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(54) METHOD FOR BLACK-PASSIVATING A ZINC LAYER, BLACK-PASSIVATION COMPOSITION, AND RESPECTIVE USE

(57) The present invention refers to a method for black-passivating a zinc layer, a respective black-passivation composition comprising one or more than one blackening agent selected from the group consisting of formula (I), salts, and stereoisomers thereof, and a respective use of such blackening agents for black-passivating a zinc layer, wherein the zinc layer is substantially free of, preferably does not comprise, nickel.

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Description

Field of the Invention

[0001] The present invention refers to a method for black-passivating a zinc layer, a respective black-passivation composition comprising one or more than one blackening agent selected from the group consisting of formula (I), salts, and stereoisomers thereof, and a respective use of such blackening agents for black-passivating a zinc layer, wherein the zinc layer is substantially free of, preferably does not comprise, nickel.

Background of the Invention

[0002] To protect metallic substrates from corrosive environmental influences, different methods are available according to the prior art. Applying a protective coating/layer of a metal or metal alloy on the metallic substrate is a widely used and established method. A well know principle is the deposition of a zinc or zinc-nickel coating/layer on a metal substrate, such as an iron substrate or iron alloy substrate (including a steel substrate). Such a coating/layer is typically obtained by a galvanization process. Among zinc and zinc-nickel galvanization, zinc galvanization has a far-reaching successful history.

[0003] Increasing further the corrosion resistance, such a coating/layer is typically in addition passivated with a passivation layer by contacting it with a passivation composition. Such passivation compositions and respective methods are widely known in the art. Usually, a passivation treatment forms insoluble reaction products on the respective coating/layer.

[0004] In many cases the passivation composition furthermore modifies the color of the coating/ layer, for example into a bluish or even dark black color. Depending on the application, such a color modification is often very much desired for optical reasons, in particular in the automotive field.

[0005] However, for certain coatings/layers a suitable color modification is either not available at all or provides an insufficient color modification such as an insufficient blackening. Particularly, a deep dark blackening of galvanized zinc without compromising excellent corrosion resistance is an ongoing demand.

[0006] EP 1 970 470 B1 refers to a treatment solution for producing substantially chromium(VI)-free black conversion layers on zinc-containing alloy layers.

[0007] Although black-passivation compositions are described in the art, there is an ongoing demand to further improve black-passivating processes for a zinc layer.

Objective of the present Invention

[0008] It was therefore the objective of the present invention to provide a method for black-passivating a zinc layer with improved blackening quality but at the same time without compromising an excellent corrosion resistance.

[0009] It is furthermore the objective to provide a respective black-passivation composition providing these benefits. Furthermore, the black-passivation composition should be easy to handle.

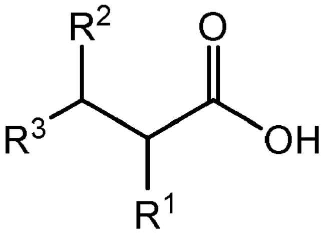
Summary of the Invention

[0010] The objectives mentioned above are solved by a method for black-passivating a zinc layer, the method comprising the steps:

(a) providing a substrate comprising the zinc layer,

(b) providing a black-passivation composition for said black-passivating, the composition comprising

(i) one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



(I),

wherein independently

R^1 denotes H, SH, or NH_2,

R^2 denotes H or SH, and

R^3 denotes COOH, SH, or CH_3,

wherein at least one of R^1, R^2, and R^3 is SH, and

(ii) trivalent chromium ions,

(c) contacting the substrate with said black-passivation composition such that the zinc layer is black-passivated.

[0011] By utilizing said one or more than one blackening agent, an excellent black-passivation of a zinc layer is obtained along with very good corrosion resistance. Moreover, the method of the present invention is simple and can be easily carried out. Own experiments have furthermore shown that the blackening obtained by means of the present invention is highly specific for zinc layers. Own experiments confirm that zinc alloy layers, such as zinc-nickel layers, are not significantly blackened. Further details are given in the examples section below in the text.

[0012] The present invention also relates to a respective black-passivation composition as further described below in the text as well as a respective use of said one or more than one blackening agent for black-passivating a zinc layer, wherein the zinc layer is substantially free of, preferably does not comprise, nickel. Generally, features described in regard to the method of the present invention, in particular features described as being preferred, apply likewise to the black-passivation composition of the present invention, most preferably to a black-passivation composition described as being preferred, and apply likewise to the use according to the present invention, most preferably to the use described as being preferred.

Detailed Description of the Invention

[0013] In the context of the present invention, the term "trivalent chromium ions" refers to chromium ions with the oxidation number +3 including the free and complexed form, respectively, preferably in a complexed form.

[0014] In the context of the present invention, the term "black-passivating" includes forming a black passivation layer or likewise forming a black-conversion layer.

[0015] Preferably, in the context of the present invention, the black-passivating (respectively the black passivation layer) has a darkness value L* of 40 or below, preferably of 35 or below, more preferably of 30 or below, even more preferably of 28 or below, yet even more preferably of 26 or below, most preferably of 25 or below, based on the CIELAB color space definition.

Step (a), providing the substrate:

[0016] As mentioned above, the method of the present invention is highly specific for a zinc layer. Preferred is a method of the present invention, wherein in the zinc layer the amount of zinc is 90 wt.-% or more, based on the total weight of the zinc layer, preferably 92 wt.-% or more, more preferably 94 wt.-% or more, even more preferably 96 wt.-% or more, yet even more preferably 98 wt.-% or more, most preferably 99 wt.-% or more, even most preferably 99.5 wt.-% or more. A very preferred amount of zinc is 99.9 wt.-% or more.

