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(54) MULTI-STAGE TREATMENT FOR ACTIVATED ZINC PHOSPHATIZING OF METALLIC COMPONENTS WITH ZINC SURFACES

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(57) ABSTRACT

The present invention relates to a process for the anti-corrosion pretreatment of a multiplicity of components in series, wherein each component in the series at least partly has surfaces of zinc and undergoes successive process steps for the deposition of iron and for zinc phosphation. In the process step for the deposition of iron, the coating layer to be established is at least 10 milligrams of elemental iron per square meter of the zinc surfaces. The zinc phosphation subsequent to this deposition of iron takes place by means of an acidic aqueous composition which in addition to zinc ions, phosphate ions and free fluoride also comprises a particulate constituent dispersed in water which is at least partly composed of hopeite, phosphophyllite, scholzite and/or hureaulite, and is provided by means of an aqueous dispersion of these crystalline solids that is stabilized with at least one polymeric organic compound.

MULTI-STAGE TREATMENT FOR ACTIVATED ZINC PHOSPHATIZING OF METALLIC COMPONENTS WITH ZINC SURFACES

[0001] The present invention relates to a process for the anti-corrosion pretreatment of a multiplicity of components in series, wherein each component in the series at least partly has surfaces of zinc and undergoes successive process steps for the deposition of iron and for zinc phosphation. In the process step for the deposition of iron, the coating layer to be established is at least 10 milligrams of elemental iron per square meter of the zinc surfaces. The zinc phosphation subsequent to this deposition of iron takes place by means of an acidic aqueous composition which in addition to zinc ions, phosphate ions and free fluoride also comprises a particulate constituent dispersed in water which is at least partly composed of hopeite, phosphophyllite, scholzite and/or hureaulite, and is provided by means of an aqueous dispersion of these crystalline solids that is stabilized with at least one polymeric organic compound.

[0002] Layer-forming phosphation is a process for applying crystalline anti-corrosion coatings to metal surfaces, in particular to materials of the metals iron, zinc and aluminum, which has been used for decades and has been studied in depth. Zinc phosphation, which is particularly well established for corrosion protection, is carried out in a layer thickness of a few micrometers and is based on corrosive pickling of the metal material in an acidic aqueous composition containing zinc ions and phosphates. In the course of the pickling, an alkaline diffusion layer forms on the metal surface, which layer extends into the interior of the solution and within which sparingly soluble crystallites form, which crystallites precipitate directly at the interface with the metal material and continue to grow there. To support the pickling reaction on materials of the metal aluminum and to mask the bath poison aluminum, which in dissolved form disturbs the layer formation on materials of the metal, water-soluble compounds that are a source of fluoride ions are often added.

[0003] The zinc phosphation is adjusted as standard in such a way that homogeneous, closed and compact crystalline coatings are achieved on the surfaces of the metals iron, zinc and aluminum. Otherwise, good corrosion protection and a good coating base cannot be achieved. Homogeneous, closed coatings in zinc phosphation are usually reliably achieved from a layer weight of 2 g/m^2. Depending on the metal surface to be phosphated, the pickling described above and the concentration of the active components in the zinc phosphation stage have to be adjusted accordingly in order to ensure correspondingly high layer weights on the surfaces of the metals iron or steel, zinc and aluminum.

[0004] Another property of zinc phosphation that is important for corrosion protection and coating adhesion, in particular for good electrocoating properties, is that the deposition process is self-limiting, i.e. the dissolution of the phosphate layer, which takes place at the acidic pH value of zinc phosphation, is in a steady-state equilibrium with the growth or continued growth of the phosphate crystallites, and the layer weight therefore no longer increases, which would be an indication of the growth of a layer coating that is crystalline but porous and therefore not compactly crystalline. In the technical zinc phosphation process, this means that, in the case of a treatment time of usually approximately 20 seconds to 5 minutes, which makes sense in terms of plant technology and cost-efficiency, in the zinc phosphation wet-chemical process step, the formation of the homogeneous, closed and crystalline zinc phosphate coating has to be completed and the self-limiting thickness of the coating is already ideally reached. This is technically ensured by the fact that coatings grow with the highest possible number density of phosphate crystallites, so that the layer formation in turn reaches the self-limiting range and thus a predetermined limit layer thickness with the lowest possible layer weights.

[0005] In order to achieve such homogeneous, closed coatings with a high degree of compactness or a high number density of phosphate crystallites, in the prior art zinc phosphation is always initiated with activation of the metal surfaces of the component to be phosphated. The activation is usually a wet-chemical process step, conventionally carried out by means of contact with colloidal aqueous solutions of phosphates (“activation stage”), which, when immobilized on the metal surface, serve as a nucleus for growth for the formation of the crystalline coating within the alkaline diffusion layer in the subsequent phosphation, so that a high number density of growing crystallites is brought about, and thus in turn a compact crystalline zinc phosphate layer is produced that also has excellent corrosion protection and, due to its high electrical charge transfer resistance, excellent electrocoating properties.

[0006] Suitable dispersions in this case are colloidal, mostly neutral to alkaline aqueous compositions based on phosphate crystallites, which have only small crystallographic deviations in their crystal structure from the type of zinc phosphate layer to be deposited. In this context, WO 98/39498 A1 teaches in particular bivalent and trivalent phosphates of the metals Zn, Fe, Mn, Ni, Co, Ca and Al, it being technically preferred for phosphates of the metal zinc to be used for activation for subsequent zinc phosphation.

[0007] An activation stage based on dispersions of bivalent and trivalent phosphates requires a high level of process control in order to keep the activation performance constantly at an optimal level, in particular when treating a series of metal components. To ensure the method is sufficiently robust, foreign ions carried over from previous treatment baths or aging processes in the colloidal aqueous solution must not lead to the activation performance deteriorating. A deterioration is initially noticeable in increasing layer weights in the subsequent phosphation and ultimately leads to the formation of defective, inhomogeneous or less compact phosphate layers. Overall, the layer-forming zinc phosphation with upstream activation is therefore a multi-stage process that is technically complex to control and has hitherto been carried out in a resource-intensive manner, both with regard to the process chemicals and the energy to be expended.

[0008] In the field of automotive manufacturing, which is particularly relevant to the present invention, various metallic materials are increasingly being used and joined together in composite structures. A wide variety of steels are still used in bodywork construction, primarily because of their specific material properties, but increasingly light metals such as aluminum are also used, in particular to significantly reduce the weight of the entire body. In particular, in the automotive industry, the challenge is often that the surfaces of zinc must be activated particularly well by the zinc phosphation processes known from the prior art in comparison to steel surfaces in order to ensure the growth of a compact crystalline phosphate layer having a coating weight of usually less than 5.0 g/m^2 in the zinc phosphation, since above such phosphate layer weights there is no satisfactory corrosion protection on the zinc surfaces, and the process is then carried out neither in a resource-saving nor economical manner, which is also due to the high phosphate consumption.

[0009] WO 2019/238573 A1 addresses a resource-saving process for zinc phosphation and indirectly also a reduction in the complexity of the multi-stage process by providing a particularly effective activation based on specifically dispersed bivalent and trivalent phosphates, which activation provides a colloidal, aqueous solution that is based on bivalent and trivalent phosphates and is excellently stabilized against sedimentation, and also makes homogeneous, closed and very compact zinc phosphate coatings possible with a relatively low particulate content in the activation stage, so that the material requirement due to the formation of layers in the zinc phosphation is also reduced.

[0010] However, there is still a need to optimize the pretreatment line for zinc phosphation, including the activation stage and phosphation stage, such that the overall process can be carried out in a less resource-intensive manner, ideally with a simultaneously simplified procedure. However, a resource-saving overall process must not be at the expense of the properties of the zinc phosphation. which must be provided as a homogeneous, closed and compact crystalline coating with high electrical charge transfer resistance in order to make good protection against corrosion and correspondingly good coverage of the coating in a subsequent electrocoating possible. In particular, this must always be ensured in the most common application, namely the series treatment of components, wherein an economically attractive and resource-saving method must also be provided for components having surfaces of zinc.

[0011] Surprisingly, this complex requirement profile can be met when an amount of a dispersion of particulate zinc phosphates is added to the acidic aqueous composition for zinc phosphation, resulting in the composition for zinc phosphation being self-activating. The activation performance of the pretreatment line for zinc phosphation of a series of components can then be maintained by the metered addition of an activating aid on the basis of the aforementioned dispersion of particulate zinc phosphates. This makes it possible to at least partially or even entirely dispense with an activation stage upstream of the zinc phosphation wet-chemical treatment stage, and in this way to conduct the overall process of zinc phosphation in a less material-intensive and energy-intensive manner and to reduce the technical complexity in the form of the separate activation stage, which has previously been absolutely necessary in the prior art. Decisive for the economical and resource-saving operation of a pretreatment line according to the invention, which serves for the satisfactory phosphation of components comprising surfaces of zinc in series, is a wet-chemical step upstream of the zinc phosphation for the deposition of an iron coating on the zinc surfaces, which results in a significant reduction of the phosphate layer weight on these surfaces, so that the object of the present invention to provide constant satisfactory corrosion protection values with low material consumption on components comprising surfaces of zinc in series is reliably achieved.

[0012] The present invention therefore relates to a process for the anti-corrosion pretreatment of a multiplicity of components in series, wherein each component in the series at least partly has surfaces of zinc and first undergoes a wet-chemical process step (i) for the deposition of iron on the zinc surfaces and subsequently undergoes a process step (ii) for zinc phosphation, wherein in process step (i), a coating layer of at least 10 milligrams of elemental iron is brought about per square meter of the zinc surfaces of the component, and wherein each component in process step (ii) is brought into contact with an acidic aqueous composition that has a free acid in points greater than zero, and contains

[0013] (A) 5-50 g/kg of phosphates dissolved in water, calculated as PO_4,

[0014] (B) 0.3-3 g/kg of zinc ions,

[0015] (C) free fluoride, and

[0016] (D) a water-dispersed particulate constituent comprising phosphates of polyvalent metal cations, wherein the phosphates are at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite,

wherein the acidic aqueous composition is obtained by adding an amount of an aqueous dispersion to an acidic aqueous composition containing the components (A)-(C), wherein the aqueous dispersion contains a water-dispersed particulate constituent (P), which comprises

[0017] at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite,

[0018] and at least one polymeric organic compound (P2).

[0019] A pretreatment in series is when the components of the series each undergo a process step for zinc phosphation according to the process according to the invention and for this purpose are brought into contact with at least one bath liquid for zinc phosphation that is provided in a system tank, the individual components being brought into contact one after the other and thus at different times. The system tank is in this case the container in which the acidic aqueous composition is located for the purpose of zinc phosphation by way of a wet-chemical pretreatment. The components can be brought into contact with the bath liquid of the system tank inside the system tank, for example by immersion, or outside the system tank, for example by spraying on the bath solution stored in the system tank.

