METHOD FOR COATING METAL SURFACES, SUBSTRATES COATED IN THIS WAY, AND USE THEREOF

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ABSTRACT

The invention relates to a method for coating metal surfaces with an acidic aqueous conversion composition which contains: in total 0.01 to 1 g/l of TiF$_5^{2+}$, ZrF$_5^{2+}$ and/or HIF$_5^2$ calculated as ZrF$_5^{2+}$, 0 or 0.01 to 1 g/l in each case of Fe$^{2+}$, Mn and/or Zn ions, of which at least one type of these ions is present in a content range from 0.01 to 1 g/l, 0 or 0.01 to 2 g/l of anion of carbonate, nitrate and/or sulphate, and 0 or 0.001 to 2 g/l of carboxylate and/or sulphonate anions, wherein the content of molybdate and/or of P-containing oxy anions is in each case <0.1 g/l or is approximately 0 g/l, and wherein the composition has a pH value in the range from 2.5 to 6.5. The invention also relates to a corresponding coating and to the use of the substrates coated in this way.
METHOD FOR COATING METAL SURFACES, SUBSTRATES COATED IN THIS WAY, AND USE THEREOF

[0001] The invention relates to a method for coating metallic surfaces with a conversion layer, optionally colored, in particular for replacing an alkaline phosphating treatment, such as, for example, iron phosphating, substrates with metallic surfaces coated accordingly, as well as the use of these coated substrates.

[0002] Methods for producing alkali phosphate coatings, in particular as pretreatment layers before painting, have been described in isolated cases. Fresh, unused alkali phosphate solutions usually have little or no aluminum, iron and zinc content. In addition to ions of at least one alkali metal and/or ammominum, the aqueous acidic alkali phosphate solutions also contain phosphate ions and, because of the pickling effect of these solutions on the metallic surfaces, they also have ion contents from the metals dissolved out of the metallic surfaces such as aluminum, iron and/or zinc as well as traces of alloy constituents of the partially pickled metallic materials. The main phases formed in the alkali phosphate layer during alkali phosphating are the corresponding phosphates, oxides and/or hydroxides of the metals from the surfaces of the basic substrates to be treated.

[0003] Alkali phosphate solutions and/or coatings are also referred to as iron phosphate solutions and/or coatings in use on iron and steel materials. Alkali phosphate coatings are also referred to in general as layers of the so-called "non-layer-forming type of phosphating" according to Werner Rausch: Die Phosphatierung von Metallen [The Phosphating of Metals], Stahlguh 1988 (see pages 109-118 in particular). This terminology is misleading because layers are also formed here, but they are much thinner than the other phosphate layers, such as the various types of zinc phosphating, for example. The alkali phosphate solution always contains an elevated amount of at least one alkali metal, for example, sodium and/or ammonium.

[0004] Alkali phosphating can usually be performed in a simple and economical manner, but high quality alkali phosphate coatings provide only limited corrosion protection, even after the second subsequent corrosion treatment, usually a) the corrosion protection is no better than, i.e., no less than 3 mm below-surface corrosion, tested in the salt spray test according to DIN 50021 NSS for 500 hours on a powder enamel coating, based on epoxy-polyester powder coating with a thickness of 60 to 80 μm on cold rolled steel plate and/or usually b) the corrosion protection is no better than, i.e., no less than, 4 mm below-surface corrosion in the salt spray test according to DIN 50021 NSS for 500 hours with a wet enamel coating, based on a polyurethane-isocyanate enamel of 60 to 80 μm thickness on a cold rolled steel plate and usually c) paint adhesion of better than, i.e., no less than GT 3 on a cross-cut test after 240 hours of testing in the condensate climate test according to DIN EN ISO 2409 with a powder enamel coating, based on epoxy-polyester powder enamel 60 to 80 μm thick on a cold rolled steel plate.

[0005] Therefore, in alkali phosphating, it is usually necessary to apply an additional second conversion layer and in most cases even at least one more subsequently applied enamel layer. Such multistep methods are not only particularly complex but also require additional baths and/or treatment zones as well as optionally also additional rinse steps and/or drying steps, in addition to being cost-intensive and time-consuming. The paint adhesion with the alkali phosphate coating is frequently also inadequate, so that then there must be an additional conversion coating, for example, based on zirconium hexafluoride and/or silane before applying the enamel. The coating process becomes especially complex and expensive in this way. The high phosphate content in alkali phosphating is also a disadvantage because phosphate in wastewater must be disposed of in a complex process.

[0006] Alkali phosphating is frequently applied in multiple steps, so that primarily only a cleaning is performed in the first step, and the layer is performed in the second step. Next the layer is rinsed and/or rerinsed.

[0007] The object of the invention was to discover aqueous compositions that could be applied easily and would have the most environmentally friendly composition possible and would also yield greater corrosion protection than high quality alkali phosphate coatings.

[0008] This object is achieved with a method for coating metallic surfaces with an aqueous acidic conversion composition, which is a solution or dispersion that is characterized in that it contains:

[0009] a total of 0.01 to 1 g/L of TiF₆²⁺, ZrF₆²⁺ and/or H₂F₆²⁺ in the form of ions, calculated as ZrF₆²⁺,
[0010] 0 or 0.01 to 1 g/L of Fe²⁺, Mn and/or Zn ions, at least one type of which may be present in the concentration range of 0.01 to 1 g/L,
[0011] wherein preferably Mn and/or Zn ions are present,
[0012] 0 or 0.01 to 2 g/L of an organic polymer and/or an organic copolymer, which is stable at a pH <6.5, based on the solids content,
[0013] 0 or 0.01 to 2 g/L of particulate SiO₂ with an average particle diameter <0.3 μm, measured on a scanning electron microscope and based on the solids content,
[0014] approx. 0 or 0.01 to 10 g/L of at least one surfactant,
[0015] approx. 0 or 0.05 to 10 g/L of ions selected from the group consisting of carbonate, nitrate and sulfate, converted to NO₃⁻ even if CO₃²⁻ or SO₄²⁻ is present and
[0016] 0 or 0.001 to 2 g/L of carboxylate and/or sulfonate anions which cause little or no impairment of the layer formation, calculated as the corresponding anions,
[0017] wherein the molybdate content, calculated as MoO₃²⁻ and/or the P-containing oxygen content calculated as PO₄³⁻ is <0.1 g/L or approx. 0 g/L each and
[0018] wherein the aqueous acidic composition has a pH in the range of 2.5 to 6.5 and preferably in the range of 3.0 to 5.5.