[0017] Preferred is a method of the present invention, wherein the zinc layer substantially only comprises zinc or consists of zinc.

[0018] More preferred is a method of the present invention, wherein the zinc layer is substantially free of, preferably does not comprise, nickel.

[0019] Preferred is a method of the present invention, wherein the zinc layer is substantially free of, preferably does not comprise, an alloying metal. Even more preferably, the zinc layer is substantially free of, preferably does not comprise, an alloying element.

[0020] In the context of the present invention, the zinc to be black-passivated is present on the substrate as a layer. Preferably, the zinc-layer is a galvanic zinc-layer. Most preferred is a method of the present invention, wherein the zinc-layer is obtained from an alkaline zinc deposition composition, preferably utilized in an electrolytic zinc deposition process.

[0021] In other words, preferred is a method of the present invention comprising a step, wherein the substrate is contacted with an alkaline zinc deposition composition such that said substrate comprising the zinc layer as defined in step (a) is obtained. This preferably is an electrolytic deposition utilizing an electrical current.

[0022] Preferred is a method of the present invention, wherein the zinc layer is distinct from the substrate. In other words, preferably the zinc layer is a coating to provide corrosion protection for the substrate.

[0023] Preferred is a method of the present invention, wherein the substrate is a metal substrate, preferably a metal substrate comprising iron, more preferably an iron substrate or an iron alloy substrate, most preferably a steel substrate. Preferably the zinc layer is deposited on such a substrate.

[0024] Preferred is a method of the present invention, wherein the substrate is selected from the group consisting of screws, bolts, nuts, rack parts, and automotive parts.

[0025] Preferred is a method of the present invention, wherein more than one substrate is provided in step (a), preferably a plurality of substrates is provided in step (a). This particularly applies if the substrate refers to screws, bolts, and nuts.

[0026] Preferred is a method of the present invention, wherein the substrate is (or preferably the substrates are) provided in a barrel or fixed on a rack. Thus, the method of the present invention is applicable to both kinds.

Step (b), providing the black-passivation composition

[0027] In the method of the present invention a black-passivation composition is utilized, preferably the black-passivation composition of the present invention (see text further below).

[0028] Preferably, the black-passivation composition is also called a conversion composition for black passivation.

[0029] Preferred is a method of the present invention, wherein the black-passivation composition is aqueous (i.e. comprises water), wherein preferably water has a concentration of more than 50 vol.-% based on the total volume of the black-passivation composition, more preferably of 75 vol.-% or more, most preferably of 90 vol.-% or more. Very preferably, water is the only solvent.

[0030] Preferably, the black-passivation composition is a solution. Thus, preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, particles (including colloids). This particularly applies, after the black-passivation composition is freshly prepared. In contrast, in some cases a method of the present invention is preferred, wherein the (preferably freshly prepared) black-passivation composition comprises particles, most preferably nano-particles.

[0031] Preferred is a method of the present invention, wherein the black-passivation composition is acidic, preferably having a pH from 0.5 to 4.5, more preferably from 0.8 to 4.0, even more preferably from 1.1 to 3.5, yet even more preferably from 1.5 to 3, most preferably from 1.8 to 2.5.

[0032] As mentioned above, the black-passivation composition comprises (i) one or more than one blackening agent as defined above.

[0033] As indicated by formula (I), the one or more than one blackening agent utilized in the black-passivation composition is an organic blackening agent.

[0034] Preferred is a method of the present invention, wherein the black-passivation composition comprises one or more than one (preferably one) blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof. According to own experiments, such a blackening agent provides excellent results (see examples below).

[0035] Preferred is a method of the present invention, wherein in the black-passivation composition the one or more than one blackening agent has a total concentration ranging from 1 mmol/L to 100 mmol/L, based on the total volume of the black-passivation composition, preferably from 2 mmol/L to 75 mmol/L, more preferably from 4 mmol/L to 50 mmol/L, even more preferably from 5 mmol/L to 35 mmol/L, yet even more preferably from 6 mmol/L to 20 mmol/L, most preferably from 8 mmol/L to 14 mmol/L. If the total concentration is significantly too high, in many cases solubility problems were observed. On the other hand, if the total concentration is too low, a reduced or at least insufficient black appearance and/or reduced NSST performance were observed in some cases.

[0036] Preferred is a method of the present invention, wherein the one or more than one blackening agent comprises (preferably at least) mercaptosuccinic acid, dimercaptosuccinic acid, mercaptopropionic acid, mercaptobutyric acid, mercapto-L-aspartic acid, salts, and/or stereoisomers thereof, most preferably in the total concentration ranges defined above.

[0037] More preferred is a method of the present invention, wherein the one or more than one blackening agent comprises (preferably at least) mercaptosuccinic acid, dimercaptosuccinic acid, 3-mercaptopropionic acid, 2-mercaptobutyric acid, 3-mercapto-L-aspartic acid, salts, and/or stereoisomers thereof, most preferably in the total concentration ranges defined above.

[0038] More preferred is a method of the present invention, wherein the one or more than one blackening agent comprises (preferably at least) mercaptosuccinic acid, most preferably in the total concentration ranges defined above.

[0039] Preferred is a method of the present invention, wherein R^1 denotes H or SH, preferably SH. This particularly comprises mercaptosuccinic acid, dimercaptosuccinic acid, mercaptopropionic acid, mercaptobutyric acid, salts, and/or stereoisomers thereof; preferably mercaptosuccinic acid, dimercaptosuccinic acid, and mercaptobutyric acid, salts, and/or stereoisomers thereof.