[0020] The components treated according to the present invention can be three-dimensional structures of any shape and design that originate from a manufacturing process, in particular also including semi-finished products such as strips, sheets, rods, pipes, etc., and composite structures assembled from said semi-finished products, the semi-finished products preferably being interconnected by means of adhesion, welding and/or flanging to form a composite structure.

[0021] In the context of the process according to the invention, a component has at least one surface of zinc or one of the metals iron or aluminum if more than 50 at. % of the metal structure on this surface, up to a material penetration depth of at least one micrometer, is composed of zinc or iron or aluminum. This generally applies to components made of corresponding metallic materials, insofar as more than 50 at. % of the metallic materials are composed of zinc or iron or aluminum as uniform materials. Components comprising surfaces of zinc are, however, also iron materials provided with metallic coatings, such as, for example, electrolytically galvanized or hot-dip galvanized steel, which can also be alloyed with iron (ZF), aluminum (ZA) and/or magnesium (ZM).

Process Step (i)—Deposition of Iron

[0022] According to the invention, the deposition of a coating layer based on elemental iron of at least 10 milligrams per square meter of the zinc surfaces of the component is required. Higher coating layers of iron are advantageous for reducing the phosphate layer weight in the subsequent process step (ii), so that in wet-chemical process step (i) of the process according to the invention, a coating layer based on elemental iron of at least 20 milligrams, particularly preferably at least 40 milligrams, very particularly preferably at least 60 milligrams, is preferred on the surfaces of the components formed by zinc. However, it can often be observed that a significantly higher coating layer of iron on the zinc surfaces proves to be disadvantageous for the process according to the invention, because, in interaction with the zinc phosphation, poorer adhesion results are achieved for organic top coats. Accordingly, it is preferred if, in the wet-chemical process step (i), the coating layer of iron is limited to less than 150 milligrams, particularly preferably less than 120 milligrams, in each case per square meter of the zinc surfaces of the component.

[0023] A wet-chemical treatment step in the sense of process step (i) is present when the components in the series are brought into contact with a water-based composition that contains the active components for the deposition of iron in the water-based phase in a dissolved or dispersed form. The composition is water-based when the proportion of water is at least 50 wt. %, preferably at least 70 wt. %, particularly preferably at least 80 wt. %, in each case based on the total composition.

[0024] Suitable wet-chemical processes for the deposition of iron in the desired coating layer are known to a person skilled in the art. Deposition typically takes place by contacting at least the surfaces of zinc with aqueous compositions containing iron(II) and/or iron(III) ions, wherein the proportion of iron ions dissolved in water is at least 50 mg/L, preferably at least 100 mg/L.

[0025] The coating layer of iron on the surfaces of zinc is determined by means of pickling and photometric analysis. For the quantitative determination, a defined sample volume of a 5 wt. % nitric acid solution is pipetted directly after process step (i) using a measuring cell ring onto a defined surface of the galvanized sheet and, after an exposure time of 30 seconds at a temperature of 25° C., transferred to a UV measuring cuvette in which 1.0% sodium thiocyanate solution is initially charged, in order to determine the absorption at a wavelength of 517 nm and a temperature of 25° C. Calibration in the two-point process takes place by determining the absorption values of two standard solutions of iron(III) nitrate in 5 wt. % nitric acid.

[0026] In order to avoid the metallic deposition of noble elements, which attenuate the positive effect of the iron coating on the zinc surfaces for zinc phosphate layer formation, and for ecological reasons, it is preferred if the aqueous compositions for the deposition of iron in process step (i) contain a total of less than 10 mg/L of ionic compounds of the metals copper, nickel, cobalt, particularly preferably a total of less than 10 mg/L of ionic compounds of the metals copper, nickel, cobalt, tin, manganese, molybdenum, chromium and/or cerium, and particularly preferably in each case less than 1 mg/L of ionic compounds of the metals nickel and cobalt, in each case based on the metal element in the aqueous composition.

[0027] Analogously, in order to avoid a layer formation competing with the deposition of iron in process step (i), it is preferred if the aqueous compositions for the deposition of iron contain a total of less than 20 mg/L of water-soluble compounds of elemental Zr, Ti, Hf and/or Si, particularly preferably in each case less than 5 mg/L, particularly preferably in each case less than 1 mg/L of water-soluble compounds of the elements Zr, Ti, Hf or Si.

[0028] A deposition of iron on zinc from acidic aqueous compositions is described in WO 2008/135478 A1 in the presence of iron(II) ions. Such a method is also suitable in the context of the present invention and is advantageous in particular due to compatibility with the pH value of the subsequent zinc phosphation in process step (ii). In this regard, preference is thus given to contacting with an acidic aqueous composition having a pH value in the range of 2.0-6.0 containing at least 50 mg/L of iron(II) ions, and preferably an a-hydroxy carboxylic acid, preferably in a molar ratio to the iron ions from 5:1 to 1:5, and particularly preferably additionally at least one reducing agent selected from oxoacids of phosphorus or nitrogen and salts thereof, wherein at least one phosphorus or nitrogen atom is present in an average oxidation state, hydrazine, hydroxylamine, nitroguanidine, N-methylmorpholine-N-oxide, glucoheptonate, ascorbic acid, and/or reducing sugars.

[0029] Alternatively and because of its particular efficiency in reducing the phosphate layer weight on the surfaces of zinc during the subsequent zinc phosphation, the deposition of the iron coating from alkaline aqueous compositions is particularly advantageous, wherein the pH value of the alkaline aqueous compositions containing iron(II) and/or iron(III) ions is preferably not below 8.5, particularly preferably not below 9.5, very particularly preferably not below 10.5, but preferably not above 13.5, particularly preferably not above 12.5, and very particularly preferably not above 11.5.

[0030] In a preferred embodiment of such an alkaline aqueous composition, in step (i) of the process according to the invention

> **[0031]** (a) at least 50 mg/L, preferably at least 100 mg/L, particularly preferably at least 200 mg/L of iron(III) ions, and
>
> **[0032]** (b) at least 100 mg/L of complexing agents selected from organic compounds (b1), which have at least one functional group selected from COOX, OPO_3X and/or PO_3X, wherein X is either an H atom or an alkali and/or alkaline earth metal atom, and/or condensed phosphates (b2) calculated as PO_4,

are present, wherein the composition preferably has a free alkalinity of at least 1 point, but preferably less than 6 points.

[0033] The term "condensed phosphates" according to component (b1) refers to the metaphosphates ($Me_n[P_nO_{3n}]$), which are water-soluble at room temperature, di-, tri- and polyphosphates ($Me_{n+2}[P_nO_{3n+1}]$ or $Me_n[H_2P_nO_{3n+1}]$), which combine isometaphosphates and cross-linked polyphosphates, wherein Me are either alkali metal atoms or alkaline earth metal atoms. Of course, instead of the water-soluble salts, the corresponding condensed acids of phosphoric acid can also be used for the formulation of the alkaline aqueous compositions, provided that the free alkalinity is set as indicated. The mass-based proportion of the "condensed phosphates" according to component (b1) is always calculated as a corresponding amount of PO_4. Analogously, when determining the molar ratios that make up an amount of condensed phosphates, this amount of condensed phosphates is always based on the equivalent amount of PO_4.

[0034] It has been found that an alkaline aqueous composition in step (i) of the process according to the invention brings about a coating layer of iron on the surfaces of zinc that is suitable for the subsequent zinc phosphation and that can grow particularly reliably compact, crystalline zinc phosphate layers when the free alkalinity is less than 5 points. For the application of the alkaline aqueous composition in the spray method, a suitable coating layer of iron is brought about in particular when the free alkalinity is less than 4 points. Surprisingly, as already mentioned, it has been found that high coating layers of iron on zinc surfaces above 150 mg/m^2 have rather proven to be disadvantageous for the process according to the invention, because, in interaction with the zinc phosphation, poorer adhesion results are achieved for organic top coats. so that the alkaline aqueous compositions in step (i) must not have an excessively high free alkalinity. However, the free alkalinity should preferably be at least 2 points in order to produce optimal coating layers on zinc surfaces of at least 20 mg/m^2 based on elemental iron. Alkaline aqueous compositions that have a free alkalinity of more than 6 points produce high coating layers of iron on the zinc surfaces; however, the adhesion to coating layers optionally applied after step (ii) is significantly reduced by high coating layers based on elemental iron, so that the corrosion protection is also less effective or inadequate.

[0035] The free alkalinity is determined by titrating 2 ml of bath solution, preferably diluted to 50 ml, with a 0.1 n acid, for example hydrochloric acid or sulfuric acid, up to a pH value of 8.5. The consumption of acid solution in ml indicates the point number of the free alkalinity.

[0036] Ideally, the alkaline aqueous composition in step (i) of the process according to the invention has a pH value of at least 9.5, particularly preferably of at least 10.5. Below a pH value of 10.5, coating layers of iron of at least 20 mg/m^2 are formed on the zinc surfaces when contacted with a composition containing iron(II) and/or iron(III) ions only in the presence of a reducing agent. Compositions of this kind for depositing an iron coating are disclosed in WO 2011/098322 A1, which contain an amino acid and additionally a reducing agent selected from oxoacids of phosphorus or nitrogen and salts thereof, wherein at least one phosphorus or nitrogen atom is present in an average oxidation state, and as such are also suitable in the context of the present invention.

[0037] In order to minimize the pickling attack on the zinc surfaces of the component, it is further preferred that the pH value in the alkaline aqueous composition in step (i) of the process according to the invention is not above 13.5, particularly preferably not above 12.5. In the event that the component has aluminum surfaces in addition to the surfaces of zinc, it is advantageous if the pH value in the composition in step (i) of the process according to the invention does not assume values above 11.5, because otherwise the increased pickling attack causes an intensive black coloration of the aluminum surfaces, so-called "well blackness," which has a disadvantageous effect on the effectiveness of a subsequent conversion treatment, for example on the zinc phosphation in step (ii) of the process according to the invention or, in the case of zinc phosphation that is adjusted so as not to form layers on aluminum in step (ii), on an acidic post-passivation on the basis of water-soluble inorganic compounds of elemental zirconium and/or titanium following the process according to the invention.

[0038] The iron ions are predominantly present as iron(III) ions at the preferably predominant pH value and in the alkaline aqueous composition when saturated with atmospheric oxygen. In step (i) of the process according to the invention, the proportion thereof is preferably not more than 2000 mg/L. Higher proportions of iron(III) ions are unfavorable for the process control, because the solubility of the iron(III) ions in the alkaline medium must be maintained by correspondingly high proportions of complexing agents, without more favorable properties being achieved with regard to the iron coating on the zinc surfaces. However, such alkaline aqueous compositions are preferred in step (i) of the process according to the invention in which the proportion of iron(III) ions is at least 100 mg/L, particularly preferably at least 200 mg/L, to ensure, on the one hand, a sufficient coating layer of iron on the zinc surfaces in step (i) of the process according to the invention within treatment times of less than two minutes which are typical for the process, and, on the other hand, to obtain phosphate layers in excellent layer quality on the surfaces of zinc in step (ii) of the process according to the invention.