[0019] The ions of TiF₆²⁺, ZrF₆²⁺ and/or H₂F₆²⁺ are largely equivalent and interchangeable in the aqueous acidic conversion composition but the ions of ZrF₆²⁺ often yield the best properties of the conversion coating produced with them. It is preferable here that in the case of a cation content of the aqueous conversion composition of only Fe²⁺ ions, based on the total Fe²⁺, Mn and Zn ion content, that this content originates at least in part from an intentional additive.

[0020] The ions of manganese and zinc as well as, to a limited extent, also those of Fe²⁺ are largely equivalent and interchangeable in the aqueous acidic conversion composition, but in many cases the ions of manganese and/or zinc
yield the best properties of the conversion coating produced with them. They preferably contain 0 or 0.01 to 0.3 g/L or 0.02 to 0.15 g/L of Fe⁺⁺⁺ ions as well as 0.01 to 1 g/L of Mn ions and/or 0.01 to 1 g/L or 0.1 to 0.6 g/L of Zn ions. It especially preferably contains 0.1 to 0.6 g/L or 0.2 to 0.4 g/L of Mn ions and/or 0.1 to 0.6 g/L or 0.2 to 0.4 g/L of Zn ions.

[0021] Adding an organic polymer and/or an organic copolymer may contribute toward a further improvement in the properties of the conversion coating produced therewith and then it may optionally be possible to omit a subsequent enamel coating. If the enamel coating is omitted, then we speak of blank corrosion protection.

[0022] Addition of extremely fine particulate SiO₂ may have a positive effect similar to that of adding an organic polymer and/or an organic copolymer but often with the difference that the layer formation and thus the coating are even more uniform.

[0023] Fundamentally at least one nonionic, anionic, cationic and/or zwitterionic surfactant may be added. Addition of at least one nonionic surfactant is especially preferred here.

[0024] The ions of manganese and zinc as well as to a limited extent also those of Fe⁺⁺⁺ are largely equivalent and interchangeable in the aqueous acidic conversion composition but the ions of manganese and/or zinc often yield the best properties of the conversion coating produced with them. The coating preferably contains 0 or 0.01 to 0.3 g/L or 0.02 to 0.15 g/L of Fe⁺⁺⁺ ions and 0.01 to 1 g/L of Mn ions and/or 0.01 to 1 g/L or 0.1 to 0.6 g/L of Zn ions. It especially preferably contains 0.1 to 0.6 g/L or 0.2 to 0.4 g/L of Mn ions and/or 0.1 to 0.6 g/L or 0.2 to 0.4 g/L of Zn ions.

[0025] Addition of an organic polymer and/or an organic copolymer may contribute toward an even further improvement in the properties of the conversion coating produced therewith and it may optionally allow the omission of a subsequent enamel coating. If an enamel coating is omitted, this is known as bare metal corrosion protection.

[0026] Addition of extremely fine particulate SiO₂ may have an effect similar to that of adding an organic polymer and/or an organic copolymer but often with the difference that layer formation and thus coating are even more uniform.

[0027] Fundamentally at least one nonionic, anionic, cationic and/or zwitterionic surfactant may be added. Addition of at least one nonionic surfactant is especially preferred here.

[0028] Anions selected from the group consisting of carbonate, nitrate and sulfate are often added by addition of cations in the form of water-soluble salts. Nitrites are especially preferred here.

[0029] Addition of carboxylate anions, for example, in the form of acetic acid and/or a manganese carboxylate is fundamentally possible as an alternative or as an addition to these ions and is often suitable for preventing or reducing the amount of the anions of mineral acids. It is fundamentally possible to use all types of carboxylic acids and their derivatives, such as the salts and esters, which are water soluble are and are stable in the pH value range, which do not have any complex substance composition, which form anions in water, which do not interfere the formation of a layer, depending on the type and quantity of anions, and which optionally form complexes with alkali and/or alkaline earth metal ions, which are not involved in the formation of the layer.

[0030] These include in particular aliphatic carboxylic acids and mono-, di- and/or polycarboxylic acids such as hydroxyacrylic acids, for example. When adding carboxylate anions, care should be taken to ensure that they do not interfere with the formation of the layer because citrate, for example, and certain other individual complexing agents may interfere with the formation of a layer, depending on the type and quantity of anions.

[0031] Addition of at least one sulfonic acid such as methane sulfonic acid, amidosulfonic acid and/or one of their derivatives, for example, may be favorable here in order to act as an accelerator and/or as an additional counterion.

[0032] Addition of molybdate has proven successful only when very small amounts are added.

[0033] Addition of oxanions that contain phosphorus, for example, orthophosphate, condensed phosphates and phosphonates, is to be avoided in particular because of the possible burden on wastewater and possibly also because of a greater production of sludge, which can result in complicated disposal of the wastewater and/or sludge. In particular in the case of P-containing oxanions, it is preferable not to add any P-containing oxanions because of reasons involving environmental safety and the need to avoid the expensive disposal associated with phosphorus, and it is preferably necessary to be sure that no P-containing oxanions are entrained into the process.

[0034] In the case of the method according to the invention, it is preferable for the aqueous acidic composition to additionally contain:

[0035] 0.03 to 5 g/L of the sum of ions of lithium, sodium and/or potassium,

[0036] 0 or 0.05 to 5 g/L of ammonium ions,

[0037] approx. 0 or 0.05 to 0.3 g/L of the sum of Co and/or Ni ions,

[0038] 0.00 to 0.1 and/or 0.8 g/L of chloride calculated as Cl⁻, nitrite, calculated as NO₂⁻ and/or peroxide, calculated as H₂O₂,

[0039] 0 or 0.01 to 0.5 g/L of fluoride, calculated as F⁻

[0040] 0 or 0.01 to 0.2 g/L of vanadate ions, calculated as VO₃⁻.

[0041] In most cases, it is fundamentally impossible to entirely avoid the presence of some lithium, sodium, potassium and ammonium content to achieve charge equalization and to avoid adding only polyvalent cations, such as heavy metal ions. Of the monovalent cations, sodium ions in particular are especially preferred. They are largely equivalent in the aqueous acidic conversion composition and can be used interchangeably and are often necessary for regulating the pH.