[0040] Preferred is a method of the present invention, wherein R^2 denotes H. This particularly comprises mercaptosuccinic acid, mercaptopropionic acid, mercaptobutyric acid, salts, and/or stereoisomers thereof.

[0041] Preferred is a method of the present invention, wherein R^3 denotes COOH or SH, preferably COOH (this particularly includes also salts thereof). This particularly comprises mercaptosuccinic acid, dimercaptosuccinic acid, mercaptopropionic acid, mercapto-L-aspartic acid, salts, and/or stereoisomers thereof; preferably mercaptosuccinic acid, dimercaptosuccinic acid, and mercapto-L-aspartic acid, salts, and/or stereoisomers thereof.

[0042] Preferably, the aforementioned preferred limitations for R^1, R^2, and R^3 are combined.

[0043] Very preferred is a method of the present invention, wherein R^1 denotes SH and R^3 denotes COOH.

[0044] Most preferred is a method of the present invention, wherein R^1 denotes SH, R^2 denotes H, and R^3 denotes COOH. Thus, most preferred is a method of the present invention, wherein the one or more than one blackening agent comprises (preferably at least, most preferably only) mercaptosuccinic acid, salts, and stereoisomers thereof.

[0045] As mentioned above, in the context of the present invention, at least one of R^1, R^2, and R^3 is SH.

[0046] Preferably, the one or more than one blackening agent comprises one (i.e. a single) SH group.

[0047] Preferably, the one or more than one blackening agent comprises two COOH groups.

[0048] Preferred is a method of the present invention, wherein said salts are independently selected from the group consisting of ammonium salts and alkaline salts, preferably selected from the group consisting of ammonium salts, sodium salts, and potassium salts.

[0049] The black-passivation composition utilized in the method of the present invention further comprises (ii) trivalent chromium ions.

[0050] Preferred is a method of the present invention, wherein the trivalent chromium ions are from an organic and/or inorganic trivalent chromium ion source, preferably from an inorganic trivalent chromium ion source. In some case, an organic trivalent chromium ion source is preferred, more preferred trivalent chromium citrate and/or trivalent chromium oxalate. A preferred inorganic trivalent chromium ion source comprises trivalent chromium chloride (most preferably trivalent chromium hexahydrate), trivalent chromium nitrate and/or trivalent chromium sulphate.

[0051] Preferred is a method of the present invention, wherein the trivalent chromium ions have a total concentration ranging from 0.1 g/L to 30 g/L, based on the total volume of the black-passivation composition, preferably from 0.5 g/L to 20 g/L, more preferably from 1 g/L to 14 g/L, even more preferably from 1.5 g/L to 10 g/L, most preferably from 2 g/L to 7 g/L. A very preferred total concentration is ranging from 3 g/L to 6 g/L. If the total concentration is significantly below 0.1 g/L, in many cases a particular desired corrosion resistance is not achieved. In contrast, if the total concentration is significantly above 30 g/L, no further benefit is identified and costs are typically unacceptably high.

[0052] In the following a number of compounds and ions are listed that preferably are not contained in the black-passivation composition utilized in the method of the present invention. Such compounds/ions are either not helpful for solving the objectives mentioned above or even have a detrimental effect and are therefore avoided.

[0053] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, hexavalent chromium. This includes any compounds and ions comprising chromium with an oxidation number of (+VI). It is a very preferred objective that the method of the present invention avoids any utilization of hexavalent chromium due to its environmental and health issues.

[0054] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, thioglycolic acid and salts thereof. However, in some cases a method of the present invention is preferred, wherein the black-passivation composition comprises thioglycolic acid and/or salts thereof in addition to said one or more than one blackening agent as defined throughout the present text.

[0055] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, nickel ions, preferably is substantially free of, preferably does not comprise, nickel.

[0056] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, intentionally added zinc ions. If zinc ions are present in the black-passivation composition, they are released/dissolved from the zinc layer upon utilizing the black-passivation composition. Thus, preferred is a method of the present invention, with the proviso that, if zinc ions are present in the black-passivation composition, they are released from the zinc layer. In other words, if zinc ions are present, the source is the zinc layer. After setting up a respective black-passivation composition no zinc ions are typically present. After starting the method of the present invention, the total concentration is very low. Upon utilizing the black-passivation composition the total concentration typically increases. Thus, preferably, zinc ions are present in a total concentration of 15 g/L or below, based on the total volume of the black-passivation composition, preferably of 12 g/L or below, most preferably of 8 g/L or below, after step (c) is carried out multiple times.

[0057] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, silver ions, preferably is substantially free of, preferably does not comprise, silver.

[0058] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, intentionally added iron ions. If iron ions are present in the black-passivation composition, they are released/dissolved from the substrate and possible damages in the zinc layer. After setting up a respective black-passivation composition no iron ions are typically present. After starting the method of the present invention, the total concentration is very low. Preferably, iron ions are present in a total concentration of 1 g/L or below, based on the total volume of the black-passivation composition, preferably of 0.8 g/L or below, most preferably of 0.5 g/L or below, after step (c) is carried out multiple times.

[0059] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, tungsten ions.

[0060] More preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, tungsten.

[0061] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, thiodiglycol.

[0062] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, silicon dioxide, silicates, a silane, and a silane containing compound, preferably is substantially free of, preferably does not comprise, a silicon-containing compound.

[0063] Only in very rare cases a method of the present invention is preferred, wherein the black-passivation composition comprises a silane and/or a silane containing compound. It is assumed that in some cases the presence of the silane and/or the silane containing compound positively affects the corrosion resistance. However, in many cases an excellent corrosion resistance is already achieved even without the presence of a silane and/or a silane containing compound.