[0039] The complexing agents according to component (b) of the alkaline aqueous composition in step (i) of the process according to the invention are preferably contained in such an amount that the molar ratio of all components (b) to iron(III) ions is greater than 1:1 and is particularly preferably at least 2:1, in particular preferably at least 5. It is found that the use of the amount of complexing agents in stoichiometric excess is advantageous for the process control, as it keeps the proportion of iron(III) ions permanently in solution. The precipitation of insoluble iron hydroxides is thus completely suppressed, so that the alkaline aqueous composition remains permanently stable and is not depleted of iron(III) ions. At the same time, sufficient deposition of an inorganic layer containing iron ions on the zinc surfaces nevertheless takes place. For reasons of economy and for resource-saving use of the complexing agents, it is nevertheless preferred that the molar ratio of the components (b) to iron(III) ions in composition (A) does not exceed the value of 10.

[0040] In a preferred embodiment, the alkaline aqueous composition can additionally contain at least 100 mg/L of phosphate ions in step (i) of the process according to the invention. This proportion of phosphate ions requires that, in addition to iron ions, phosphate ions are also a substantial constituent of the iron-containing coating layer produced on the zinc surfaces in step (i). It has been found that such layers are advantageous for the subsequent zinc phosphation and, in interaction with zinc phosphation, provide good adhesion to subsequently applied coating layers. Accordingly, it is further preferred in step (i) of the process according to the invention that the alkaline aqueous composition contains at least 200 mg/L, particularly preferably at least 500 mg/L, of phosphate ions. The properties of the passive layer, which, when the zinc surface of the component is contacted with compositions (A) in step (i) of the process according to the invention, are not further positively influenced above a proportion of phosphate ions of 4 g/L, so that, for reasons of economic efficiency, the proportion of phosphate ions in the alkaline aqueous composition in step (i) of the process according to the invention should preferably be below 10 g/L.

[0041] The ratio of iron(III) ions to phosphate ions can thereby be varied within a wide range. The mass-based ratio of iron(III) ions to phosphate ions in the alkaline aqueous composition in step (i) of the process according to the invention is preferably in a range from 1:20 to 1:2, particularly preferably in a range from 1:10 to 1:3. Alkaline aqueous compositions that have such a mass ratio of iron (III) ions to phosphate ions provide homogeneous black-gray layers containing phosphate ions having readily adjustable coating layers in the range of 20-150 mg/m^2 based on elemental iron after being brought into contact with a zinc surface.

[0042] Condensed phosphates (b2) are capable of keeping iron(III) ions in solution in an alkaline medium by complexation. Although there are no particular restrictions on the type of condensed phosphates that can be used for alkaline aqueous compositions in step (i) of the process according to the invention, those condensed phosphates selected from pyrophosphates, tripolyphosphates and/or polyphosphates, particularly preferably from pyrophosphates, are preferred because they are particularly readily water-soluble and very easily accessible.

[0043] As organic compounds (b1) that are likewise present or present as an alternative to the condensed phosphates (b2) as complexing agents in the alkaline aqueous composition, preference is given in step (i) of the process according to the invention to compounds that have an acid number of at least 250 in their acid form (X═H atom). Lower acid numbers give the organic compounds surface-active properties, so that organic compounds (b1) having acid numbers below 250 can have a strong emulsifying effect as anionic surfactants. In this context, it is further preferred that the organic compounds are not high molecular and do not exceed a number average molecular weight of 5,000 u, particularly preferably of 1,000 u. If the preferred acid number and optionally the preferred molecular weight are exceeded, the emulsifying effect of the organic compounds (b1) can be so pronounced that impurities in the form of oils and drawing greases carried over from the cleaning stage via the component can only be removed from the treatment stage by means of complex separation processes for the deposition of the iron coating, for example by the metered addition of cationic surfactants, so that further process parameters have to be controlled. It is therefore more advantageous to adjust the alkaline aqueous composition in step (i) of the process according to the invention so that it is only slightly emulsifying in order to allow conventional separation of the floating oils and fats. Anionic surfactants also have a tendency to cause pronounced foaming, which is particularly disadvantageous during spray application of the alkaline aqueous composition. Therefore, organic complexing agents (b1) having acid numbers of at least 250 are preferably used in the composition in step (i) of the process according to the invention. The acid number indicates the amount of potassium hydroxide in milligrams which is required to neutralize 1 g of the organic compound (b1) in 100 g of water according to DIN EN ISO 2114.

[0044] Preferred organic complexing agents (b1) in the alkaline aqueous composition in step (i) of the process according to the invention are selected from α-, β- and/or γ-hydroxycarboxylic acids, hydroxyethane-1,1-diphosphonic acid, [(2 hydroxyethyl)(phosphonomethyl)amino]-methylphosphonic acid, diethylenetriaminepentakis(methylene phosphonic acid) and/or amino-tris-(methylene phosphonic acid) and salts thereof, particularly preferably hydroxyethane-1,1-diphosphonic acid, [(2 hydroxyethyl)(phosphonomethyl)amino]-methylphosphonic acid, diethylenetriaminepentakis(methylene phosphonic acid) and/or amino-tris-(methylene phosphonic acid) and salts thereof.

[0045] According to the invention, such alkaline aqueous compositions containing exclusively condensed phosphates (b2), exclusively contain organic complexing agents (b1) or a mixture of both are thus explicitly included in step (i) of the process according to the invention. However, the proportion of organic complexing agent (b1) in the alkaline aqueous composition can be reduced to the extent that complexing agent (b2) selected from condensed phosphates is present. In a particular embodiment of the process according to the invention, the alkaline aqueous composition in step (i) contains complexing agents (b2) selected from condensed phosphates and organic complexing agents (b1), wherein the molar ratio of all components (b) to iron(III) ions is greater than 1:1, but the molar ratio of components (b1) to iron(III) ions is less than 1:1, particularly preferably less than 3:4, but preferably at least 1:5. A mixture of the two complexing agents (b1) and (b2) is advantageous in that the condensed phosphates in the alkaline medium are in equilibrium with the phosphate ions of the alkaline aqueous composition at an elevated temperature, so that phosphate ions consumed by layer formation on the zinc surfaces are slowly replenished from the condensed phosphates. Conversely, however, the presence of condensed phosphates alone is not sufficient to bring about a coating layer based on iron and phosphate on the zinc surfaces, so that a proportion of phosphate ions in the alkaline aqueous composition in step (i) of the process according to the invention is always preferred. In the presence of the condensed phosphates, however, the precipitation of sparingly soluble phosphates, for example iron phosphates, is in particular suppressed by the interaction with the organic complexing agents (b1), even at high pH values above 10.5, so that alkaline aqueous compositions containing a mixture of the complexing agents in step (i) of the process according to the invention are preferred, wherein it is preferably to be ensured that the molar ratio of components (b1) to iron(III) ions is at least 1:5.

[0046] In order to increase the cleaning capacity for the components in the series to be treated in the process according to the invention, the alkaline aqueous composition can additionally contain non-ionic surfactants in step (i). In this case, the non-ionic surfactants are preferably selected from one or more ethoxylated and/or propoxylated C10-C18 fatty alcohols having a total of at least two but no more than 12 alkoxy groups, particularly preferably ethoxy and/or propoxy groups, some of which may be present such that they are end-capped with an alkyl functional group, particularly preferably with a methyl, ethyl, propyl or butyl functional group.

[0047] In a particular embodiment of the process according to the invention, the alkaline aqueous composition in step (i) contains

[0048] a) 0.05 to 2 g/L of iron(III) ions,

[0049] b) at least 0.1 g/L of complexing agents selected from organic compounds (b1), which have at least one functional group selected from COOX, OPO_3X and/or PO_3X, wherein X is either an H atom or an alkali and/or alkaline earth metal atom, and/or condensed phosphates (b2) calculated as PO_4,

[0050] c) 0.1 to 4 g/L of phosphate ions,

[0051] d) a total of 0.01 to 10 g/L of non-ionic surfactants, which are preferably selected from one or more ethoxylated and/or propoxylated C10-C18 fatty alcohols having a total of at least two but no more than 12 alkoxy groups, particularly preferably ethoxy and/or propoxy groups, some of which may be present such that they are end-capped with an alkyl functional group, particularly preferably with a methyl, ethyl, propyl or butyl functional group,

[0052] e) a total of less than 10 mg/L of ionic compounds of the metals copper, nickel, cobalt, tin, manganese, molybdenum, chromium, and/or cerium, in particular in each case less than 1 mg/L of ionic compounds of the metals nickel and cobalt, in each case based on the metal element,

wherein no more than 10 g/L of condensed phosphates (b2) are present as PO_4, and the molar ratio of the sum of components (b1) and (b2) to iron(III) ions is greater than 1:1, and wherein the free alkalinity is at least 1 point, but less than 6 points, and the pH value is at least 10.5.

[0053] In a preferred embodiment of the process according to the invention, during the treatment in series in step (i), the component is brought into contact with an aqueous composition for the deposition of iron, in particular an alkaline aqueous composition containing iron(II) and/or iron(III) ions, for at least 30 seconds, but not more than 4 minutes, at a temperature of at least 30° C., particularly preferably at least 40° C., but not more than 70° C., particularly preferably not more than 60° C. The preferred treatment or contact times in step (i) of the process according to the invention should be selected such that the coating layer of iron of at least 10 mg/m^2, preferably of at least 20 mg/m^2 is achieved. The treatment and contact times for implementing a minimum coating layer of this kind vary depending on the type of application and depend in particular on the flow of the aqueous fluid acting on the metal surface to be treated. In processes in which the composition is applied by spraying, the minimum coating layer of iron develops more quickly than in dipping applications.

Process Step (ii)—Activated Zinc Phosphation

[0054] The zinc phosphation of the components in the series carried out in process step (ii) is effected by means of acidic aqueous compositions for zinc phosphation containing phosphates of polyvalent metal cations dispersed as a particulate constituent, wherein the phosphates are at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite. The acidic aqueous zinc phosphation is thus self-activating, requiring no prior separate activation, and is obtained as such by corresponding addition of an amount of an aqueous dispersion to an acidic aqueous composition containing components (A)-(C) according to claim **1** of the present invention.

[0055] The aqueous dispersion contains a particulate constituent (P) in water-dispersed form, which comprises

[0056] at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite,

[0057] and at least one polymeric organic compound (P2),

wherein the aqueous dispersion for providing the acidic aqueous composition for the zinc phosphation of process step (ii) is preferably added in such an amount that the proportion by weight of phosphates from the particulate constituent of the aqueous dispersion, based on the acidic aqueous composition containing components (A)-(C), is at least 0.004 g/kg, preferably at least 0.01 g/kg, particularly preferably at least 0.05 g/kg and very particularly preferably at least 0.08 g/kg.

