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(54) Zinc phosphate-containing conditioning agent for phosphate conversion-treatment of steel plate and corresponding product

(57) A zinc phosphate-containing surface conditioning agent to be used for surface conditioning as pretreatment for zinc phosphate conversion coating of a metallic material, which contains from 500 to 20,000 ppm of zinc phosphate and which has a pH of from 3 to 11, wherein said zinc phosphate has an average particle size of at most 3 μm and D_{90} of at most 4 μm.

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Description

BACKGROUND OF THE INVENTION

FIELD OF THE INVENTION

[0001] The present invention relates to a surface conditioning agent to be used for pretreatment for zinc phosphate conversion treatment of a metallic material.

DISCUSSION OF BACKGROUND

[0002] Automobile bodies, electric appliances, etc., are prepared by forming metallic materials such as steel plates or zinc-plated steel plates into shaped metal products, followed by painting and assembling. Painting of such shaped metal products is carried out via various steps such as degreasing, surface conditioning, conversion treatment and electropainting.

[0003] The surface conditioning treatment is a treatment applied for such a purpose that in the subsequent step of phosphate conversion treatment, a coating film made of crystals of a phosphate will be formed uniformly, quickly and with a high density over the entire metal surface. Usually, a metallic material is immersed in a surface conditioning bath to let crystal nuclei of a phosphate form on the metal surface. In such a surface conditioning step, it is usual that a titanium phosphate colloid is formed on the metal surface, so that by this colloid, a conversion coating will be formed well on the metal surface in the conversion treatment.

[0004] As a surface conditioning agent to be used for such surface conditioning, for example, JP-A-9-249978 discloses a high durability surface conditioning agent which is an aqueous solution having a pH of from 8.5 to 10.0, wherein titanium ions are from 1 to 50 ppm, phosphate radical ions are from 50 to 1,000 ppm, tripolyphosphate radical ions are from 50 to 400 ppm or from 20 to 1,500 ppm, and the value of (weight of tripolyphosphate radical ions)/(weight of titanium ions) is from 10 to 100.

[0005] However, various such titanium phosphate colloids proposed as surface conditioning agents, have a nature such that they tend to undergo dissolution or coagulation as the time passes, and they are in the form of a powder which is inconvenient in handling.

[0006] Further, JP-A-2000-96256 discloses a surface conditioning treatment solution containing bivalent or trivalent metal phosphate particles and a monosaccharide or polysaccharide as an accelerator component. However, by a study by the present inventors, it has been made clear that such a surface conditioning treatment solution is poor in stability and has a problem such that the treating property is not fully satisfactory against an aluminum alloy, against a pocket portion of a component having a complex structure or against a steel plate to be hardly conversion treated, such as a black-skin steel plate.

SUMMARY OF THE INVENTION

[0007] Under these circumstances, it is an object of the present invention to provide a surface conditioning agent which is liquid and excellent in stability and which shows an excellent treating property also against a pocket portion or against a steel plate to be hardly conversion treated, such as a black-skin steel plate.

[0008] The present inventors have conducted an extensive study in view of the above problems. As a result, they have found it possible to obtain a conversion steel plate having an excellent surface state by employing, as a surface conditioning agent, one having zinc phosphate dispersed in a specific state, and have arrived at the present invention.

The present invention provides:

[0009]

(1) A zinc phosphate-containing surface conditioning agent to be used for surface conditioning as pretreatment for zinc phosphate conversion coating of a metallic material, which contains from 500 to 20,000 ppm of zinc phosphate and which has a pH of from 3 to 11, wherein said zinc phosphate has an average particle size of at most 3 μm and D_{90} of at most 4 μm.

(2) A process for producing a phosphate conversiontreated steel plate, which comprises immersing a metallic material in the zinc phosphate-containing surface conditioning agent as defined in the above item (1), followed by phosphate conversion treatment.

(3) A process for producing a painted steel plate, which comprises immersing a metallic material in the zinc phosphate-containing surface conditioning agent as defined in the above item (1), followed by phosphate conversion

treatment and further by painting.

(4) A zinc phosphate dispersion to be used for preparation of a zinc phosphate-containing surface conditioning agent to be used for surface conditioning as pretreatment for zinc phosphate conversion coating of a metallic material, which contains from 0.5 to 50 wt% of zinc phosphate and which has a pH of from 3 to 11, wherein said zinc phosphate has an average particle size of at most 3 μm and D_{90} of at most 4 μm.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0010] Now, the present invention will be described in detail with reference to the preferred embodiments.