[0064] Also, only in rare cases it is preferred that the black-passivation composition comprises silicon dioxide, preferably as silicon dioxide nano-particles.

[0065] Also, only in rare cases it is preferred that the black-passivation composition comprises one or more than one silicate.

[0066] Preferred is a method of the present invention, wherein the black-passivation composition is substantially free of, preferably does not comprise, formic acid, acetic acid, and salts thereof, more preferably is substantially free of, preferably does not comprise, a sulfur-free mono-carboxcylic acid and salts thereof.

[0067] Preferred is a method of the present invention, wherein the black-passivation composition is further comprising

(iii) one or more than one (preferably one) species of halogen ions;

(iv) one, two, or more than two (preferably two or more than two) carboxylic acids and/or salts thereof;

(v) phosphate anions;

(vi) nitrate anions; and/or

(vii) cobalt ions.

[0068] More preferred is a method of the present invention, wherein the black-passivation composition comprises at least all of (iii) to (vi), most preferably all of (iii) to (vii).

[0069] Preferred is a method of the present invention, wherein the black-passivation composition comprises (iii) one or more than one (preferably one) species of halogen ions.

[0070] Preferably, said one or more than one species of halogen ions are the counter anions of the trivalent chromium ions. Preferably, the one or more than one species of halogen ions comprises chloride ions. A preferred trivalent chromium ion source is chromium (III) chloride. Bromide ions are preferably not comprised in the black-passivation composition.

[0071] Preferred is a method of the present invention, wherein the one or more than one species of halogen ions has a total concentration from 1 g/L to 50 g/L, based on the total volume of the black-passivation composition, preferably from 3 g/L to 35 g/L, even more preferably from 5 g/L to 25 g/L, most preferably from 7 g/L to 20 g/L, even most preferably from 9 g/L to 16 g/L. This most preferably applies to chloride ions. Most preferably, chloride ions are the only species of halogen ions in the black-passivation composition.

[0072] Preferred is a method of the present invention, wherein the black-passivation composition comprises (iv) one, two, or more than two (preferably two or more than two, most preferably two) carboxylic acids and/or salts thereof. Compounds according to (iv) are different and distinct from one or more than one blackening agent according to (i). This means that compounds according to (iv) are (at least) sulfur-free.

[0073] Said one, two, or more than two carboxylic acids and/or salts thereof typically serve as complexing agents for the trivalent chromium ions, preferably additionally for the cobalt ions (if cobalt ions are present).

[0074] Preferred is a method of the present invention, wherein said one, two, or more than two carboxylic acids and/or salts thereof comprise a dicarboxylic acid, a tricarboxylic acid, and/or salts thereof. Most preferably, said one, two, or more than two carboxylic acids and/or salts thereof comprise only dicarboxylic acids and/or salts thereof.

[0075] A preferred dicarboxylic acid and/or salts thereof comprises a C2 to C6 dicarboxylic acid and/or salts thereof, preferably oxalic acid, malonic acid, succinic acid, glutaric acid, adipic acid, and/or salts thereof, most preferably oxalic acid, malonic acid, succinic acid, and/or salts thereof.

[0076] A preferred tricarboxylic acid and/or salts thereof comprises citric acid and/or salts thereof.

[0077] Preferred is a method of the present invention, wherein the one, two, or more than two carboxylic acids and salts thereof have a total concentration from 10 mmol/L to 500 mmol/L, based on the total volume of the black-passivation composition, preferably from 25 mmol/L to 400 mmol/L, even more preferably from 55 mmol/L to 300 mmol/L, most preferably from 80 mmol/L to 200 mmol/L, even most preferably from 100 mmol/L to 160 mmol/L. More preferably, the above total concentration ranges apply with the proviso that the black-passivation composition comprises at least one, two, or more than two (preferably two or more than two, most preferably two) sulfur-free dicarboxylic acids and/or salts thereof, most preferably at least oxalic acid.

[0078] Most preferably, oxalic acid, succinic acid, and/or salts thereof are the only sulfur-free dicarboxylic acids and salts thereof in the black-passivation composition, preferably the only sulfur-free carboxylic acids and salts thereof in the black-passivation composition.

[0079] Preferred is a method of the present invention, wherein the black-passivation composition comprises (v) phosphate anions. The presence of phosphate anions typically supports the blackening effect and roughens the surface for subsequent formation of the black passivate as an insoluble precipitate on the zinc layer.

[0080] A preferred phosphate anion source comprises phosphoric acid.

[0081] Preferred is a method of the present invention, wherein the phosphate anions have a total concentration ranging from 1 g/L to 100 g/L, based on the total volume of the black-passivation composition, preferably from 4 g/L to 75 g/L, even more preferably from 8 g/L to 50 g/L, most preferably from 12 g/L to 35 g/L, even most preferably from 15 g/L to 25 g/L.

[0082] Preferred is a method of the present invention, wherein the black-passivation composition comprises (vi) nitrate anions.

[0083] Nitrate ions preferably act as oxidizing agent in the black-passivation composition.

[0084] Preferred is a method of the present invention, wherein the nitrate anions have a total concentration ranging from 0.1 g/L to 20 g/L, based on the total volume of the black-passivation composition, preferably from 0.3 g/L to 15 g/L, even more preferably from 0.5 g/L to 10 g/L, most preferably from 0.8 g/L to 5 g/L, even most preferably from 1 g/L to 2 g/L.