[0058] In an alternative or preferred embodiment, the components in the series in step (ii) of the process according to the invention are brought into contact with an acidic aqueous composition, wherein the acidic aqueous composition contains

[0059] (A) 5-50 g/kg of phosphates dissolved in water, calculated as PO_4,

[0060] (B) 0.3-3 g/kg of zinc ions, and

[0061] (C) free fluoride,

and has a free acid in points greater than zero,

wherein in process step (ii) for zinc phosphation an activating aid is added continuously or discontinuously to the acidic aqueous composition in an amount that, under the selected conditions of zinc phosphation process step (ii), is sufficient to maintain the property of the acidic aqueous composition of depositing a zinc phosphate layer having a layer weight of less than 5.0 g/m^2, preferably less than 4.5 g/m^2, particularly preferably less than 4.0 g/m^2, very particularly preferably less than 3.5 g/m^2, on a hot-dip galvanized steel surface (Z),

wherein the activating aid contains a particulate constituent (P) in water-dispersed form, which constituent comprises

[0062] at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite,

[0063] and at least one polymeric organic compound (P2).

[0064] The inventive property of the acidic aqueous composition for zinc phosphation in process step (ii) on hot-dip galvanized steel surfaces (Z) of bringing about the growth of a zinc phosphate layer having a layer weight below 5.0 g/m^2, preferably below 4.5 g/m^2, particularly preferably below 4.0 g/m^2 and very particularly preferably below 3.5 g/m^2, (hereinafter referred to as "phosphation quality") is to be checked on substrates that have been cleaned and degreased (Z) and are not subjected to any further wet-chemical pretreatment step before being brought into contact with the acidic aqueous composition of the process according to the invention in step (ii) and after the deposition of iron on the zinc surfaces in step (i). In order to check the phosphation quality of the acidic aqueous composition, hot-dip galvanized steel (Z) is thus first cleaned using an alkaline cleaning agent prepared as 2 wt. % Bonderite® C-AK 1565 A and 0.2 wt. % Bonderite® C-AD 1270 in deionized water ($k<1\ \mu Scm^{-1}$) at pH 11.0 and 55° C. for 5 minutes by immersion. The substrates cleaned and degreased (Z) in this way are rinsed with deionized water ($k<1\ \mu Scm^{-1}$) at room temperature and are then supplied to the treatment stages according to process steps (i) and (ii) according to the selected process conditions. According to the selected process conditions means at a relevant identical temperature, application duration and bath circulation and using the wet-chemical treatment stages for which the phosphation quality specified according to the invention is to apply, i.e., the resulting target layer weights on hot-dip galvanized steel (Z) are to be below 5.0 g/m^2, preferably below 4.5 g/m^2, particularly preferably below 4.0 g/m^2 and very particularly preferably below 3.5 g/m^2. The phosphation quality can therefore be determined in the current process according to the invention by cleaned and degreased sheets of hot-dip galvanized steel (Z) also being introduced, together with the components in the series, for process steps (i) and (ii), and the layer weight of zinc phosphate on the sheets, and thus the phosphation quality of the acidic aqueous composition for zinc phosphation, then being determined in process step (ii). The cleaned and degreased sheets of hot-dip galvanized steel (Z), in their function as test sheets for determining phosphation quality, are preferably rigidly connected to the component or the conveying frame in order to ensure that the flow conditions during transport of the component together with the conveying frame through the phosphating bath are reproduced as similarly as possible for the test sheet. For this purpose, the test sheets should ideally be connected to the component or the conveying frame in such a way that the transport of a test sheet together with the component and the conveying frame, compared to the transport of the component and the conveying frame without such a test sheet, has no influence on the flow conditions that is to be considered, and that the flow conditions are substantially identical in both cases and thus substantially correspond to the flow conditions of at least a portion of the components of the series. This can be achieved, for example, by adapting the size and/or the shape of the test sheet to the size and shape of the component and/or of the conveying frame which is arranged adjacent to the test sheet in each case. It is conceivable in this case, in particular when a test sheet is arranged on an outer surface portion of the component or the conveying frame, for the dimensions of the test component to correspondingly be smaller than those of said surface portion, for example in order to prevent the test component from protruding beyond the surface portion. Alternatively or additionally, the test component may follow a curvature or other planar deviation of the surface portion or the conveying frame. It has proven to be particularly expedient to select a sheet portion that is sufficiently small compared to the size of a suitable outer surface of the component, with an outer surface being particularly suitable if it is located at a location that has a particularly low curvature or at the location that has the lowest curvature of the component, and the test sheet metal then being mounted substantially in parallel so as to be spaced apart along the surface normal of such an outer surface. The phosphation quality is obtained directly during the series treatment of such components, which also have a surface of hot-dip galvanized steel (Z) as the surfaces of zinc. Such components are preferred in a preferred embodiment of the process.

[0065] It is additionally preferred for the phosphation quality that, if the contact is extended by one minute, the layer weight on hot-dip galvanized steel (Z) increases by no more than 0.2 g/m^2, and thus the layer formation under the selected conditions is already in the range of self-limitation, so that the property of the acidic aqueous composition for zinc phosphation of producing compact, crystalline zinc phosphate layers in step (ii) of the process according to the invention is ensured. Accordingly, it is preferred that in the zinc phosphation process step, an amount of activating aid is added that, under the selected conditions of the zinc phosphation process step in the process according to the invention, is sufficient to maintain the property of the acidic aqueous composition of depositing a zinc phosphate layer having a layer weight of less than 5.0 g/m^2, preferably less than 4.5 g/m^2, particularly preferably less than 4.0 g/m^2 and very particularly preferably less than 3.5 g/m^2 on a hot-dip galvanized steel surface (Z), wherein the layer weight achieved under the selected conditions of zinc phosphation process step (ii) in the process according to the invention increases by no more than 0.2 g/m^2 when the contact time with the acidic aqueous composition is extended by 60 seconds.

[0066] Usually, the phosphation quality is determined and monitored in the process according to the invention by hot-dip galvanized steel (Z), which has been cleaned and degreased as described above, also undergoing the zinc phosphation process step at regular intervals during the series treatment and then being subjected to a layer weight determination. As already mentioned, the phosphation quality is obtained directly during the series treatment of such components, which also have at least one surface of hot-dip galvanized steel (Z) as the surfaces of zinc. Insofar as the phosphation quality of the acidic aqueous composition is ensured by the metered addition of the activating aid, homogeneous, closed and compact crystalline zinc phosphate coatings are deposited on the components having surfaces of the metals zinc, iron and aluminum in the usual treatment times of 20 seconds to 5 minutes.

[0067] The layer weight of zinc phosphate is determined within the scope of the present invention by removing the zinc phosphate layer using aqueous 5 wt. % CrO_3 as a pickling solution that is brought into contact with a defined area of the phosphated material or component at 25° C. for 5 min immediately following the zinc phosphation and rinsing with deionized water ($\kappa<1\ \mu Scm^{-1}$), and subsequently determining the phosphorus content in the same pickling solution by means of ICP-OES. The layer weight of zinc phosphate can be found by multiplying the amount of phosphorus relative to surface area by a factor of 6.23.

[0068] In the process according to the invention, the activating aid is added to the acidic aqueous composition for zinc phosphation for the purpose of maintaining the phosphation quality in the process step (ii) for zinc phosphation. In order to maintain the phosphation quality in the series treatment process, the addition can take place by means of continuous or discontinuous metering into the system tank. Continuous metering is preferred if the pretreatment of the components in series directly follows one another and the decrease in the phosphation quality over time can be determined, so that a quantity of the activating agent can in turn be continuously metered in over time. This process has the advantage that, after the start-up of the pretreatment line and the determination of the material flows for the metered addition of the activating aid and other active components, the phosphation quality does not have to be checked further as long as the series treatment remains unchanged in terms of timing and properties of the components to be treated and the treatment parameters in zinc phosphation process step (ii). However, if a constant mode of operation in the series treatment cannot be ensured or is not desirable due to the system, discontinuous metering of the activating aid is advantageous and may even be advisable. In this case, the phosphation quality of the acidic aqueous composition is preferably monitored continuously or at defined time intervals in step (ii), and a specified amount of the activating aid is then metered in if the layer weight on hot-dip galvanized steel (Z) reaches a certain value below 5.0 g/m^2. preferably below 4.5 g/m^2, particularly preferably below 4.0 g/m^2 and very particularly preferably below 3.5 g/m^2. The continuous or quasi-continuous determination of the phosphation quality, which takes place at defined time intervals, can also be carried out using proxy data that correlate with the actual zinc phosphate layer weight. The non-destructive determination of the layer thickness, for example using the eddy current process or even contact-free optical determination methods such as ellipsometry or spectral reflectivity measurement, provides suitable proxy data for the layer weight of zinc phosphate, which data can be reliably measured on the surfaces of zinc of the components in a pretreatment line and can be correlated with the actual layer weight on hot-dip galvanized parts steel (Z). The crystallite size and thus the determination of the roughness by means of optical profilometry can also provide proxy data for the layer weight, since a higher layer weight on hot-dip galvanized steel (Z) is associated with a low number density of crystallites, which, however, are relatively larger, so that the roughness increases with the layer weight.

[0069] It has been found that the phosphation quality is already adequate in most cases if the activating aid is metered in continuously or discontinuously in such an amount that is suitable for maintaining a steady-state amount of preferably at least 0.001 g/kg, particularly preferably at least 0.005 g/kg, more particularly preferably at least 0.01 g/kg, of particulate constituent (P) in the acidic aqueous composition during the pretreatment of the components in series. This applies in particular to the contacting of the acidic aqueous composition by spraying, whereas in the case of dip application, a steady-state amount of preferably at least 0.002 g/kg, particularly preferably 0.01 g/kg and more particularly preferably 0.02 g/kg of particulate constituent (P) should be contained in the acidic aqueous composition for zinc phosphation.

[0070] The present invention thus surprisingly shows that by the metered addition of an activating aid, as is known in the prior art and described, for example, in WO 98/39498 A1, directly to the acidic aqueous treatment solution for zinc phosphation in step (ii), activation of the metal surfaces can take place, so that homogeneous, closed and compact crystalline zinc phosphate coatings having a high electrical charge transfer resistance grow on the metal surfaces, wherein such high quality phosphate coatings for corrosion protection and coating adhesion are achieved on the surfaces of zinc due to the deposition of iron brought about in process step (i). The present invention makes use of this effect in that the series treatment of components is based on zinc phosphation by means of an acidic aqueous composition that, in addition to zinc ions, phosphate ions and free fluoride, also contains a particulate constituent (P) dispersed in water, and/or on maintaining the phosphation quality by the metered addition of the activating aid to the acidic aqueous composition for zinc phosphation. For the desired phosphation quality, it is in this case possible to switch to solely adding the aqueous dispersion or metering the activating aid, each containing the particulate constituent (P), without the components in the series having to go through a wet-chemical activation stage, for example based on the aqueous dispersion or activating aid, prior to the zinc phosphation process step. This can save a complete process step, including the necessary bath maintenance, circulation, temperature management and chemical additivation, e.g. using water-soluble condensed phosphates, so that an extremely resource-saving and economical operation of a pretreatment line for zinc phosphation is possible for the first time.