[0011] The zinc phosphate-containing surface conditioning agent of the present invention is one which deposits a zinc phosphate colloid on a metal surface of e.g. iron, zinc or aluminum type and is one which accelerates formation of a zinc phosphate coating with the above colloid serving as crystal nuclei in the subsequent zinc phosphate conversion treatment step, to let a good zinc phosphate coating form.

Zinc phosphate

[0012] The surface conditioning agent of the present invention contains zinc phosphate. Here, zinc phosphate is one represented by $Zn_3(PO_4)_2$ and is usually a colorless crystallizable solid, but a commercial product in a powder form is available.

[0013] To obtain zinc phosphate, zinc sulfate and a dilute solution of disodium hydrogen phosphate may be mixed and heated in a molar ratio of 3:2, whereby a tetrahydrate of zinc phosphate will be formed as a crystallizable precipitate. Otherwise, a tetrahydrate of zinc phosphate may be obtained by reacting a dilute phosphoric acid aqueous solution with zinc oxide or zinc carbonate. Crystals of the tetrahydrate are of rhombic system, and there are three types of transformation. When heated, it becomes a dihydrate at 100°C, a monohydrate at 190°C and an anhydrate at 250°C. Zinc phosphate in the present invention may be either a tetrahydrate, a dihydrate, a monohydrate or an anhydride, but usually a tetrahydrate which is readily available, may be used as it is.

[0014] Otherwise, as zinc phosphate, one subjected to various surface treatment may be employed. For example, it may be one surface-treated with e.g. a silane coupling agent, rosin, a silicone compound or a metal alkoxide such as silicon alkoxide or aluminum alkoxide.

[0015] It is known to obtain finely particulated zinc phosphate by adding silica and polyphosphoric acid at the time of reacting a zinc compound with phosphoric acid (e.g. JP-B-49-2005), or to replace a part of zinc in zinc phosphate by a metal such as magnesium, calcium or aluminum by kneading zinc phosphate with various types of a metal compound in a wet system by a mechanical means to complete the reaction mechanochemically (e.g. JP-A-4-310,511). For example, it may be one having a component other than phosphorus, oxygen and zinc, such as silica, calcium or aluminum, introduced by such a means, or one commercially available as a silicate-modified zincphosphate. In such a case, it preferably contains zinc phosphate corresponding to at least 25 mass% as calculated as ZnO and at least 15 mass% as calculated as P_2O_5.

[0016] The form of zinc phosphate is also not particularly limited. Its commercial product is usually in a white powder form. However, the form of the powder may be any form such as a fine particulate form, a plate form or a scaly form. The particle size is also not particularly limited, but it is usually a powder having an average particle size of about a few μm. It is particularly preferred to use one commercially available as an antirust pigment such as a product having the buffering function increased by treatment to impart basicity. As described hereinafter, in the present invention, it is possible to prepare a stable dispersion having zinc phosphate finely dispersed, whereby a constant surface treatment effect can be obtained irrespective of the primary particle size or the form of the powder.

Preparation of the dispersion

[0017] It is preferred that zinc phosphate as described above is preliminarily formed into a dispersion, so that it is used in a finely dispersed state.

[0018] The method for preparing an aqueous dispersion having zinc phosphate dispersed in an aqueous medium, is not particularly limited. However, it is preferred to mix zinc phosphate into a dispersion medium such as water or an organic solvent and carry out pulverization in a wet system in the presence of a dispersant.

Dispersion medium

[0019] As the dispersion medium in which zinc phosphate is dispersed, an aqueous medium containing at least 80 wt% of water may be mentioned. As a medium other than water, various organic solvents may be employed, but it is advisable to control the content of the organic solvent at a low level, preferably at most 10 wt%, more preferably at

most 5 wt% in the aqueous medium. In the present invention, the dispersion may be one which contains no dispersion medium other than water.

[0020] The water-soluble organic solvent is not particularly limited. For example, it may be an alcohol solvent such as methanol, isopropanol, ethylene glycol or ethylene glycol monopropyl ether, a hydrocarbon solvent such as hexane, heptane, xylene, toluene, cyclohexane or naphtha, a ketone solvent such as methyl isobutyl ketone, methyl ethyl ketone, isophorone or acetophenone, an amide solvent such as dimethyl acetamide or methyl pyrrolidone, or an ester solvent such as ethyl acetate, isobutyl acetate, octyl acetate, ethylene glycol monomethyl ether acetate, or diethylene glycol monomethyl ether acetate.

[0021] Such organic solvents may be used alone or in combination as a mixture of two or more of them.