[0085] Preferred is a method of the present invention, wherein the black-passivation composition comprises (vii) cobalt ions, preferably Co (II) ions.

[0086] Cobalt ions typically improve corrosion resistance after a heat treatment.

[0087] Preferred is a method of the present invention, wherein the cobalt ions have a total concentration ranging from 0.1 g/L to 20 g/L, based on the total volume of the black-passivation composition, preferably from 0.5 g/L to 15 g/L, even more preferably from 1 g/L to 10 g/L, most preferably from 1.5 g/L to 7 g/L, even most preferably from 2 g/L to 4 g/L.

Step (c), contacting with the black-passivation composition

[0088] In step (c) the substrate with the zinc layer is contacted with the black-passivation composition such that the zinc layer is black-passivated.

[0089] Preferred is a method of the present invention, wherein in step (c) the black-passivation composition has a temperature in a range from 15°C to 70°C, preferably from 20°C to 55°C, even more preferably from 25°C to 45°C, most preferably from 30°C to 40°C. If the temperature is significantly exceeding 70°C, in many cases an undesired rapid dissolution (stripping) of the zinc layer is observed impairing the corrosion resistance. However, if the temperature is too low, in many cases the contacting in step (c) is undesirably long.

[0090] Preferred is a method of the present invention, wherein in step (c) the contacting is performed for a time period from 5 seconds to 200 seconds, preferably from 10 seconds to 150 seconds, even more preferably from 20 seconds to 100 seconds, most preferably from 30 seconds to 80 seconds. If the time period is significantly exceeding 200 seconds, in many cases an undesired roughening of the surface is observed up to a rapid dissolution (stripping) of the zinc layer, impairing the corrosion resistance. However, if the time period is too low, typically the blackening is insufficient and thus, the optical appearance is impaired.

[0091] Preferred is a method of the present invention, wherein step (c) is performed without applying an electrical current. Preferably, in step (c) the substrate is dipped into the black-passivation composition or sprayed with the black-passivation composition.

Post-treatment

[0092] As shown in the examples below, a very good corrosion resistance is obtained if after step (c) the substrate is further treated in order to preferably further increase corrosion resistance.

[0093] Generally preferred is a method of the present invention, wherein the substrate obtained after step (c) of the method of the present invention is additionally treated with a post-dip composition and/or a sealer composition, preferably as outlined below, either in this order or in reversed order (i.e. first sealer and subsequently post-dip).

[0094] Thus, preferred is a method of the present invention, wherein step (c) is followed by step

(d) contacting the substrate obtained after step (c) with a post-dip composition such that a post-dipped substrate is obtained.

[0095] Preferably, step (d) is optional. Depending on the substrate, in some cases step (d) is required.

[0096] Preferred is a method of the present invention, wherein the post-dip composition is acidic, preferably has a pH ranging from 2 to 6.8, more preferably from 2.5 to 6.3, even more preferably from 3 to 6, most preferably from 3.5 to 5.5.

[0097] Preferred is a method of the present invention, wherein the post-dip composition comprises trivalent chromium ions.

[0098] Preferred is a method of the present invention, wherein the post-dip composition is substantially free of, preferably does not comprise, compounds and ions comprising hexavalent chromium.

[0099] Preferred is a method of the present invention, wherein the post-dip composition comprises phosphate anions.

[0100] Preferred is a method of the present invention, wherein the post-dip composition comprises one or more than one wetting agent.

[0101] Preferred is a method of the present invention, wherein the post-dip composition comprises one or more than one complexing agent, preferably for the trivalent chromium ions.

[0102] Preferred is a method of the present invention, wherein in step (d) the post-dip composition has a temperature in a range from 18°C to 60°C, preferably 20°C to 58°C, more preferably from 28°C to 56°C, even more preferably from 33°C to 54°C, most preferably from 38°C to 50°C.

[0103] Preferred is a method of the present invention, wherein in step (d) the contacting is performed for a time period from 4 seconds to 100 seconds, preferably from 6 seconds to 80 seconds, even more preferably from 8 seconds to 50 seconds, most preferably from 10 seconds to 30 seconds.

[0104] Preferred is a method of the present invention, wherein step (d) is followed by step

(e) contacting the substrate obtained after step (d) with a sealer composition such that a sealed substrate is obtained.

[0105] Preferably, step (e) is optional. Depending on the substrate, in some cases step (e) is required.

[0106] In some cases, a method of the present invention is preferred, wherein step (e) follows on step (c), i.e. no step (d) is carried out after step (c) but rather step (e) after step (c). This optionally is followed by step (d).

[0107] Preferred is a method of the present invention, wherein the sealer composition has a pH ranging from 5 to 14, more preferably from 6 to 13, even more preferably from 7 to 12.

[0108] In some cases, preferred is a method of the present invention, wherein the sealer composition is alkaline, preferably has a pH of 9 or higher, more preferably in a range from 9.1 to 12, even more preferably from 9.3 to 11, most preferably from 9.5 to 10.5.

[0109] Preferred is a method of the present invention, wherein the sealer composition comprises two or more than two organic compounds.

[0110] Preferred is a method of the present invention, wherein the sealer composition is substantially free of, preferably does not comprise, trivalent chromium ions.

[0111] Preferred is a method of the present invention, wherein the sealer composition comprises at least one organic polymer, preferably comprising a polyurethane, a polyalkylene (preferably polyethylene), a polyfluoroalkylene (preferably polytetrafluoroethylene) and/or a polyacrylate. However, in some cases, a method of the present invention is preferred, wherein the sealer composition is substantially free of, preferably does not comprise, an organic polymer. Such sealers are preferably known as inorganic sealer. Preferably, they comprise at least one silicon-based compound, preferably at least one silicate, most preferably at least one poly-silicate.