[0071] For the dispersed particulate constituent (P) and the at least one particulate inorganic compound (P1) or polymeric organic compound (P2), the definitions and preferred specifications set forth below apply regardless of whether the dispersed particulate constituent (P) is a part of the aqueous dispersion for providing the self-activating acidic aqueous composition for zinc phosphation or the activating aid for maintaining the activation performance of the acidic aqueous composition in process step (ii) of the process according to the invention. In the following, for the sake of simplicity, reference is made only to the activating aid. The statements regarding the activating aid therefore also apply accordingly to the aqueous dispersion for providing the self-activating acidic aqueous composition for zinc phosphation.

[0072] Activating aids that can be used according to the invention, i.e., that maintain the phosphation quality during metered addition to the acidic aqueous composition of the zinc phosphation, or provide the acidic aqueous composition for zinc phosphation in step (ii) for the first time, are aqueous dispersions and thus contain a particulate constituent (P) in water-dispersed form which comprises at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite, and at least one polymeric organic compound (P2).

[0073] The use of polyvalent metal cations in the form of phosphates is responsible for the good activation performance or suitability of the activating aid for maintaining the phosphation quality of the acidic aqueous composition for zinc phosphation, and said phosphates should therefore be contained in the activating aid in a sufficiently high proportion in the dispersed particulate constituent (P). Accordingly, the proportion of phosphates contained in the at least one particulate inorganic compound (P1), based on the dispersed particulate constituent (P) in the activating aid, is preferably at least 25 wt. %, particularly preferably at least 35 wt. %, more particularly preferably at least 40 wt. %, very particularly preferably at least 45 wt. %. The dispersed particulate constituent (P) of the activating aid is the solids content that remains after drying the retentate of an ultrafiltration of a defined partial volume of the activating aid with a nominal cutoff limit of 10 kD (NMWC: nominal molecular weight cutoff). Ultrafiltration is carried out by adding deionized water ($\kappa<1$ μScm^{-1}) until a conductivity of below 10 $\mu Scm^{-}1$ is measured in the filtrate. The inorganic particulate constituent in the activating aid is, in turn, that which remains when the particulate constituent (P) obtained from the drying of the ultrafiltration retentate is pyrolyzed in a reaction furnace by supplying a CO_2-free oxygen flow at 900° C. without admixture of catalysts or other additives until an infrared sensor provides a signal identical to the CO_2-free carrier gas (blank value) in the outlet of the reaction furnace. The phosphates contained in the inorganic particulate constituent are determined as phosphorus content by means of atomic emission spectrometry (ICP-OES) after acid digestion of the constituent with aqueous 10 wt. % HNO_3 solution at 25° C. for 15 min, directly from the acid digestion.

[0074] The active components of the activating aid, which—as soon as they are added in a sufficient amount to the acidic aqueous composition for zinc phosphation—promote the formation of a homogeneous, closed and compact crystalline phosphate coating on the metal surfaces and in particular on the surfaces of zinc, and, in this sense, activate the metal surfaces, are, as already mentioned, mainly composed of phosphates, which, in turn, are at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite, preferably at least partly selected from hopeite, phosphophyllite, and/or scholzite, particularly preferably at least partly selected from hopeite and/or phosphophyllite, and very particularly preferably at least partly selected from hopeite. The maintenance of the phosphation quality in the acidic aqueous composition is therefore substantially based on the metered phosphates in particulate form which are contained in the activating aid. Without taking into account water of crystallization, hopeites stoichiometrically comprise $Zn_3(PO_4)_2$ and the nickel-containing and manganese-containing variants $Zn_2Mn(PO_4)_3$, $Zn_2Ni(PO_4)_3$, whereas phosphophyllite consists of $Zn_2Fe(PO_4)_3$, scholzite consists of $Zn_2Ca(PO_4)_3$ and hureaulite consists of $Mn_3(PO_4)_2$. The existence of the crystalline phases hopeite, phosphophyllite, scholzite and/or hureaulite in the activating aid can be demonstrated by means of X-ray diffractometric methods (XRD) after separation of the particulate constituent (P) by means of ultrafiltration with a nominal cutoff limit of 10 kD (NMWC: nominal molecular weight cutoff), as described above, and drying of the retentate to constant mass at 105° C.

[0075] Due to the preference for the presence of phosphates comprising zinc ions and having a certain crystallinity, it is preferred for the formation of firmly adherent crystalline zinc phosphate coatings, in the process according to the invention, for the activating aid to contain at least 20 wt. %, particularly preferably at least 30 wt. %, more particularly preferably at least 40 wt. %, of zinc in the inorganic particulate constituent, based on the phosphate content of the inorganic particulate constituent, calculated as PO_4.

[0076] However, the activating aid should preferably not additionally contain any titanium phosphates, since these do not have a positive effect on the phosphation quality when metered in. In a preferred embodiment of the process according to the invention, the proportion of titanium in the inorganic particulate constituent of the activating aid is therefore less than 0.01 wt. %, particularly preferably less than 0.001 wt. %, based on the activating aid. In a particularly preferred embodiment, the activating aid contains a total of less than 10 mg/kg, particularly preferably less than 1 mg/kg of titanium.

[0077] The polymeric organic compound (P2) that stabilizes the particulate constituent has a major influence on the effectiveness of the particulate constituent (P) metered in via the activating aid. It is found that the selection of the polymeric organic compound is decisive for the extent of the activation of the metal surfaces in the acidic aqueous composition for zinc phosphation in step (ii), which activation is known to be brought about by the dispersed polyvalent phosphates and which, as the present invention shows, surprisingly can also take place simultaneously with the layer formation.

[0078] In the context of the present invention, an organic compound is polymeric if its weight-average molar mass is greater than 500 g/mol. The molar mass is in this case determined using the molar mass distribution curve of a sample of the relevant reference value, which curve is established experimentally at 30° C. by means of size-exclusion chromatography using a concentration-dependent refractive index detector and calibrated against polyethylene glycol standards. The average molar masses are evaluated with the aid of a computer according to the strip method using a third-order calibration curve. Hydroxylated polymethacrylate is suitable as a column material, and an aqueous solution of 0.2 mol/L sodium chloride, 0.02 mol/L sodium hydroxide, and 6.5 mmol/L ammonium hydroxide is suitable as an eluent.

[0079] It is found that the maintenance of the phosphation quality and thus an activation of the metal surfaces in the zinc phosphation process step when brought into contact with the acidic aqueous composition is particularly well achieved, i.e., using relatively small amounts of active components of the activating aid, if the polymeric organic compound (P2) used for dispersing the particulate inorganic compound (P1) is at least in part composed of styrene and/or an ⌋-olefin having not more than 5 carbon atoms, wherein the polymeric organic compound (P2) additionally has units of maleic acid, the anhydride and/or the imide thereof, and preferably additionally polyoxyalkylene units, particularly preferably polyoxyalkylene units, in its side chains. Such polymeric organic compounds (P2) are therefore preferred according to the invention in the particulate constituent (P) of the activating aid.

[0080] The α-olefin in this case is preferably selected from ethene, 1-propene, 1-butene, isobutylene, 1-pentene, 2-methyl-but-1-ene and/or 3-methyl-but-1-ene and particularly preferably selected from isobutylene. It is clear to a person skilled in the art that the polymeric organic compounds (P2) contain these monomers as structural units in unsaturated form covalently linked to one another or to other structural units.

[0081] Suitable commercially available representatives of polymeric organic compounds (P2) are, for example, Dispex® CX 4320 (BASF SE), a maleic acid-isobutylene copolymer modified with polypropylene glycol, Tego® Dispers 752 W (Evonik Industries AG), a maleic acid-styrene copolymer modified with polyethylene glycol, or Edaplan® 490 (Münzing Chemie GmbH), a maleic acid-styrene copolymer modified with EO/PO and imidazole units.

[0082] In the context of the present invention, polymeric organic compounds (P2) that are composed at least partly of styrene are preferred.

[0083] The polymeric organic compounds (P2) used for colloidal stabilization of the particulate constituent (P) of the activating aid preferably have polyoxyalkylene units that in turn are preferably composed of 1,2-ethanediol and/or 1,2-propanediol, particularly preferably of both 1,2-ethanediol and 1,2-propanediol, the proportion of 1,2-propanediols in the entirety of the polyoxyalkylene units being preferably at least 15 wt. %, but particularly preferably not exceeding 40 wt. %, based on the entirety of the polyoxyalkylene units. Furthermore, the polyoxyalkylene units are preferably contained in the side chains of the polymeric organic compounds (P2). A proportion of the polyoxyalkylene units in the entirety of the polymeric organic compounds (P2) of preferably at least 40 wt. %, particularly preferably at least 50 wt. %, but preferably no more than 70 wt. %, is advantageous for the dispersibility of said compounds.

[0084] For anchoring the polymeric organic compound (P2) with the inorganic particulate constituent (P1) of the activating aid, which is at least partly formed of polyvalent metal cations in the form of phosphates selected from hopeite, phosphophyllite, scholzite and/or hureaulite, and increased stability and ability of the particulate constituent (P) to activate in the acidic aqueous composition of the zinc phosphation, the organic polymeric compounds (P2) also have imidazole units, preferably in the side chains, particularly preferably as a constituent of the polyoxyalkylene units of the polymeric organic compounds (P2).

[0085] In a preferred embodiment, the amine value of the organic polymeric compounds (P2) is at least 25 mg KOH/g, particularly preferably at least 40 mg KOH/g, but preferably less than 125 mg KOH/g, particularly preferably less than 80 mg KOH/g, and therefore, in a preferred embodiment, the entirety of the polymeric organic compounds in the particulate constituent (P) of the activating aid also have these preferred amine values. The amine value is determined in each case by weighing out approximately 1 g of the relevant reference value—organic polymeric compounds (P2) or the entirety of the polymeric organic compounds in the particulate constituent (P)—in 100 mL of ethanol, titration being carried out using 0.1 N HCl titrant solution against the indicator bromophenol blue until the color changes to yellow at a temperature of the ethanolic solution of 20° C. The amount of HCl titrant solution used in milliliters multiplied by the factor 5.61 divided by the exact mass of the weight in grams corresponds to the amine value in milligrams KOH per gram of the relevant reference value.