[0042] As in many coating processes, here again, the addition of cobalt and/or nickel is advantageous to achieve better corrosion protection, although these elements are problematical with respect to environmental safety and occupational hygiene.

[0043] It is sometimes necessary to add at least one accelerator, in particular to add a chlorate, nitrite and/or peroxide. However, it is important to add a suitable amount, for example, an NO₃⁻ content of much less than 1 g/L. When adding at least one accelerator, the formation of a layer may be accelerated and the properties of the coating produced in this way can be improved. Overdosing of accelerator should be avoided so as not to interfere with the formation of a
layer, as in the case of Example B40. Addition of nitroguanidine has not proven to be advantageous.

[0044] The complex fluoride content alone often leads to a lower free fluoride content. Addition of at least one fluoride may lead to a slightly higher free fluoride content. The free fluoride content, which is favorable for substrate surfaces that contain aluminum in particular, is often in the range of 0.01 to 9.5 g/L, calculated as F.

[0045] Addition of at least one vanadium compound can significantly increase the corrosion protection.

[0046] The possibility cannot be ruled out that additional element concentrations of the metallic surfaces of the substrates and of the installation may enter the bath due to the pickling effect of the aqueous acidic conversion composition and may optionally even accumulate in the bath composition, in particular Fe^{2+} ions and alloying elements and their ions.

[0047] On the other hand, the possibility is usually also not ruled out in the case of today's coating methods and installations that amounts of ions and substances from other areas of the installation such as a cleaning step used in the past, for example, may perhaps be entrained in small amounts, even despite the use of a water rinse. Amounts of alkaline metals, ammonium, complexing agents, surfactants, anionic contaminants of the cleaning bath and/or additional impurities and/or ions in particular may be entrained into the bath composition according to the invention in this way. However, it is not absolutely necessary to provide a separate previous cleaning step so that the input of foreign ions can be mostly ruled out by means of a chemical treatment solution. In the best case, a cleaning step may be performed with water containing a surfactant but without any buffer content.

[0048] On the one hand, the cleaning may be performed before the corrosion coating step, so that the cleaning is performed prior to contacting the substrate with the aqueous composition. On the other hand, the aqueous composition may also contain at least one surfactant in addition to or instead of this cleaning step, so that the cleaning and conversion coating are (also) performed in the same process step.

[0049] Preferably little or none of the following are intentionally added to the aqueous conversion composition: 0.1 g/L carboxylic acids, phosphates, phosphonates and/or compounds and/or ions of calcium, chromium, chromate, cobalt, copper, magnesium, molybdenum, nickel, vanadium and/or tin and/or silane, silanol, siloxane, polysiloxane. Silane, silanol, siloxane and polysiloxane refer to silane, silanol, siloxane and/or polysiloxane because in water and in coating starting with a silane, for example, it can very rapidly yield silanols and/or siloxanes, which can sometimes also yield polysiloxanes, depending on the chemical definition of each.

[0050] The aqueous acidic conversion composition of alkaline earth metals such as calcium and/or magnesium is preferably a total of no more than 0.2 g/L to prevent precipitation in the presence of fluorides if possible.

[0051] The following variants are especially preferred:

[0052] The acidic aqueous conversion composition has a pH in the range of 2.5 to 6.5 and contains consists of or essentially a total of:

[0053] Variant A: 0.01 to 1 g/L of TiF_{4}^{2-}, ZrF_{6}^{2-} and/or HF F_{5}^{2-} in the form of ions, calculated as ZrF_{5}^{2-} and 0 or 0.01 to 1 g/L of Fe^{2+}. Mn and/or Zn ions, such that at least one species of these ions is present in the content range from 0.01 to 1 g/L, as well as optionally 0.01 to 2 g/L of particulate SiO$_2$ with an average particle diameter <0.3 μm, based on the solids content, and/or optionally 0.01 to 10 g/L of at least one surfactant and with a phosphate content <0.1 g/L PO$_4$.

[0054] Variant B:

[0055] 0.01 to 1 g/L of TiF_{4}^{2-}, ZrF_{6}^{2-} and/or HfF_{6}^{2+} in the form of ions, calculated as ZrF_{6}^{2-}.

[0056] 0 or 0.01 to 1 g/L of Fe^{2+}, Mn and/or Zn ions, of which at least one species of these ions is present in the content range of 0.01 to 1 g/L, and 0.01 to 2 g/L of organic polymer and/or copolymer which is stable at a pH <6.5, based on the solids content,

[0057] and optionally 0.01 to 2 g/L of particulate SiO$_2$ with an average particle diameter <0.3 μm, based on the solids content,

[0058] and optionally 0.01 to 10 g/L of at least one surfactant,

[0059] and optionally 0.05 to 10 g/L of anions, selected from the group consisting of carbonate, nitrate and sulfate, converted to NO$_3$ and even if CO$_3$ and SO$_4$ is present and

[0060] optionally 0.001 to 2 g/L of carboxylate and/or sulfonate anions, which cause little or no impairment of the layer-forming process, calculated as the corresponding anions,

[0061] wherein the molybdate content, calculated as MnO$_2$ and/or the P-containing oxygen content, calculated as PO$_4$ is <0.1 g/L or approx. 0 g/L.

[0062] Variant C:

[0063] 0.01 to 1 g/L of TiF_{4}^{2-}, ZrF_{6}^{2-} and/or HfF_{6}^{2+} in the form of ions, calculated as ZrF_{6}^{2-}.

[0064] 0 or 0.01 to 1 g/L of Fe^{2+}, Mn and/or Zn ions, of which at least one species of these ions is present in the content range from 0.01 to 1 g/L, and a molybdate content, calculated as MoO$_2$ in the range of 0.01 to <0.5 g/L plus optionally 0.01 to 2 g/L of organic polymer and/or copolymer which is stable at a pH <6.5, based on the solids content, and optionally 0.01 to 2 g/L of particulate SiO$_2$ with an average particle diameter <0.3 μm, based on the solids content,

[0065] and optionally 0.01 to 10 g/L of at least one surfactant,

[0066] and optionally 0.05 to 10 g/L of anions, selected from the group consisting of carbonate, nitrate and sulfate, converted to NO$_3$, even if CO$_3$ and SO$_4$ is present and

[0067] wherein the molybdate content, calculated as MnO$_2$ in the range of 0.01 to <0.5 g/L and the P-containing oxygen content, calculated as PO$_4$ is <0.1 g/L or approx. 0 g/L.