[0112] In some cases, preferred is a method of the present invention, wherein the sealer composition comprises one or more than one wax. However, in some cases, a method of the present invention is preferred, wherein the sealer composition is substantially free of, preferably does not comprise, a wax, most preferably is substantially free of, preferably does not comprise, any lubricant.

[0113] Preferred is a method of the present invention, wherein the sealer composition comprises one or more than one silicon-containing compound, preferably at least one silane and/or at least one inorganic silicate. Preferably, the at least one inorganic silicate is a colloid.

[0114] Generally preferred is a method of the present invention, wherein in step (e) the sealer composition has a temperature in a range from 15°C to 65°C, preferably 17°C to 60°C, more preferably from 19°C to 55°C, most preferably from 21°C to 50°C.

[0115] Preferred is a method of the present invention, wherein in step (e) the contacting is performed for a time period from 5 seconds to 500 seconds, preferably from 10 seconds to 400 seconds, even more preferably from 20 seconds to 300 seconds, most preferably from 30 seconds to 200 seconds.

[0116] More preferred is a method of the present invention, wherein in step (e) the contacting is performed for a time period from 5 seconds to 200 seconds, preferably from 10 seconds to 140 seconds, even more preferably from 20 seconds to 100 seconds, most preferably from 30 seconds to 70 seconds.

[0117] When performing steps (d) and (e) as outlined above in this order, not only a very good black-passivation is obtained but additionally also an excellent corrosion resistance, most preferably up to 72 hours, based on ISO 9227, with max. 1% white rust formation. However, a significantly increased corrosion resistance can be already achieved by at least performing one of steps (d) and (e).

[0118] Preferred is a method of the present invention, wherein step (e) is followed by step
(f) drying the substrate obtained after step (e).

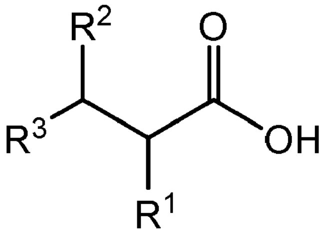
[0119] Preferred is a method of the present invention, wherein step (f) is carried out at a temperature ranging from 55°C to 95°C, preferably 58°C to 90°C, more preferably from 58°C to 85°C, most preferably from 60°C to 80°C.

[0120] Preferred is a method of the present invention, wherein step (f) is carried out for a time period from 2 minutes to 20 minutes, preferably from 4 minutes to 18 minutes, even more preferably from 6 minutes to 15 minutes, most preferably from 8 minutes to 13 minutes.

[0121] Preferably, a drying step, preferably as defined above, is also carried out after one or more than one of the previous steps, e.g. after step (c), step (d), etc. Very preferred is a method of the present invention, wherein a drying step, preferably as defined in step (f), is carried out after step (d) and prior to step (e). This is very preferred because in step (d) the post-dip composition is acidic, wherein in step (e) the sealer composition is alkaline.

[0122] The present invention furthermore refers to a black-passivation composition comprising

(i) one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



(I),

wherein independently

R^1 denotes H, SH, or NH_2,

R^2 denotes H or SH, and

R^3 denotes COOH, SH, or CH_3,

wherein at least one of R^1, R^2, and R^3 is SH,

and further comprising

(ii) trivalent chromium ions;

(iii) one or more than one species of halogen ions;

(iv) one, two, or more than two (preferably two or more than two, most preferably two) carboxylic acids and/or salts thereof;

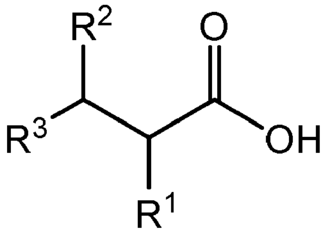
(v) phosphate anions;

(vi) nitrate anions, and

(vii) optionally cobalt ions.

[0123] Preferably, the aforementioned regarding the black-passivation composition utilized in the method of the present invention (in particular what is defined as being preferred) and what is defined for the method of the present invention applies likewise to the black-passivation composition of the present invention.

[0124] The present invention furthermore refers to the use of one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



(I),

wherein independently

R^1 denotes H, SH, or NH_2,

R^2 denotes H or SH, and

R^3 denotes COOH, SH, or CH_3,

wherein at least one of R^1, R^2, and R^3 is SH,
for black-passivating a zinc layer, wherein the zinc layer is substantially free of, preferably does not comprise, nickel.

[0125] Preferably, the aforementioned regarding the one or more than one blackening agent (in particular what is defined as being preferred) used in the black-passivation composition according to the present invention as well as what is defined for the method of the present invention applies likewise to the use of the present invention.

[0126] The present invention is described in more detail by the following non-limiting examples.

Examples

[0127] In each experiment, as substrates a plurality of steel screws (M8x55) was used, galvanized in an alkaline zinc or alkaline zinc nickel deposition composition (in Table 1 abbreviated as Zn and ZnNi, respectively).

[0128] Prior to zinc or zinc nickel galvanization, the screws were degreased, pickled with hydrochloric acid, electro cleaned, and activated with hydrochloric acid to obtain pre-treated screws, ready for galvanization.

[0129] In a second step, the pre-treated screws were galvanized in an alkaline zinc deposition composition (Protolux 3000, product of Atotech) or alkaline zinc nickel deposition composition (Reflectalloy ZNA, product of Atotech), each composition comprising about 10 g/L zinc ions. In each case, the resulting zinc layer as well as zinc nickel layer had a thickness of about 8 μm ± 2 μm. The nickel content in the zinc nickel layer was about 12% to 13%.