[0086] It has also been proven to be advantageous for the polymeric organic compounds (P2), preferably also the entirety of the polymeric organic compounds in the particulate constituent (P), to have an acid number according to DGF C-V 2 (06) (as of April 2018) of at least 25 mg KOH/g, but preferably of less than 100 mg KOH/g, particularly preferably of less than 70 mg KOH/g, to ensure a sufficient number of polyoxyalkylene units. It is also preferred for the polymeric organic compounds (P2), preferably also the entirety of the polymeric organic compounds in the particulate constituent (P), to have a hydroxyl number of less than 15 mg KOH/g, particularly preferably of less than 12 mg KOH/g, more particularly preferably of less than 10 mg KOH/g, determined according to method A of 01/2008: 20503 from European Pharmacopoeia 9.0 in each case.

[0087] For a stable dispersion of the inorganic particulate constituents in the activating aid, it is sufficient for the proportion of the polymeric organic compounds (P2), preferably the entirety of the polymeric organic compounds in the particulate constituent (P), based on the particulate constituent (P), to be at least 3 wt. %, particularly preferably at least 6 wt. %, but preferably not exceeding 15 wt. %. The dispersed particulate constituent (P) of the activating aid is the solids content that remains after drying the retentate of an ultrafiltration of a defined partial volume of the activating aid with a nominal cutoff limit of 10 kD (NMWC: nominal molecular weight cutoff). Ultrafiltration is carried out by adding deionized water ($\kappa<1\ \mu Scm^{-1}$) until a conductivity of below 10 μScm^{-1} is measured in the filtrate.

[0088] The activating aid preferably contains no more than 40 wt. % of particulate constituent (P), based on the agent, since otherwise the stability of the dispersion and the technical handling behavior for a continuous or discontinuous metered addition of the agent to the acidic aqueous composition of the zinc phosphation by means of metering pumps are no longer ensured or are at least complex. This applies in particular with regard to the overall low amounts of particulate constituents (P) required to maintain the phosphation quality of a reference amount of the acidic aqueous composition for zinc phosphation. However, it is advantageous for the activating aid to be provided as a dispersion that is as stable as possible and at the same time as highly concentrated as possible. This can be achieved in particular when using the preferred polymeric organic compounds (P2) to disperse the particulate inorganic compound (P1), so that activating aids are preferably used which contain at least 5 wt. %, but preferably no more than 30 wt. %, of particulate constituent (P) based on the agent.

[0089] In such concentrated aqueous dispersions of the activating aid, i.e., those having a proportion of 5 wt. % of particulate constituent (P) based on the agent, the activating aid can, in the process according to the invention, additionally be characterized by its D50 value of more than 10 μm, which is correspondingly preferred. The agglomerates of the dispersed particles contained in the dispersion bring about the thixotropic flow properties that are favorable for the handling behavior of the activating aid. The tendency of the agglomerates to be highly viscous at low shear is favorable for their long shelf life, while the loss of viscosity when sheared makes them pumpable. Favorable flow properties are also obtained if the dispersion does not significantly exceed a D90 value of 150 μm: therefore, according to the invention, a D90 value of the aqueous dispersion of less than 150 μm, preferably less than 100 μm, in particular less than 80 μm, is preferred. In the context of the present invention, the D50 value or the D90 value denotes the particle diameter that is not exceeded by 50 vol. % or 90 vol. %, respectively, of the particulate constituents contained in the aqueous dispersion. According to ISO 13320:2009, the D50 value or D90 value can be determined from volume-weighted cumulative particle size distributions by means of scattered light analysis according to Mie theory immediately after dilution of the activating aid, in the form of the concentrated aqueous dispersion, to a dispersed particulate constituent of 0.05 wt. % with a corresponding amount of deionized water ($\kappa<1\ \mu Scm^{1}$) at 20° C., using spherical particles and a refractive index of the scattering particles of $n_D=1.52-i\cdot 0.1$. The dilution is carried out in such a way that an amount of the concentrated dispersion corresponding to a volume of 200 ml of deionized water is added to the sample vessel of the LA-950 V2 particle size analyzer from the manufacturer Horiba Ltd., and is mechanically circulated there into the measuring chamber (setting of the circulating pump on the LA-950 V2: level 5=1167 rpm for a volume flow of 3.3 liters/minute). The particle size distribution is measured within 120 seconds after the dispersion has been added to the dilution volume.

[0090] The presence of a thickener can be advantageous for preventing the irreversible agglomeration of primary particles of the particulate constituent (P), in particular if the activating aid is present as the concentrated dispersion described above. In a preferred embodiment of the process according to the invention, the activating aid therefore contains a thickener, preferably in an amount which, in the shear rate range of from 0.001 to 0.25 reciprocal seconds, gives the activating aid a maximum dynamic viscosity of at least 1000 Pa·s, but preferably below 5000 Pa·s, at a temperature of 25° C., and preferably leads to shear-thinning behavior, i.e., a decrease in viscosity with increasing shear rate, resulting at 25° C. at shear rates above those present at the maximum dynamic viscosity, so that the activating aid has an overall thixotropic flow behavior. The viscosity over the specified shear rate range can in this case be determined by means of a cone and plate viscometer having a cone diameter of 35 mm and a gap width of 0.047 mm.

[0091] A thickener, within the meaning of the present invention, is a polymeric chemical compound or a defined mixture of chemical compounds which, as a 0.5 wt. % constituent in deionized water ($k<1\ \mu Scm^{-1}$) at a temperature of 25° C., has a Brookfield viscosity of at least 100 mPa·s at a shear rate of 60 rpm (=rounds per minute) using a size 2 spindle. When determining this thickener property, the mixture should be mixed with water in such a way that the corresponding amount of the polymeric chemical compound is added to the water phase at 25° C. while stirring and the homogenized mixture is then freed of air bubbles in an ultrasonic bath and left to stand for 24 hours. The measurement value of the viscosity is then read within 5 seconds immediately after application of a shear rate of 60 rpm by the number 2 spindle.

[0092] The activating aid preferably contains a total of at least 0.5 wt. %, but preferably no more than 4 wt. %, particularly preferably no more than 3 wt. %, of one or more thickeners, the total proportion of polymeric organic compounds in the non-particulate constituent of the aqueous dispersion furthermore preferably not exceeding 4 wt. % (based on the dispersion). The non-particulate constituent is the solids content of the aqueous dispersion in the permeate of the above-described ultrafiltration after it has been dried to constant mass at 105° C., i.e., the solids content after the particulate constituent has been separated by means of ultrafiltration.

[0093] Certain classes of polymeric compounds are particularly suitable thickeners and are also readily commercially available. Thus, the thickener is preferably selected from polymeric organic compounds, which, in turn, are preferably selected from polysaccharides, cellulose derivatives, aminoplasts, polyvinyl alcohols, polyvinylpyrrolidones, polyurethanes and/or urea urethane resins, and particularly preferably from urea urethane resins, in particular urea urethane resins that are a mixture of polymeric compounds resulting from the reaction of a polyvalent isocyanate with a polyol and a mono- and/or diamine. In a preferred embodiment, the urea urethane resin results from a polyvalent isocyanate, preferably selected from 1,4-tetramethylene diisocyanate, 1,6-hexamethylene diisocyanate, 2.2(4),4-trimethyl-1.6-hexamethylene diisocyanate, 1,10-decamethylene diisocyanate, 1,4,-cyclohexylene diisocyanate, p-phenylene diisocyanate, m-phenylene diisocyanate, 2,6-toluene diisocyanate, 2.4-toluene diisocyanate and mixtures thereof, p- and m-xylylene diisocyanate, and 4-4'-diisocyanatodicyclohexylmethane, particularly preferably selected from 2,4-toluene diisocyanate and/or m-xylylene diisocyanate. In a particularly preferred embodiment, the urea urethane resin results from a polyol selected from polyoxyalkylene diols, particularly preferably from polyoxyethylene glycols, which in turn are preferably composed of at least 6, particularly preferably at least 8, more particularly preferably at least 10, but preferably less than 26, particularly preferably less than 23, oxyalkylene units.

[0094] Urea urethane resins that are particularly suitable and therefore preferred according to the invention can be obtained by first reacting a diisocyanate, for example toluene-2,4-diisocyanate, with a polyol, for example a polyethylene glycol, to form NCO-terminated urethane prepolymers, followed by further reaction with a primary monoamine and/or with a primary diamine, for example m-xylylenediamine. Urea urethane resins that have neither free nor blocked isocyanate groups are particularly preferred. As a constituent of the activating agent, such urea urethane resins promote the formation of loose agglomerates of primary particles, which are protected against further agglomeration and, when metered into the acidic aqueous composition for zinc phosphation, dissociate into primary particles. To further promote this property profile, urea urethane resins that have neither free or blocked isocyanate groups nor terminal amine groups are preferably used as the thickener. In a preferred embodiment, the thickener, which is a urea urethane resin, therefore has an amine value of less than 8 mg KOH/g, particularly preferably of less than 5 mg KOH/g, more particularly preferably of less than 2 mg KOH/g, determined in each case according to the method as previously described for the organic polymeric compound (P2). Since the thickener is substantially dissolved in the aqueous phase of the activating aid and can thus be assigned to the non-particulate constituent, while component (P2) is substantially bound in the particulate constituent (P), an activating aid in which the entirety of the polymeric organic compounds in the non-particulate constituent preferably has an amine value of less than 16 mg KOH/g, particularly preferably of less than 10 mg KOH/g, more particularly preferably of less than 4 mg KOH/g, is preferred. It is further preferred for the urea urethane resin to have a hydroxyl number in the range of from 10 to 100 mg KOH/g, particularly preferably in the range of from 20 to 60 mg KOH/g, determined according to method A of 01/2008:20503 from European Pharmacopoeia 9.0. With regard to the molecular weight, a weight-average molar mass of the urea urethane resin in the range of from 1000 to 10000 g/mol, preferably in the range of from 2000 to 6000 g/mol, is advantageous according to the invention and therefore preferred, in each case determined experimentally, as previously described in connection with the definition according to the invention of a polymeric organic compound.

[0095] The activating aid is an aqueous dispersion that preferably has a pH value in the range of 6.5-8.0 and particularly preferably does not contain any pH-regulating, water-soluble compounds with a pK_S value of less than 6 or a pK_B value of less than 5.

[0096] The activating aid can also contain auxiliaries, for example selected from preservatives, wetting agents and defoamers, which are contained in the amount necessary for the relevant function. The proportion of auxiliaries, particularly preferably of other compounds in the non-particulate constituent which are not thickeners, is preferably less than 1 wt. %.

[0097] The activating aid can preferably be obtained as a concentrated aqueous dispersion by

[0098] i) providing a pigment paste by triturating 10 parts by mass of an inorganic particulate compound (P1) with 0.5 to 2 parts by mass of the polymeric organic compound (P2) in the presence of 4 to 7 parts by mass of water and grinding until a D50 value of less than 1 μm has been reached, as determined by means of dynamic light scattering after dilution with water by a factor of 1000, for example by means of Zetasizer® Nano ZS from Malvern Panalytical GmbH;

[0099] ii) diluting the pigment paste with such an amount of water, preferably deionized water (k<1 μScm^{-1}) or service water and a thickener that a dispersed particulate constituent (P) of at least 5 wt. % and a maximum dynamic viscosity of at least 1000 Pa·s at a temperature of 25° C. in the shear rate range of from 0.001 to 0.25 reciprocal seconds is set,

wherein preferred embodiments of the activating aid are obtained in an analogous manner by selecting corresponding components (P1), (P2) and the thickener in the amount that may be provided or required in each case. Such a concentrated aqueous dispersion has excellent stability and, due to its thixotropic flow behavior, also good pumpability, so that the concentrated dispersion can be metered directly into the zinc phosphation system tank in a controlled manner.