[0068] With all three variants, it is preferable for Mn and/or Zn ions to be added, while the Fe$^{2+}$ ion content is pickled out of the iron-rich metallic substrate preferably by a pickling effect of the acidic conversion composition. The coating is optionally then enumerated at least once.

[0069] An aqueous acidic conversion composition which is a solution or dispersion containing the following is especially preferred:

[0070] a total of 0.01 to 1 g/L of TiF$_4$, ZrF$_6$ and/or HfF$_6$ in the form of ions, calculated as ZrF$_6$,
0 or 0.01 to 1 g/L of Mn and/or Zn ions, at least one type of these ions being present in the concentration range of 0.01 to 1 g/L.

0 or 0.01 to 0.5 g/L of Fe^{2+} ions.

wherein preferably Mn and/or Zn ions are present,

0 or 0.01 to 1 g/L of an organic polymer and/or an organic copolymer which is stable at a pH of <6.5, based on the solids content,

0 or 0.01 to 1 g/L of particulate SiO2 with an average particle diameter of <0.3 μm, measured with a scanning electron microscope and based on the solids content,

approx. 0 or 0.01 to 6 g/L of at least one surfactant,

approx. 0 or 0.05 to 6 g/L of anions selected from the group consisting of carbonate, nitrate and sulfate, converted to NO3^-, even if CO3^{2-} or SO4^{2-} is present and

0 or 0.001 to 1 g/L of carboxylate and/or sulfonate anions, which have little or no negative effect on the formation of a layer, calculated as the corresponding anions,

wherein the molybdate composition, calculated as MoO4^{2-} and/or the P-containing oxanion content, calculated as PO4^{3-}, each amounts to <0.1 g/L or approx. 0 g/L, and

wherein the aqueous composition has a pH in the range of 2.5 to 6.5 and preferably in the range of 3.0 to 5.5.

The aqueous acidic composition especially preferably contains, consists of or essentially comprises:

0.01 to 5 g/L of the total of ions of lithium, sodium and/or potassium,

0 or 0.05 to 5 g/L of ammonium ions,

approx. 0 or 0.05 to 0.2 g/L of the total of Ca and/or Ni ions,

0 or 0.01 to 0.4 g/L of chloride, calculated as ClO4^-, nitrite, calculated as NO2^- and/or peroxide, calculated as H2O2,

0 or 0.01 to 0.5 g/L of free fluoride, calculated as F^- and

0 or 0.01 to 0.1 g/L of vanadate ions, calculated as VO3^{2-}.

The bath composition according to the invention may preferably also be prepared by diluting one or two concentrates with water by a dilution factor in the range of 5:1 to 40:1. The second concentrate may contain a surfactant, for example, and may also be aqueous. Fluoride may also be added as a nonfluoride, a bifluoride and/or in the form of the corresponding acids. The free fluoride content is often in the range of 0.01 to 0.2 g/L.

For the aqueous acidic conversion composition, it is preferably possible to work with municipal water having a conductance of approx. 200 to 600 μS/cm, for example, or with deionized water for the bath as well as for supplementing the liquid level in the bath as well as for the first rinse after the conversion coating.

After this first rinse step, a deionized rinse using deionized water is necessary as a standard only as a final rinse to prevent drying of the salt load, which can result in inferior corrosion protection.

The paint adhesion and anticorrosion effect on hot-dip galvanized (HDG) steel plate tend to be somewhat inferior to that on cold rolled steel (CRS) plate. If the zinc content in the aqueous acidic conversion composition is decreased or even omitted entirely, then the properties of the coating on hot-dip galvanized steel plate are often improved.

An Fe^{2+} ion content often has a negative effect on the properties of the coating, but it has been found that Fe^{3+} ions are gradually oxidized to Fe^{3+} and form a sludge sediment in the bath. It is therefore preferable for the aqueous acidic conversion composition to have a manganese and/or zinc ion content.

A surfactant-containing aqueous composition can help to either further improve the cleaning effect after degreasing and/or pickling or to at least omit the degreasing step before conversion coating, so that it is possible to perform the cleaning in a one-pot process.

With the method according to the invention, it is preferable for at least one substrate having metallic surfaces to be brought in contact with the aqueous composition for a period of time in the range of 1 second to 10 minutes, in particular 0.5 to 10 minutes in treatment of parts. A period of time in the range of 1 to 10 minutes is especially preferred, in particular in dipping, or preferably 0.5 to 6 minutes, in particular in spraying. Thus even with these compositions the same treatment times may be used as in alkali phosphating, which facilitates switching from alkali phosphating installations to the conversion coating according to the invention, because in alkali phosphating, 3 to 5 minutes are frequently also used. Alternatively, the composition according to the invention may also be applied to strip steel metal if it is still rinsed with water after the strip coating (rinse process). In strip coating, the metal strip is preferably brought in contact with the aqueous composition over a period of time in the range of 1 second to 2 minutes.

With the method according to the invention, it is preferable for the substrate having metallic surfaces to be a temperature in the range of 5 to 90° C., preferably in the range of 15 to 70° C. or 30 to 60° C. when brought in contact with the aqueous composition. On the other hand, it is also preferable for the aqueous composition to have a temperature in the range of 35 to 70° C. or 45 to 60° C. when brought in contact with the substrate having metallic surfaces. Then the temperatures used with these compositions may be the same as those as in alkali phosphating, where temperatures of 50 to 55° C. are often used.

This object is also achieved with a coated substrate having metallic surfaces that have been coated according to the invention.

It is preferable here for the coating thereby produced to have a layer thickness of 0.3 to 3 μm and/or for the total of the application of zirconium, measured as an element and/or titanium in the conversion coating, to be in the range of 1 to 300 mg/m² or preferably in the range of 15 to 150 mg/m², measured by X-ray fluorescence analysis (RFA).

It is also preferable for the coating produced in this way to be colored, iridescent or gray. Interference colors of the first order or of a higher order or colors in which the interference color has superimposed on it the color of ions preferably occur with the coating produced in this way. These colors are similar to those which are obtained in alkali phosphate coating. The colors often help to approximately estimate the thickness and to some extent even the uniformity and/or quality of a coating. If this is even possible at a greater distance of viewing, then it is especially advantageous with a coating process.
For particularly high quality application purposes in particular, it is preferable for the conversion coating thereby produced according to the invention to next be rinsed with water or with an aqueous after-rinse solution, in particular one containing silane, an organic polymer and/or an organic copolymer and optionally also to be enameled. The after-rinse may be performed using aqueous after-rinse solutions, for example, Gardolene® D95, which contains a phenolic resin or Gardolene® D6890, based on silane.