[0130] In a third step, the galvanized screws were rinsed with water (2x 30 seconds) and pre-treated for passivation; either by contacting with hydrochloric acid (for ZnNi galvanized screws) or strongly diluted nitric acid (for Zn galvanized screws).

[0131] In a fourth step, the screws were passivated in various acidic (pH about 1.5 to 2.5), aqueous passivation compositions for blackening. The tests are numbered as summarized in Table 1 below. All concentrations given in Table 1 are in mmol/L, based on the total volume of the respective passivation composition. Furthermore, in Table 1 "E" refers to examples according to the invention, wherein "CE" denotes a comparative example.

[0132] All passivation compositions comprise trivalent chromium ions in a concentration ranging from 4 to 10 g/L; experiments E1, CE1, CE2, and CE3, and CE6 to CE8 about 5 g/L, and CE4 and CE5 about 10 g/L.

[0133] Furthermore, cobalt (II) ions are contained in a concentration range from 0.5 g/L to 4 g/L.

[0134] In addition, nitrate anions are present in a concentration from 1 g/L to 2 g/L (E1, CE1, CE2, and CE3 as well as CE6 to CE8) and of about 30 g/L (CE4 and CE5).

[0135] Experiments E1, CE1 to CE3 as well as CE6 to CE8 additionally comprise phosphate anions in a concentration ranging from 15 g/L to 25 g/L and furthermore 7 g/L to 20 g/L chloride ions.

[0136] Passivation was carried out by contacting the galvanized screws with the respective passivation composition for 60 seconds at a temperature of about 35°C (CE4 and CE5 at about 25°C). Afterwards, the screws were rinsed with water and optionally dried at 70°C to 80°C if not further treated. Otherwise, screws were further contacted with a post-dip composition.

Table 1:

									Corrosion test (hours)		
No.	**OxAc[1]**	**SucAc[2]**	**MsAc[3]**	**MaAc[4]**	**AcAc[5]**	**TgAc[6]**	**Galvanization**	**L***	**72**	**96**	**168**
E1	126	5	**10**	0	0	0	Zn	25	7	4	2
CE 1	126	5	0	0	0	10	Zn	27	5	3	1
CE 2	126	5	0	0	0	33	Zn	26	4	2	2
CE 3	126	5	**10**	0	0	0	ZnNi	53	--	--	--
CE 4	16	0	0	18	33	0	Zn	78	4	2	2
CE 5	16	0	0	18	33	0	ZnNi	27	9	9	9
CE 6	126	5	0	0	0	0	Zn	72	3	3	2
CE 7	126	5	0	0	10	0	Zn	70	5	4	3
CE 8	126	5	0	0	20	0	Zn	68	6	5	4

"[1]" denotes: Oxalic acid; "[2]" denotes: Succinic acid; "[3]" denotes: Mercaptosuccinic acid (i.e. Thiomalic acid); "[4]" denotes Maleic acid (as anhydride); "[5]" denotes Acetic acid, "[6]" denotes Thioglycolic acid
"Corrosion test" refers to white rust formation if not specified otherwise, based on NSS test according to EN ISO 9227 (50 g/L sodium chloride solution, about pH 7 at 35°C, Liebish SMT-1000 spray cabinet). Corrosion was evaluated after 72 hours, 96 hours, and 168 hours. The corrosion rating is as follows, referenced to the total surface area of a respective screw:
10 denotes no white rust at all,
9 denotes >0% to 0.1%,
8 denotes >0.1% to 0.25%,
7 denotes >0.25% to 0.5%,
6 denotes >0.5% to 1.0%,
5 denotes >1.0% to 2.5%,
4 denotes >2.5% to 5.0%
3 denotes >5.0% to 10.0%,
2 denotes >10.0% to 25.0%,
1 denotes >25% to 50%,
0 denotes >50%

[0137] The darkness/blackening effect was evaluated by parameter L* according to the CIELAB color space definition (L*a*b* color system) and was determined via a Konica Minolta CM-700d device (sphere (SCE mode)).

[0138] As shown in Table 1, experiment E1 shows a very dark and desired blackening (L* of 25), which is even the darkest value obtained for all experiments. Furthermore, a very good corrosion resistance is obtained for a galvanic zinc layer (7 @ 72 hours). In some cases, experiments even showed a corrosion test rating after 168 hours of 4 (data not shown).

[0139] Comparative examples CE1 and CE2 refer to a commonly used blackening agent known in the art, thioglycolic acid instead of mercaptosuccinic acid. In fact, thioglycolic acid also provides a very acceptable darkness (L* of 26 and

27, respectively), although they are slightly less dark/black compared to E1. More important, E1 exhibits a significantly increased corrosion resistance compared to CE1 and CE2. In fact, CE2 even showed about 3% red rust formation after 168 hours.

[0140] Comparative example CE3 applies the inventive black-passivation composition to a galvanic zinc nickel layer. However, as shown in Table 1, no significant blackening effect was observed at all (L* of 53; no further corrosion test was carried out). This confirms that the black passivation composition utilized in the context of the present invention is specific for a zinc layer but not for a zinc nickel layer.

[0141] Comparative examples CE4 and CE5 are based on compositions disclosed in EP 1 970 470 B1. Comparative Example CE4 shows that such a respective composition does not provide any blackening/darkness on a zinc layer (additionally showing about 3% red rust formation after 168 hours), wherein comparative Example CE5 confirms that excellent blackening/darkness and corrosion resistance is obtained on a zinc nickel layer with such passivation compositions. Thus, it is again showed that the black-passivation composition utilized in the context of the present invention is specific for a zinc layer.

