of at least one holder element, in the inside room of the bath container.

Preferably, the phosphating plant additionally comprises

c) an acidic aqueous phosphating composition filled in the phosphating bath container such that the at least one iron-containing body is at least partially immersed in the phosphating composition.

[0041] According to a preferred embodiment, the at least one magnet is attached onto the outside wall of the phosphating bath container, wherein the at least one magnet is more preferably at least two magnets and even more preferably exactly two magnets.

[0042] According to another preferred embodiment, the at least one magnet is hung, each one by means of at least one holder element, into the inside room of the bath container, wherein the at least one magnet is more preferably one magnet, for example one spherical magnet, which is more preferably hung into the inside room of the bath container by means of exactly one holder element.

[0043] For further preferred embodiments as well as preferred features of the phosphating plant, reference is made to the description of the method according to the present invention herein above.

Summary of the Figures:

[0044] According to an especially preferred embodiment, iron powder (1a, 1b) is attached to two permanent magnets (2a, 2b; grey sections) which are attached on the outside wall (3) of the phosphating bath container (4) below the surface (5; dotted line) of the phosphating composition. A corresponding phosphating plant is shown in **Fig. 1**. The walls of the bath container (4) as well as the first magnet (2a) are depicted as being transparent.

[0045] According to another especially preferred embodiment, iron powder (1) is attached to a spherical permanent magnet (2; grey disc) which, by means of a holder element (3), is immersed in the phosphating bath, this means below the surface (5; dotted line) of the phosphating composition in the phosphating bath container (4). A corresponding phosphating plant is shown in **Fig. 2**. The walls of the bath container (4) are depicted as being transparent.

Claims

1. Method for increasing the concentration of iron(II) ions in iron side phosphating systems, **characterized in that** it comprises the following steps:

i) at least one magnet is attached onto the inside

and/or outside wall of a phosphating bath container and/or hung, by means of at least one holder element, into the inside room of the bath container,

ii) at least one iron-containing body is attached to the at least one magnet by means of magnetic forces, and

iii) the phosphating bath container is filled with an acidic aqueous phosphating composition such that the at least one iron-containing body is at least partially immersed in the phosphating composition,

as well as, subsequently, the following step:

iv) iron(II) ions are dissolved out of the at least one iron-containing body into the phosphating composition such that the concentration of iron(II) ions in the phosphating composition is increased to a concentration of at least 0.5 g/l.

2. Method according to claim 1, **characterized in that**, subsequent to step iv), it comprises the following additional step:

v) At least one optionally pickled and/or cleaned metal substrate is immersed into the phosphating composition and phosphatized by an iron side phosphating process, wherein a concentration of iron(II) ions in the phosphating composition of up to 5 g/l or even up to 7 g/l is obtained.

3. Method according to claim 1 or 2, **characterized in that** the phosphating bath container exhibits at least one element for continuous stirring and mixing of the phosphating composition.

4. Method according to one of the preceding claims, **characterized in that** the at least one magnet is attached onto the outside wall of the phosphating bath container, wherein the at least one magnet is preferably at least two magnets.

5. Method according to one of claims 1 to 3 **characterized in that** the at least one magnet is hung, each one by means of at least one holder element, into the inside room of the bath container.

6. Method according to claim 5, **characterized in that** the at least one magnet is one magnet, for example one spherical magnet, which is hung into the inside room of the bath container by means of exactly one holder element.

7. Method according to one of the preceding claims, **characterized in that** the at least one iron-containing body is selected from the group consisting of iron powder, iron wool, steel powder and steel wool, preferably from the group consisting of iron powder and iron wool.

8. Method according to claim 7, **characterized in that** the at least one iron-containing body is iron powder.

9. Method according to claim 8, **characterized in that** it has an average particle size of less than 90 μm .

10. Iron side phosphating plant according to one of the preceding claims **characterized in that** it comprises

a) a phosphating bath container, and

b) at least one magnet which is attached to the inside and/or outside wall of the bath container and/or hung, each one by means of at least one holder element, in the inside room of the bath container

and, preferably additionally comprises

c) an acidic aqueous phosphating composition filled in the phosphating bath container such that the at least one iron-containing body is at least partially immersed in the phosphating composition.

Fig. 1:

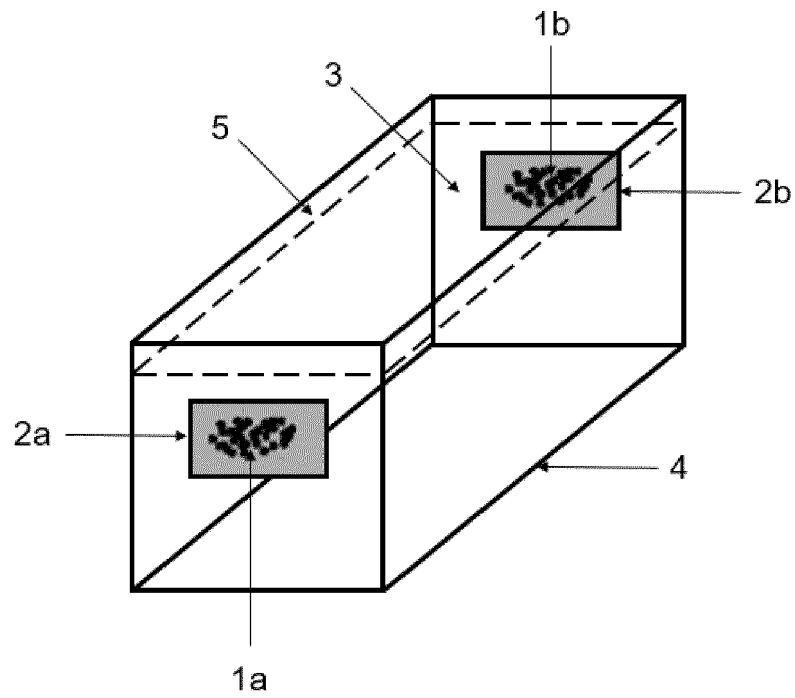
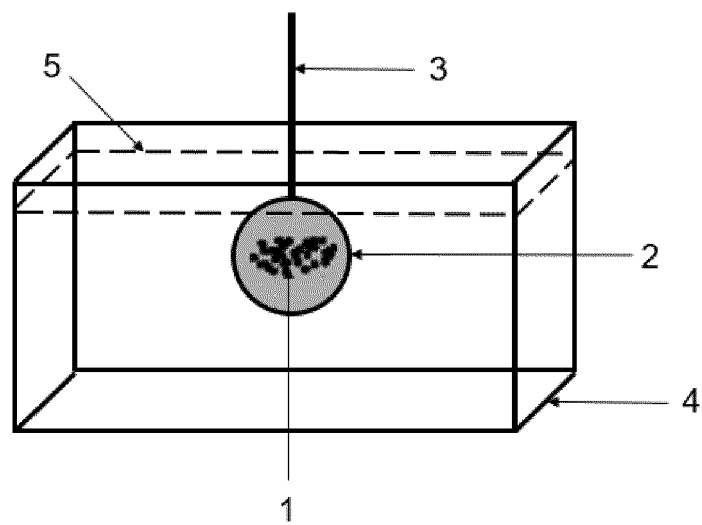


Fig. 2:





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Application Number
EP 20 16 2034

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**ANNEX TO THE EUROPEAN SEARCH REPORT
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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