The aqueous after-rinse solution especially preferably contains at least one a) cation selected from alkaline earth metal cations, aluminum cations, titanium cations, yttrium cations and heavy metal cations, b) an organic polymer and/or an organic copolymer, c) silane, silanol, siloxane and/or polycondensate and/or d) a complex fluoride, where “complex fluoride” also stands for the corresponding fluorine-containing acid. In particular aminosilanes with one, two or even more amino groups and/or bis-silyl silanes are the preferred silanes here.

In a particularly preferred process according to the invention, a coating is applied with an aqueous acidic composition according to the invention, then optionally rinsed with water thereafter and/or optionally rerinsed thereafter with an aqueous composition, and the at least one coating prepared in this way is then enameled at least once.

In a particularly preferred process according to the invention, a coating is applied with an aqueous acidic composition according to the invention, based on 0.01 to 1 g/L of TiF$_4^{2-}$, ZrF$_6^{2-}$ and/or H$_2$TiF$_6^{2-}$ or only ZrF$_6^{2-}$ in the form of ions, calculated as ZrF$_6^{2-}$ and 0 or 0.01 to 1 g/L of Fe$^{3+}$, Mn and/or Zn ions, of which at least one species of these ions is present in the content range from 0.01 to 1 g/L, as well as optionally 0.01 to 2 g/L of particulate SiO$_2$ with an average particle diameter <0.3 μm, based on the solids content and/or optionally 0.01 to 10 g/L of at least one surfactant, which is essentially phosphate-free and essentially phosphonate-free, then the coating is optionally rinsed with water and/or optionally thereafter rerinsed with an aqueous composition, based on zirconium complex fluoride, silane and/or organic polymer copolymer, which is stable at a pH of <6.5, and the at least one coating produced in this way can next be enameled at least once. Because of the surfactant content in the aqueous acidic composition according to the invention, it may optionally be possible to omit a previous cleaning step.

The conversion coating thereby produced according to the invention may contain no organic polymer and no organic copolymer, preferably without subsequent rinsing with water or preferably with an aqueous after-rinse solution, in particular one that contains silane, an organic polymer and/or an organic copolymer, then dried and optionally also enameled.

Alternatively, if the conversion coating produced in this way according to the invention contains an organic polymer and/or an organic copolymer, preferably used without coating it with a primer, enamel or adhesive.

The conversion coating produced in this way according to the invention may optionally also be coated preferably at least once with a primer, enamel or adhesive, optionally after at least one rinsing with water and/or an aqueous after-rinse solution. Thus, the same treatment steps, sequences and methods as in alkali phosphating may be successfully used, as needed, even with these compositions.

The coating produced in this way may in an excellent manner represent a substitute for an alkali phosphate coating such as an iron phosphate coating, for example.

The at least one substrate having metallic surfaces coated according to the invention is preferably used as an architecture element, as a container, as a construction or connecting element, as a profile element, as a heating body element, as a molding body with a complex shape and/or as a component in construction, energy technology, automotive engineering, equipment design, household appliances or mechanical engineering.

It was surprising that excellent coatings, which have an excellent corrosion resistance, excellent paint adhesion and in most cases also a definite color are obtained with the aqueous conversion compositions according to the invention. The corrosion resistance on steel surfaces is almost as good as that of a high quality zinc phosphating and is thus definitely superior to the corrosion resistance of a high quality alkali phosphating treatment without having used an after-rinse solution subsequently to improve the properties of the coating. When using an additional after-rinse solution, the corrosion resistance of a high quality zinc phosphating can even be achieved.

It was also surprising that an excellent substitute for alkali phosphating can be obtained in a comparatively simple process, which is simple and environmentally friendly and in some cases even yields fully similar results.

The composition according to the invention and the process according to the invention are particularly advantageous in the chemical pretreatment of surfaces of various steel substrates, which are used in the metal-working industry, where it is possible to perform a cleaning in one step and at the same time to apply a conversion layer that can be enameled, which is why this three-step process of cleaning with conversion coating, rinse with tap water and rinsing with deionized water is fully sufficient. In particular the bath analysis is very simple to handle because an accurate determination of anions and cations is rarely necessary since the pH and the conductivity usually provide sufficient information about the chemical condition of the bath.

The process according to the invention can be used to produce a colored, iridescent, gray or colorless (as in the case of B40) passivation layer (without enameling) or a colored, iridescent, gray or colorless (as in the case of B40) conversion coating (with enameling). A passivation layer per se is also a coating produced by conversion. Therefore, the term “conversion coating” in the sense of this patent application also includes the term “passivation layer,” if or as long as no enamel layer has been applied even in the claims, for example.

The process according to the invention may be used as a substitute for an alkali phosphating process or in isolated cases may even be used to replace a zinc phosphating process. The products produced with the inventive process may be used in a variety of ways, in particular as architectural elements, as containers, as construction elements or connecting elements, as profile elements, as heating elements, as molded parts having a complex shape and/or as components in construction engineering, energy technology, automotive engineering, equipment manufacture, household appliance manufacture or mechanical engineering.
neering and, for example, as heating elements, as frames, as sheets, as linings, as angles or as components in the interior of motor vehicles or aircraft.

**EXAMPLES AND COMPARATIVE EXAMPLES**

**[0113]** The subject matter of the invention will now be explained in greater detail on the basis of exemplary embodiments. These examples were carried out using the substrates, process step, substances and mixtures discussed below.

**[0114]** The following standard sheet metal plates were used: Gardobond® C of cold rolled steel, CRS, from St14 DC05, Gardobond® HDG/5 from the corresponding hot-dip galvanized steel or Gardobond® F from AA 5005 from AlMg1 from Chemetall GmbH for coating. Unless otherwise indicated, standard Gardobond® C plates were used.