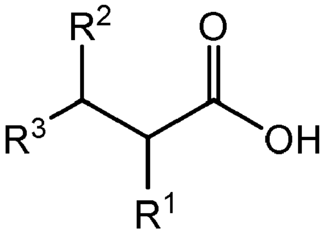
[0142] Comparative examples CE6 to CE8 confirm that the blackening/darkening effect is obtained by means of the mercaptosuccinic acid. In CE6 the passivation composition of E1 is applied with the only difference that no mercaptosuccinic acid is utilized. As a result, no blackening (L* about 70) and no useful corrosion resistance was obtained. In CE7 and CE8 mercaptosuccinic acid is replaced by acetic acid. Again, no blackening was obtained (L* about 70).

Claims

1. A method for black-passivating a zinc layer, the method comprising the steps:

   (a) providing a substrate comprising the zinc layer,
   (b) providing a black-passivation composition for said black-passivating, the composition comprising

      (i) one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



(I),

      wherein independently

         R^1 denotes H, SH, or NH_2,
         R^2 denotes H or SH, and
         R^3 denotes COOH, SH, or CH_3,

      wherein at least one of R^1, R^2, and R^3 is SH, and

      (ii) trivalent chromium ions,

   (c) contacting the substrate with said black-passivation composition such that the zinc layer is black-passivated.

2. The method of claim 1, wherein the substrate is a metal substrate, preferably a metal substrate comprising iron, more preferably an iron substrate or an iron alloy substrate, most preferably a steel substrate.

3. The method of claim 1 or 2, wherein the zinc layer is obtained from an alkaline zinc deposition composition.

4. The method of anyone of claims 1 to 3, wherein the zinc layer is substantially free of, preferably does not comprise,

nickel.

5. The method of anyone of claims 1 to 4, wherein the black-passivation composition is acidic, preferably having a pH from 0.5 to 4.5, more preferably from 0.8 to 4.0, even more preferably from 1.1 to 3.5, yet even more preferably from 1.5 to 3, most preferably from 1.8 to 2.5.

6. The method of anyone of claims 1 to 5, wherein in the black-passivation composition the one or more than one blackening agent has a total concentration ranging from 1 mmol/L to 100 mmol/L, based on the total volume of the black-passivation composition, preferably from 2 mmol/L to 75 mmol/L, more preferably from 4 mmol/L to 50 mmol/L, even more preferably from 5 mmol/L to 35 mmol/L, yet even more preferably from 6 mmol/L to 20 mmol/L, most preferably from 8 mmol/L to 14 mmol/L.

7. The method of anyone of claims 1 to 6, wherein R^1 denotes H or SH, preferably SH.

8. The method of anyone of claims 1 to 7, wherein R^2 denotes H.

9. The method of anyone of claims 1 to 8, wherein R^3 denotes COOH or SH, preferably COOH.

10. The method of anyone of claims 1 to 9, wherein the one or more than one blackening agent comprises mercapto-succinic acid, salts, and stereoisomers thereof.

11. The method of anyone of claims 1 to 10, wherein the black-passivation composition is substantially free of, preferably does not comprise, formic acid, acetic acid, and salts thereof, more preferably is substantially free of, preferably does not comprise, a sulfur-free mono-carboxcylic acid and salts thereof.

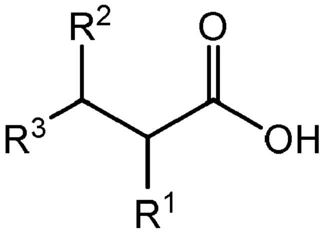
12. The method of anyone of claims 1 to 11, wherein the black-passivation composition is further comprising

(iii) one or more than one species of halogen ions;
(iv) one, two, or more than two carboxylic acids and/or salts thereof;
(v) phosphate anions;
(vi) nitrate anions; and/or
(vii) cobalt ions.

13. The method of anyone of claims 1 to 12, wherein in step (c) the black-passivation composition has a temperature in a range from 15°C to 70°C, preferably from 20°C to 55°C, even more preferably from 25°C to 45°C, most preferably from 30°C to 40°C.

14. A black-passivation composition comprising

(i) one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



(I),

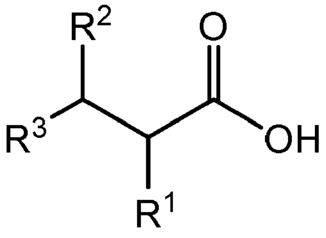
wherein independently

R^1 denotes H, SH, or NH_2,
R^2 denotes H or SH, and
R^3 denotes COOH, SH, or CH_3,

wherein at least one of R^1, R^2, and R^3 is SH,

and further comprising
(ii) trivalent chromium ions;
(iii) one or more than one species of halogen ions;
(iv) one, two, or more than two carboxylic acids and/or salts thereof;
(v) phosphate anions;
(vi) nitrate anions, and
(vii) optionally cobalt ions.

15. Use of one or more than one blackening agent selected from the group consisting of compounds of formula (I), salts, and stereoisomers thereof



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wherein independently

R^1 denotes H, SH, or NH_2,
R^2 denotes H or SH, and
R^3 denotes COOH, SH, or CH_3,

wherein at least one of R^1, R^2, and R^3 is SH,

for black-passivating a zinc layer, wherein the zinc layer is substantially free of, preferably does not comprise, nickel.

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EUROPEAN SEARCH REPORT

Application Number
EP 22 17 1011

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C23C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
The Hague	10 November 2022	Panitz, J

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