[0100] With regard to the acidic aqueous composition for zinc phosphation, it is imperative for the formation of homogeneous, closed zinc phosphate layers that, in step (ii) of the process according to the invention, said composition contains at least

[0101] (A) 5-50 g/kg of phosphates dissolved in water, calculated as PO_4,

[0102] (B) 0.3-3 g/kg of zinc ions, and

[0103] (C) free fluoride,

and a free acid in points greater than zero.

[0104] In this context, the amount of phosphate ions includes orthophosphoric acid and the anions, dissolved in water, of the salts of orthophosphoric acid, calculated as PO_4.

[0105] The proportion of the free acid in points in the acidic aqueous composition of the zinc phosphation in step (ii) of the process according to the invention is preferably at least 0.4, but preferably no more than 3.0, particularly preferably no more than 2.0. The proportion of the free acid in points is determined by diluting 10 ml sample volume of the acidic aqueous composition to 60 ml and titrating with 0.1 N sodium hydroxide solution to a pH value of 3.6. The consumption of ml of sodium hydroxide solution indicates the point number of free acid.

[0106] The preferred pH value of the acidic aqueous composition is usually above 2.5, particularly preferably above 2.7, but preferably below 3.5, particularly preferably below 3.3. The “pH value,” as used in the context of the present invention, corresponds to the negative decadic logarithm of the hydronium ion activity at 20° C. and can be determined by means of pH-sensitive glass electrodes.

[0107] A quantity of free fluoride or a source of free fluoride ions is essential for the layer-forming zinc phosphation process. Insofar as components comprising surfaces of iron or aluminum, in addition to surfaces of zinc, are to be zinc-phosphated in a layer-forming manner, as is necessary, for example, in the zinc phosphation of automobile bodies that are at least partly made of aluminum, it is advantageous if the amount of free fluoride in the acidic aqueous composition in step (ii) is at least 0.5 mmol/kg, particularly preferably at least 2 mmol/kg. The concentration of free fluoride should not exceed values above which the phosphate coatings have loose adhesions that can be easily wiped off, since this defect frequently cannot be compensated for even by an increased metered addition of the activating aid or by an increased steady-state amount of particulate constituents (P) in the acidic aqueous composition for zinc phosphation. Therefore, it is advantageous, and therefore preferred, for the concentration of free fluoride in the acidic aqueous composition of the zinc phosphation to be below 15 mmol/kg, particularly preferably below 10 mmol/kg and more particularly preferably below 8 mmol/kg, in step (ii) of the process according to the invention.

[0108] The amount of free fluoride is to be determined potentiometrically by means of a fluoride-sensitive measuring electrode at 20° C. in the relevant acidic aqueous composition after calibration with fluoride-containing buffer solutions without pH buffering. Suitable sources of free fluoride ions are hydrofluoric acid and the water-soluble salts thereof, such as ammonium bifluoride and sodium fluoride, as well as complex fluorides of the elements Zr, Ti and/or Si, in particular complex fluorides of the element Si. In a phosphation process according to the present invention, the source of free fluoride is therefore preferably selected from hydrofluoric acid and the water-soluble salts thereof and/or complex fluorides of the elements Zr, Ti and/or Si. Salts of hydrofluoric acid are water-soluble within the meaning of the present invention if their solubility in deionized water (k<1 μScm^{-1}) at 60° C. is at least 1 g/L, calculated as F.

[0109] In order to suppress what is known as “pin-holing” on the surfaces of the metal materials that are made of zinc, it is preferred, in such processes according to the invention, for the source of free fluoride in step (ii) to be at least partly selected from complex fluorides of the element Si, in particular from hexafluorosilicic acid and the salts thereof. The term pin-holing is understood by a person skilled in the art of phosphation to mean the phenomenon of local deposition of amorphous, white zinc phosphate in an otherwise crystalline phosphate layer on the treated zinc surfaces or on the treated galvanized or alloy-galvanized steel surfaces.

[0110] The accelerators known in the prior art can be added to the acidic aqueous composition in the process according to the invention for more rapid layer formation. These accelerators are preferably selected from 2-hydroxymethyl-2-nitro-1,3-propanediol, nitroguanidine, N-methylmorpholine-N-oxide, nitrite, hydroxylamine and/or hydrogen peroxide. It is found that when nitroguanidine or hydroxylamine is used as an accelerator, a comparatively lower metered addition of activating aid is required or a lower steady-state amount of particulate constituents (P) must be maintained in the acidic aqueous composition for zinc phosphation in step (ii), so that nitroguanidine or hydroxylamine, in particular nitroguanidine is particularly preferred as an accelerator in the acidic aqueous composition in step (ii) of the process according to the invention in view of a particularly low material use of the activating aid for maintaining the phosphation quality.

[0111] An embodiment in which less than 10 ppm of nickel and/or cobalt ions are contained in total in the acidic aqueous composition for zinc phosphation in step (ii) of the process according to the invention is particularly preferred from an ecological point of view.

[0112] Furthermore, in the process according to the invention, the additivation well known in the art in zinc phosphation processes can also be used.

Optional Process Steps

[0113] In a preferred embodiment of the process according to the invention, before being brought into contact with the acidic aqueous composition in zinc phosphation process step (ii), the components in the series are therefore not brought into contact with a colloidal, aqueous activation solution containing, in the particulate constituent, hopeite, phosphophyllite, scholzite and/or hureaulite, preferably phosphates of polyvalent metal cations, or sparingly soluble salts of the element Ti. Before being brought into contact with the acidic aqueous composition in zinc phosphation process step (ii), the components in the series are particularly preferably not brought into contact with a colloidal, aqueous solution for activating the surfaces of the components for zinc phosphation, and the components in the series very particularly preferably do not go through an activation stage for activating the surfaces of the components for zinc phosphation before being brought into contact in process step (ii).

[0114] However, it is usually not possible to dispense with a cleaning and degreasing stage as a process step upstream of the zinc phosphation in step (ii) and the deposition of iron in step (i). In order to achieve reproducible layer coatings that are as uniform as possible, in a preferred embodiment of the process according to the invention, before process step (i), at least the metal surfaces of the components are cleaned and if necessary degreased in a separate cleaning stage or together with process step (i). The cleaning is preferably carried out by contact with an aqueous, preferably neutral or alkaline cleaning agent, wherein process step (i) immediately follows the cleaning stage, with or without an intermediate rinsing step, preferably without an intermediate rinsing step.

[0115] In the context of cleaning and optionally degreasing the components, the alkaline cleaning is characterized by the fact that the metal surfaces, in particular the surfaces that contain metal aluminum, whether as a material or as an alloy component of hot-dip galvanized steel, are pickled, which leads to an additional standardization of the metal surfaces and is therefore advantageous for the growth of homogeneous zinc phosphate coatings.

[0116] The cleaning stage—or combined cleaning and ironizing stage—preferably does not take place by means of contact with an aqueous, preferably neutral or alkaline cleaning agent containing a particulate constituent comprising hopeite, phosphophyllite, scholzite and/or hureaulite or sparingly soluble salts of the element Ti, since, as explained above, any activation of the metal surfaces before the zinc phosphation in step (ii) can be dispensed with according to the invention. A rinsing step after the cleaning is, as already mentioned, optional and, in the context of the present invention, is used exclusively for the complete or partial removal of soluble residues, particles and active components that are carried over by adhering to the component from a previous wet-chemical treatment step—in this case the cleaning and degreasing stage—from the component to be treated, without metal-element-based or semi-metal-element-based active components, which are already consumed merely by bringing the metal surfaces of the component into contact with the rinsing liquid, being contained in the rinsing liquid itself. For example, the rinsing liquid can simply be city water or deionized water or, if necessary, can also be a rinsing liquid that contains surface-active compounds to improve the wettability by means of the rinsing liquid.

Components

[0117] Since the phosphation quality in the process according to the invention on hot-dip galvanized steel is technically optimized, processes are naturally also preferred according to the invention in which the components in the series that at least partly have surfaces of zinc also comprise surfaces of hot-dip galvanized steel. In principle, the phosphation quality of the acidic aqueous composition, which is maintained in step (ii) by adding the activating aid, is such that components that are manufactured in a multi-metal construction, such as automobile bodies, can also be zinc-phosphated with very good properties, and very homogeneous, closed and compact zinc phosphate coatings can also be obtained on the surfaces of iron and aluminum. In the process according to the invention, it is therefore preferred for the components in the series to also have surfaces of the metal iron or, specifically for lightweight construction in car body manufacturing, additional aluminum. In a particularly preferred embodiment, specifically in car body manufacturing, the components have surfaces of the metals zinc, iron and aluminum next to one another.

[0118] In the process according to the invention, it is preferred for the components in the series to be brought into contact with the acidic aqueous composition in step (ii) for at least a period of time that is sufficient to deposit a layer weight of at least 1.0 g/m^2 on the surfaces of zinc, since it is then ensured that a sufficiently homogeneous, closed zinc phosphate coating is formed on all metal surfaces of the components selected from zinc, iron, or aluminum. Accordingly, preference is given to a process according to the invention in which a zinc phosphate layer having a layer weight of at least 1.0 g/m^2, preferably at least 1.5 g/m^2, is deposited on the surfaces of zinc. Because the phosphation quality of the acidic aqueous composition for zinc phosphation in step (ii) is preferably maintained as a control variable in the process according to the invention, or the acidic aqueous composition has an inherent activation performance, it is also always ensured that the zinc surfaces of the component have a homogeneous, closed and compact crystalline zinc phosphate layer, the layer thickness of which is in the range of self-limitation, so that, according to the invention, the layer weight of the zinc phosphate layer on the zinc surfaces of the component, as required by the object spectrum, is preferably also below 5.0 g/m^2, preferably below 4.5 g/m^2, particularly preferably below 4.0 g/m^2 and very particularly preferably below 3.5 g/m^2.

[0119] In the process according to the invention, a good coating base for a subsequent dip coating or powder coating, in the course of which a substantially organic cover layer is applied, is produced. Accordingly, in a preferred embodiment of the process according to the invention, the zinc phosphation in step (ii), with or without an intermediate rinsing and/or drying step, but preferably with a rinsing step and without a drying step, is followed by dip coating or powder coating, particularly preferably electrocoating, more particularly preferably cathodic electrocoating, which preferably contains water-soluble or water-dispersible salts of yttrium and/or bismuth in addition to the dispersed resin, which preferably comprises an amine-modified polyepoxide.