**[0115]** Aqueous conversion coatings corresponding to those listed in Table 1 were prepared using as the surfactant a nonionic surfactant of the Gardobond® additive H7438 which ensured an additional cleaning of the metal surface. The alkaline potassium hydroxide-stabilized SiO₂ dispersion Gardobond® additive H7157 from Chemetall GmbH had a solids content of 20% and an average particle size of 0.2 μm. The polymer dispersion 1 AC 2773, based on acrylate from Alberdingk had a solids content of 53%. The copolymer dispersion 2 VA 294 VP containing acrylate from Alberdingk had a solids content of 47%. The acrylate-containing copolymer dispersion 3 AS 2084 VP from Alberdingk had a solids content of 59%. Copolymer, SiO₂ particles and/or surfactant were added separately to the previously prepared aqueous conversion composition toward the end of the mixing process. In individual experiments ammonium molybdate was added.

**[0116]** The plates were conversion coated at 55°C for 3 minutes with a cleaning effect. Then they were rinsed once with process water and then with deionized water before drying the coated plates at 120°C in a drying cabinet for at least 10 minutes. When using a different temperature, no definite difference in quality was observed.

**[0117]** Next, one and only one enamel layer was applied to the conversion coated plates. Either an epoxy-polyester powder coating of Interpon® 700 from Akzo Nobel Powder Coatings GmbH was applied in a layer thickness of 60 to 80 μm, or a wet coating of Alexit® Monolayer, based on polyurethane and isocyanate from Mankiewicz, was applied in a layer thickness of 60 to 80 μm or Catholuard® 350, a black cathodic dip coat from BASF, was applied in a layer thickness of 20 μm.

**[0118]** The enamel adhesion of the enamelled samples was determined in the cross-cut method according to DIN EN ISO 2409 before and after 240 hours of alternating climate test. The corrosion resistance of the enamelled samples was determined in the salt spray test according to DIN 50021 over 500 hours in the neutral salt spray test NSS in which case a single enamel layer was applied—unlike what is customary in the Asian and North American markets.

**[0119]** The layer weight was measured in mg/m² using X-ray fluorescence analysis for an application of elemental zirconium. The element zirconium is often the indicator element for the quality of the coating, wherein different applications of metal to zirconium were deposited using the same aqueous composition but different metal substrates.

**[0120]** In the Comparative Examples VB1 and VB2, the examples according to the invention were compared with high quality alkali phosphating, which is widely used internationally on Gardobond® C plates made of cold rolled steel; the typical procedure in alkali phosphating, which is also known as iron phosphating, when used on iron and steel materials, was performed using Gardobond® WH =Gardobond® A 4976 on steel surfaces at 55°C for 3 minutes, rinsing with deionized water and optionally with a subsequent after-rinse for 5 minutes with a Gardolene® D 6800 after-rinse based on ZrF₄ before drying for at least 10 minutes in a drying cabinet at 120°C.

### Table 1

<table>
<thead>
<tr>
<th>Content in g/L</th>
<th>VB1</th>
<th>VB2</th>
<th>VB3</th>
<th>VB4</th>
<th>VB5</th>
<th>VB6</th>
<th>B1</th>
<th>B2</th>
<th>B3</th>
<th>B4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron phosphating GB</td>
<td>A 4976</td>
<td>A 4976</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Zr as ZrF₄</td>
<td>—</td>
<td>—</td>
<td>0.50</td>
<td>1.00</td>
<td>0.05</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Surfactant: GBA H7438</td>
<td>4</td>
<td>4</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
<td>3</td>
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<td>3</td>
</tr>
<tr>
<td>pH</td>
<td>5.4</td>
<td>5.4</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>4.8</td>
<td>3.5</td>
<td>4.2</td>
<td>4.8</td>
<td>5.4</td>
</tr>
<tr>
<td>After-rinse with Gardolene® D6800/6</td>
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<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Color of the layer</td>
<td>blue</td>
<td>purple</td>
<td>blue</td>
<td>purple</td>
<td>lightly golden</td>
<td>yellow</td>
<td>blue*</td>
<td>light golden</td>
<td>yellow</td>
<td>blue</td>
</tr>
<tr>
<td>Layer weight of Zr in mg/m²</td>
<td>0</td>
<td>7</td>
<td>41</td>
<td>77</td>
<td>55</td>
<td>46</td>
<td>79</td>
<td>105</td>
<td>134</td>
<td>81</td>
</tr>
</tbody>
</table>

Enamel adhesion in the cross-cut test after 240 hours of condensate climate test according DIN EN ISO 2409:

<table>
<thead>
<tr>
<th>In wet paint 60-80 μm</th>
<th>GT 4</th>
<th>GT 1</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
<th>GT 0</th>
</tr>
</thead>
<tbody>
<tr>
<td>In powder coating 60-80 μm</td>
<td>GT 3</td>
<td>GT 2</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

Corrosion resistance in a salt spray test according to DIN 50021 500 h NSS in mm:

<table>
<thead>
<tr>
<th>In wet paint 60-80 μm</th>
<th>8.0</th>
<th>3.0</th>
<th>3.0-4.5</th>
<th>2.0-3.0</th>
<th>1.0-2.5</th>
<th>2.0</th>
<th>0.0-2.0</th>
<th>1.0</th>
<th>2.0-2.5</th>
<th>3.0</th>
</tr>
</thead>
<tbody>
<tr>
<td>In powder coating 60-80 μm</td>
<td>5.0</td>
<td>2.0</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>In cathodic dip coating</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Layer weight of Zr in mg/m²</td>
<td>1.0</td>
<td>2.0-2.5</td>
<td>3.0</td>
<td>4.0</td>
<td>5.0</td>
<td>6.0</td>
<td>7.0</td>
<td>8.0</td>
<td>9.0</td>
<td>10.0</td>
</tr>
</tbody>
</table>
### TABLE 1-continued

Overview of the compositions of the aqueous baths and the properties of the respective coated samples and the coatings

<table>
<thead>
<tr>
<th>Content in g/L</th>
<th>B9</th>
<th>B10</th>
<th>B11</th>
<th>B12</th>
<th>B13</th>
<th>B14</th>
<th>B15</th>
<th>VB16</th>
<th>B17</th>
<th>B18</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr as H₂ZrF₆</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>—</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>0.05</td>
<td>0.15</td>
<td>0.50</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.025</td>
<td>0.15</td>
<td>0.50</td>
</tr>
<tr>
<td>Zn</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>0.05</td>
<td>0.15</td>
<td>0.50</td>
<td>0.025</td>
<td>0.15</td>
<td>0.50</td>
</tr>
<tr>
<td>Ti as H₂TiF₆</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.10</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Layer application Zr</td>
<td>44</td>
<td>59</td>
<td>96</td>
<td>55</td>
<td>60</td>
<td>112</td>
<td>46</td>
<td>63</td>
<td>88</td>
<td>112</td>
</tr>
</tbody>
</table>

*unevenly blue

Enamed adhesion in the cross-cut test after 240 hours in the condense climate test according DIN EN ISO 2409:

<table>
<thead>
<tr>
<th>Content in g/L</th>
<th>B19</th>
<th>B20</th>
<th>B21</th>
<th>B22</th>
<th>B23</th>
<th>B24</th>
<th>B25</th>
<th>B26</th>
<th>B27</th>
<th>B28</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr as H₂ZrF₆</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.10</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>Layer application Zr</td>
<td>44</td>
<td>59</td>
<td>96</td>
<td>55</td>
<td>60</td>
<td>112</td>
<td>46</td>
<td>63</td>
<td>88</td>
<td>112</td>
</tr>
</tbody>
</table>

Enamed adhesion in the cross-cut test after 240 hours in the condense climate test according DIN EN ISO 2409:

<table>
<thead>
<tr>
<th>Content in g/L</th>
<th>B29</th>
<th>B30</th>
<th>B31</th>
<th>B32</th>
<th>B33</th>
<th>B34</th>
<th>B35</th>
<th>B36</th>
<th>B37</th>
<th>B38</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr as H₂ZrF₆</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.10</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
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<tr>
<td>Layer application Zr</td>
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<td>59</td>
<td>96</td>
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<td>60</td>
<td>112</td>
<td>46</td>
<td>63</td>
<td>88</td>
<td>112</td>
</tr>
</tbody>
</table>

Enamed adhesion in the cross-cut test after 240 hours in the condense climate test according DIN EN ISO 2409:

<table>
<thead>
<tr>
<th>Content in g/L</th>
<th>B39</th>
<th>B40</th>
<th>B41</th>
<th>B42</th>
<th>B43</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr as H₂ZrF₆</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
<td>0.30</td>
</tr>
<tr>
<td>Mn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Zn</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
<td>0.15</td>
</tr>
<tr>
<td>Fe²⁺</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
<tr>
<td>NO₃ as NaNO₃</td>
<td>0.10</td>
<td>1.00</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>
These examples illustrate that excellent coatings which have an excellent corrosion resistance, an excellent paint adhesion and usually also a distinct color are obtained by using the aqueous conversion compositions according to the invention. The corrosion resistance on steel surfaces is almost as good as that of the high quality zinc phosphating and is therefore far superior to the corrosion resistance of a high quality alkali phosphating (e.g., B3 in comparison with VB1).

In the comparative example VB2, the coating properties were determined only after an additional second conversion treatment—unlike the examples according to the invention. The paint adhesion on steel surfaces is almost as good as that with a high quality zinc phosphating and is thus very definitely superior to a high quality alkali phosphating. In addition, the aqueous conversion compositions according to the invention have a very environmentally friendly composition, are advantageous from the standpoint of occupational health and are phosphate-free.

If an after-rinse solution was used, for example, such as solution with a silane content, an organic polymer content and/or an organic copolymer content after the corrosion conversion coating according to the invention and after at least one rinsing with water, then paint adhesion to steel surfaces achieved in this way is at least as good as that with a high quality zinc phosphating and a corrosion resistance at least as good as that of a high quality zinc phosphating was also achieved.

On the whole, it has been found that the aqueous acidic conversion compositions according to the invention are excellent for replacement of alkali phosphating on a variety of types of metallic substrate surfaces and not only...
for iron phosphating on iron and steel surfaces. A multimetal capability in the treatment has even been found so that a mix of different types of metallic surfaces can be treated either simultaneously or in succession in the same bath.

If ZrF₆⁻₅ is replaced by TiF₆²⁻, there may optionally be a minor impairment in corrosion protection when used on steel in particular. When only zinc was used as the heavy metal cation, high quality coatings were obtained even when the zinc content of the coatings remained unexpectedly extremely low. When using only manganese as the heavy metal cation, high quality coatings were obtained although the manganese content of the coatings was also unexpectedly extremely low. If manganese and zinc were used at the same time, minor impairments were observed in some cases in comparison with the use of only one of these types of heavy metal cations.

When using only Fe²⁺ as a heavy metal cation or in addition to Mn and/or Zn ions, high quality coatings were also obtained. Fe²⁺ can be resupplied from the bath of substrate surfaces containing iron through a reaction-induced pickling process. However, the iron is then frequently oxidized to Fe³⁺ due to the circulation of the bath and is then withdrawn from the bath as a reactive constituent. Despite the addition of Fe³⁺, a steady-state Fe³⁺ concentration is often established in the range of 0.025 to 0.1 g/L Fe³⁺, as also occurs in Examples B41 and B42.

In the case of longer-lasting coatings with a plurality of substrates, for example, the main elements and some of the alloying elements are removed by pickling in the aqueous acidic conversion composition and can accumulate in the bath composition to some extent, so that in case there are frequently more cations in the bath at the same time and can have subordinate effects on their properties, in particular affecting the composition of the coating.

If no heavy metal cations at all were added in Comparative Examples VB3 and VB4, in most cases inferior coatings were obtained. Zn and Mn are deposited only in insignificant immeasurable quantities, based on measurements by X-ray fluorescence analysis, in contrast with Zr. However, Zr is the main component of the layer and may be present as Zr(OH)₂Feₓ, for example. Zn often acts as a fluoride scavenger in the interface between the metal and the coating, so that less fluoride can be incorporated into the layer, which is understood to mean leads to better properties, based on the information available to the present applicant. Zn and Mn are components of the layer only in relatively small amounts and can therefore be detected analytically with some accuracy only by means of photoelectron spectroscopy XPS/ESCA.

The properties of the coatings to be produced are then the best when the Zr layer is the thickest in comparative tests. However, the Zr layer varies with different grades of steel and also in the case of the same grade of steel with different surface properties.

In the experiments, a nonionic surfactant that was added further improved the cleanliness of the metallic surface of the standard plates of CRS cardboard® C that were used. The prior cleaning step may therefore be omitted. If the addition of the surfactant was omitted by comparison with the former, the properties of the coating were fundamentally the same but the risk that the metallic surfaces would not be cleaned adequately was increased, and this may also have a negative influence on the properties of a layer.