EXEMPLARY EMBODIMENTS

[0120] To illustrate the advantages of the process according to the invention, the process sequence described in detail below was applied to the layer-forming phosphation of various metallic substrates and the suitability thereof for the treatment of components composed of these metallic substrates in series was illustrated.

[0121] a) Alkaline cleaning by means of 3.5% Bonderite® C-AK 2020-1, mixed with 0.8% Bonderite® M-FE 2020 MU, 1.2% Bonderite® M-AD ZN-2, 0.5% Bonderite® M-AD FE-1 and 0.5% Bonderite® C-AD 1561, which are each process chemicals from Henkel AG & Co. KGaA, and with fully deionized water (k<1 μScm^{-1}), was applied to the proportion as indicated. After setting a pH value of 11.8-11.9 and a temperature of 55° C., the sheets were first spray degreased for 1 minute at a pressure of 1 bar, then

[0122] a1) a variant without iron deposition: dip degreased for 3 minutes with the same cleaning solution while stirring, or

[0123] a2) a variant with iron deposition: dip degreased for 2 minutes while stirring by dipping the sheets in 3.6 wt. % Bonderite® C-AK 2020-1, mixed with 0.8 wt. % Bonderite® M-FE 2020 MU, 0.7 wt. % Bonderite® M-AD ZN-2, 0.5 wt. % Bonderite® M-AD FE-1 and 0.5 wt. % Bonderite® C-AD 1561, which are each process chemicals from Henkel AG & Co. KGaA, and with fully deionized water (k<1 μScm^{-1}), was applied to the proportion as indicated. The treatment was carried out after setting a pH value of 12.0 and a temperature of 60° C.

[0124] b) The substrates were then thoroughly washed with fully deionized water (k<1 μScm^{-1}) for approximately 1 minute. Under these conditions, a closed water layer remained on the substrates for at least 30 seconds, indicating the absence of grease and oil on the substrates.

[0125] c) The substrate surfaces were then wetted in water and dipped directly, without treatment in a separate activation bath, into a hydroxylamine-accelerated phosphating bath on the basis of fully deionized water (k<1 μScm^{-1}) and 4.6 wt % Bonderite® M—Zn 1994 MU-1 and 1 wt % Bonderite® M-AD 565, which are each process chemicals from Henkel AG & Co. KGaA and were applied with deionized water (k<1 μScm^{-1}) to the proportion as indicated, for 3 min at 52° C. while stirring (free acid: 1.1 points, total acid: 26.5 points, zinc content: 0.13 wt. %, accelerator content: 0.1 wt. %), to which

[0126] c1) 1 g/L Bonderite® M-AC 3000 (Henkel AG & Co. KGaA) of an aqueous dispersion of zinc phosphates, which is prepared as described in the example of WO 2021/104973 A1, was added (this corresponds to a proportion of particulate zinc phosphate of 0.2 g/kg based on the phosphating bath), or

[0127] c2) 3 g/L Bonderite® M-AC 3000 (Henkel AG & Co. KGaA) of an aqueous dispersion of zinc phosphates, which is prepared as described in the example of WO 2021/104973 A1, was added (this corresponds to a proportion of particulate zinc phosphate of 0.6 g/kg based on the phosphating bath).

[0128] d) the substrates were then thoroughly washed under fully deionized water (k<1 μScm^{-1}) for about 1 minute, then

[0129] e) blown with compressed air at room temperature and then dried in an oven at 50° C.

[0130] The metallic substrates coated according to this process sequence were sheets of cold-rolled steel (CRS), electrolytically galvanized steel (EG), hot-dip galvanized steel (HDG), zinc-magnesium hot-dip coated steel (ZM), and aluminum (AA6014), which were cleaned after process step a1) or a2) and then pretreated after successive process steps b)-e).

[0131] Closed, homogeneous zinc phosphate layers were produced in all cases. Coating layers in the range of 82 to 105 mg/m^2 of iron were produced on the HDG, EG and ZM sheets in the process sequences with an ironizing stage (a2-b-c1-d-e/a2-b-c2-d-e). The iron coating was quantitatively determined after substrate pickling with 5 wt. % HNO$_3$ and subsequent photometric concentration determination based on the formation of a colored thiocyanate complex.

[0132] A further reduction in the phosphate layer weight could be achieved on all galvanized sheets in processes according to the invention having an ironizing stage prior to the activated zinc phosphation (see Table 1), which is advantageous both in terms of process economy and in terms of downstream electrocoating and the improved coverage that can then be achieved there. At the same time, the layer weight produced on the aluminum and cold-rolled steel sheets remains almost constant to slightly increased, so that the process according to the invention for zinc phosphation of components composed of the aforementioned material mix is suitable.

TABLE 1

Method sequence	Coating weight[#]/gm^{-2}				
	HDG	ZM	EG	CRS	AA6014
a1-b-c1-d-e	4.2	4.1	4.3	2.9	2.1
a1-b-c2-d-e	4.2	3.8	4.1	2.7	2.3
a2-b-c1-d-e	3.2	3.5	3.3	2.8	2.2
a2-b-c2-d-e	3.2	3.2	3.1	2.8	2.5

[#] determined by differential gravimetric analysis after stripping the zinc phosphate layer in 5 wt. % of chromic acid.

1. A process for the anti-corrosion pretreatment of a plurality of components in series, wherein each component in the series at least partly has surfaces of zinc wherein each component first undergoes a wet-chemical process step (i) for the deposition of iron on the zinc surfaces and subsequently undergoes a process step (ii) for zinc phosphation,

wherein in process step (i), a coating layer of at least 10 milligrams of elemental iron is deposited per square meter of the zinc surfaces of the component, and

wherein each component in process step (ii) is brought into contact with an acidic aqueous composition that has a free acid in points greater than zero, and contains

(A) 5-50 g/kg of phosphates dissolved in water, calculated as PO$_4$,

(B) 0.3-3 g/kg of zinc ions,

(C) free fluoride, and

(D) a water-dispersed particulate constituent comprising phosphates of polyvalent metal cations, wherein the phosphates are at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite, wherein the acidic aqueous composition is obtained by adding an amount of an aqueous dispersion to an acidic aqueous composition containing the components (A)-(C);

wherein the aqueous dispersion contains a water-dispersed particulate constituent (P) that comprises:

at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite; and

at least one polymeric organic compound (P2).

2. The process according to claim **1**, wherein the aqueous dispersion to provide the acidic aqueous composition for process step (ii) is added in such an amount that a proportion by weight of phosphates from the particulate constituent (P) of the aqueous dispersion, based on the acidic aqueous composition, is at least 0.004 g/kg.

3. The process according claim **1**, wherein an amount of an activating aid containing a particulate constituent (P) in water-dispersed form is added continuously or discontinuously to the acidic aqueous composition in process step (ii) of the zinc phosphation, said particulate constituent (P) comprising:

at least one particulate inorganic compound (P1) composed of phosphates of polyvalent metal cations at least partly selected from hopeite, phosphophyllite, scholzite and/or hureaulite,

and at least one polymeric organic compound (P2),

said amount being sufficient, under the conditions of process step (ii), to maintain a property of the acidic aqueous composition of depositing a zinc phosphate layer having a layer weight of less than 5.0 g/m^2 on a hot-dip galvanized steel surface (Z).

4. The process according to claim **1**, wherein, in process step (ii), the polymeric organic compound (P2) in the particulate constituent (P) of the aqueous dispersion or of the activating aid is at least partly composed of styrene and/or an alpha-olefin having no more than 5 carbon atoms; and the polymeric organic compound (P2) additionally comprises units of maleic acid, an anhydride of the maleic acid, an imide of the maleic acid or a combination of one or more thereof.

5. The process according to claim **1**, wherein, in process step (ii), the acidic aqueous composition for zinc phosphation has a pH value below 3.6 and free acid greater than 0.5 points.

6. The process according to claim **1**, wherein, in process step (ii), the acidic aqueous composition for zinc phosphation contains a source of free fluoride; and at least 10 mg/kg, but no more than 200 mg/kg of free fluoride.

7. The process according to claim **1**, wherein, in wet-chemical process step (i), a coating layer based on elemental iron of at least 20 milligrams, but less than 150 milligrams per square meter of the zinc surfaces of the component is deposited on the surfaces of the component formed by zinc.

8. The process according to claim **1**, wherein wet-chemical process step (i) is carried out by contacting at least the surfaces of zinc of the components in the series with an aqueous composition containing iron(II) and/or iron(III) ions, wherein the proportion of iron ions dissolved in water is at least 50 mg/L, but in total less than 10 mg/L of ionic compounds of the metals copper, nickel, cobalt, tin, manganese, molybdenum, chromium, and/or cerium are contained in the aqueous composition in each case relative to the metal element.

9. The process according to claim **8**, wherein wet-chemical process step (i) is carried out by contact with an alkaline aqueous composition, having a pH value not below 8.5, but not above 13.5; and which contains

(a) at least 50 mg/L of iron(III) ions, and

(b) at least 100 mg/L of complexing agents selected from organic compounds (b1), which have at least one functional group selected from COOX, OPO_3X and/or PO_3X, wherein X is either an H atom or an alkali and/or alkaline earth metal atom, and/or condensed phosphates (b2) calculated as PO_4,

wherein the composition has a free alkalinity of at least 1 point, but less than 6 points.

10. The process according to claim **9**, wherein the alkaline aqueous composition additionally contains at least 100 mg/L, but no more than 10 g/L of phosphate ions, wherein a mass-based ratio of iron(III) ions to phosphate ions in the alkaline aqueous composition is in a range from 1:20 to 1:2.

11. The process according to claim **10**, wherein a molar ratio of all components (b) to iron(III) ions in the alkaline aqueous composition is greater than 1:1.

12. The process according to claim **1**, wherein prior to contact with the acidic aqueous composition in process step (ii) of the zinc phosphation, the components in the series are not brought into contact with a colloidal aqueous solution containing hopeite, phosphophyllite, scholzite and/or hureaulite or sparingly soluble salts of elemental Ti in the particulate constituent, and are not brought into contact with a colloidal aqueous solution for activating the surfaces of the components for zinc phosphation prior to being brought into contact with the acidic aqueous composition in process step (ii), and do not undergo an activation stage for activating the surfaces of the components for zinc phosphation.

13. The process according to claim **1**, wherein the components in the series are cleaned and optionally degreased in a cleaning stage prior to or together with process step (i), in particular by contact with an aqueous, alkaline cleaning agent, wherein process step (i) immediately follows the cleaning stage with or without an intermediate rinsing step.

14. The process according to claim **1**, wherein the components in the series additionally have surfaces of the metal aluminum, and optionally surfaces of iron.

15. The process according to claim **1**, wherein a zinc phosphate layer having a layer weight of at least 1.0 g/m^2 is deposited on the surfaces of zinc.

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