In the case of larger amounts of molybdenum added, the possibility of a slight separation of the coating must be considered.

Addition of an organic polymer, an organic copolymer and SiO₂ nanoparticles have proven to be particularly successful. It should be noted here that when amounts in excess of 0.5 g/L are added, there is no foaming and there are no encrustations on spray nozzles and walls to cause interference.

23. A method of contacting a substrate comprising the steps of:

- contacting a metallic surface with an aqueous acidic conversion composition to produce a coating on the metallic surface, wherein the aqueous acidic conversion composition is a solution or a dispersion comprising:
  a total content of 0.01 to 1 g/L of TiF₆²⁺, ZrF₆²⁺ and/or HfF₆²⁺ ions, calculated as ZrF₆²⁺;
  0 or 0.01 to 1 g/L of at least one type of ions selected from the group consisting of Mn and Zn ions;
  0 or 0.01 to 2 g/L of an organic polymer and/or an organic copolymer which is stable at a pH of <6.5, based on the solids content;
  0 or 0.01 to 2 g/L of particulate SiO₂ with an average particle diameter <0.3 μm, based on the solids content;
  about 0 or 0.01 to 10 g/L of at least one surfactant; and
  about 0 or 0.05 to 10 g/L of anions selected from the group consisting of carbonate, nitrate, and sulfate, 0 or 0.001 to 2 g/L of at least 1 type of anions selected from the group consisting of carboxylate and sulfate,

- wherein the aqueous acidic conversion composition has a pH in the range of 2.5 to 6.5.

24. The method according to claim 23, wherein the aqueous acidic conversion composition further comprises:

- a total content of 0.03 to 5 g/L of lithium, sodium and/or potassium ions;
- 0 or 0.05 to 5 g/L of ammonium ions;
- a total content of about 0 or 0.05 to 0.3 g/L of Co and/or Ni ions;
- 0 or 0.01 to 0.8 g/L of chloride, calculated as ClO₃⁻, nitrite, calculated as NO₂⁻ and/or peroxide, calculated as H₂O₂;
- 0 or 0.01 to 0.5 g/L of free fluoride, calculated as F⁻; and
- 0 or 0.01 to 0.2 g/L of vanadate ions, calculated as VO₄⁻³.

25. The method according to claim 23, wherein the coating has a layer thickness of 0.3 to 3 μm.

26. The method according to claim 25, wherein the coating has a total content of anions selected from the group consisting of elemental zirconium and/or titanium, measured as an element, in a range 1 to 300 mg/m² as measured by X-ray fluorescence analysis.

27. The method according to claim 23, wherein the coating is colored, iridescent or gray.

28. The method according to claim 23, wherein the coating is a replacement for an alkali phosphate coating.
29. The method according to claim 23 further comprising diluting one or two concentrates with water by a dilution factor in a range of 5:1 to 40:1 to prepare the aqueous acidic conversion composition used in the coating step.

30. The method according to claim 23, wherein the step of contacting the metallic surface of the substrate with the aqueous acidic conversion composition occurs for a period of time in a range of 1 second to 10 minutes.

31. The method according to claim 23, wherein the metallic surface is at a temperature in a range of 5° C. to 90° C. when brought into contact with the aqueous acidic conversion composition.

32. The method according to claim 23, wherein the aqueous acidic conversion composition is at a temperature in a range of 35° C. to 70° C., when brought into contact with the metallic surface of the substrate.

33. The method according to claim 23 further comprising cleaning the metallic surface of the substrate before the contacting step.

34. The method according to claim 23, wherein the aqueous acidic conversion composition further comprises at least one surfactant thereby enabling cleaning of the metallic surface of the substrate in the same step as the contacting step.

35. The method according to claim 23 further comprising (i) rinsing the coating with water or with an aqueous after-rinse solution comprising at least one component selected from the group consisting of silane, an organic polymer and an organic copolymer; and (ii) optionally enameling the coating.

36. The method according to claim 23 further comprising (i) drying the coating if the coating does not contain an organic polymer or an organic copolymer; and (ii) optionally enameling the coating without a subsequent rinsing with water or with an aqueous after-rinse solution comprising at least one component selected from the group consisting of silane, an organic polymer and an organic copolymer.

37. The method according to claim 23 wherein, if the coating does contain an organic polymer and/or an organic copolymer, then the coating is not further contacted with a primer, enamel or adhesive.

38. The method according to claim 23 further comprising (i) rinsing the coating with at least one of water and an aqueous after-rinse solution; and (ii) subsequently contact-

ing the coating with at least one component selected from the group consisting of primer, enamel and adhesive.

39. The method according to claim 38, wherein the aqueous after-rinse solution comprises at least one of each: a) cation selected from alkaline earth metal, aluminum, titanium, yttrium and heavy metal cations, b) an organic polymer and/or an organic copolymer, c) silane, silanol, siloxane and/or polysiloxane and/or d) complex fluoride.

40. A method for coating a substrate comprising the steps of:

- contacting a metallic surface of the substrate with an aqueous acidic conversion composition to produce a coating on the metallic surface;
- optionally rinsing the coating with water, and/or optionally rinsing with an aqueous composition comprising an organic polymer and/or organic copolymer that is stable at a pH of <6.5, a zirconium complex fluoride and/or silane; and
- enameling the coating;

wherein the aqueous acidic conversion composition is a solution or a dispersion consisting essentially of:

- a total content of 0.01 to 1 g/L of $\text{H}_6\text{ZrF}_6^{2+}$ and/or $\text{H}_4\text{ZrF}_6^{2+}$ ions, or only $\text{ZrF}_6^{2+}$ ions, calculated as $\text{ZrF}_6^{2+}$;
- 0 or 0.01 to 1 g/L of at least one type of ions selected from the group consisting of Mn and Zn ions;
- 0 or 0.01 to 2 g/L of an organic polymer and/or an organic copolymer which is stable at a pH of <6.5, based on the solids content;
- optionally 0.01 to 2 g/L of particulate SiO$_2$ with an average particle diameter <0.3 μm, based on the solids content;
- optionally 0.01 to 10 g/L of at least one surfactant that is essentially phosphate-free and essentially phosphonate-free.

41. A metallic surface of a substrate coated by the method of claim 1.

42. The method according to claim 23, wherein the method is a substitute for an alkali phosphating method or a zinc phosphating method.

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