[0022] To obtain an aqueous dispersion of zinc phosphate, it is convenient from the viewpoint of the process to mix zinc phosphate to an aqueous medium, followed by pulverization in wet system, at the time of the preparation of the dispersion. However, pulverization in a wet system may be carried out in a dispersion medium other than an aqueous medium, followed by substitution of the solvent to obtain the aqueous dispersion.

Dispersant

[0023] In the preparation of the dispersion, a dispersant may be employed. Such a dispersant is not particularly limited, and for example, a polymer dispersant, a surfactant or a coupling agent may be used.

[0024] As a preferred example of the polymer dispersant, a natural polymer may be mentioned, and its specific examples include a protein such as hide glue, gelatin, casein or albumin, a natural rubber such as gum arabic or tragacanth gum, a glucoxide such as saponin, alginic acid, an alginic acid derivative such as alginic acid propylene glycol ester, alginic acid triethanolamine or ammonium alginate, and a cellulose derivative such as methyl cellulose, carboxymethyl cellulose, hydroxyethyl cellulose or ethylhydroxy cellulose.

[0025] Such dispersants may be used alone or in combination as a mixture of two or more of them. Among them, it is particularly preferred to use methyl cellulose, or more preferred to use carboxymethyl cellulose, hydroxyethyl cellulose or the like.

[0026] Further, as another preferred example of a polymer dispersant, a synthetic polymer may be mentioned. Its specific examples include a polyamine resin, a polycarboxylic acid resin, a polyolefin resin, a polyester resin, a polyurethane resin, a polyvinyl alcohol, a polyvinyl pyrrolidone, an acrylic resin such as a polyacrylic acid resin, an acrylic acid/acrylonitrile copolymer, a potassium acrylate/acrylonitrile copolymer, a vinyl acetate/acrylate copolymer or an acrylic acid/acrylate copolymer, a styrene/acrylic acid resin such as a styrene/acrylic acid copolymer, a styrene/methacrylic acid copolymer, a styrene/methacrylic acid/acrylate copolymer, a styrene/α-methyl styrene/acrylic acid copolymer or a styrene/α-methylstyrene/acrylic acid/acrylate copolymer, a styrene/maleic acid copolymer, a styrene/maleic anhydride copolymer, a vinyl naphthalene/acrylic acid copolymer, a vinyl naphthalene/maleic acid copolymer, and a vinyl acetate copolymer such as a vinyl acetate/ethylene copolymer, a vinyl acetate/fatty acid vinyl ethylene copolymer, a vinyl acetate/maleate copolymer, a vinyl acetate/crotonic acid copolymer or a vinyl acetate/acrylic acid copolymer, and their salts.

[0027] These polymer dispersants may be used alone or in combination as a mixture of two or more of them. Among them, it is particularly preferred to use a polyamine resin, a polycarboxylic acid resin, a polyester resin, a polyurethane resin, a polyvinyl alcohol, a polyvinyl pyrrolidone, a styrene/acrylic acid resin, a polyacrylic acid resin, or a styrene/maleic acid copolymer.

[0028] More specifically, there may be mentioned UNISENCE CP-102 (manufactured by Senka Company) or KZ-125K (manufactured by Senka Company), as a polyamide resin; AJISPER PB821 (manufactured by Ajinomoto Co., Inc.), SOLSPERSE 24000GR (manufactured by Zinneka Company), SOLSPERSE 32550 (manufactured by Zinneka Company) or Disperbyk 190 (manufactured by BYK-Chemie Japan KK), as a polyester resin; EFKA-4046 (manufactured by Wilbur-Ellis Company), Disperbyk 161 (manufactured by BYK-Chemie Japan KK), Disperbyk 163 (manufactured by BYK-Chemie Japan KK) or Disperbyk 165 (manufactured by BYK-Chemie Japan KK), as a polyurethane resin; PVP K-90 (manufactured by Gokyo Trading Co., Ltd.) as a polyvinyl alcohol or a polyvinyl pyrrolidone; Johncryl 61J as a styrene/acrylic acid resin; Disperbyk 191 (manufactured by BYK-Chemie Japan KK) or EFKA-4550 (manufactured by Wilbur-Ellis Company) as a polyacrylic acid resin; or SMA resin 1440H (manufactured by ATO Company) or MALIALIM AKM-0531 (manufactured by NOF Corporation), as a styrene/maleic acid resin.

[0029] Further, as a preferred example of the surfactant, a nonionic surfactant may be mentioned, such as a polyoxyethylene alkyl ether, a polyoxyalkylene alkyl ether, a polyoxyethylene derivative, an oxyethyleneoxypropylene block copolymer, a sorbitan fatty acid ester, a polyoxyethylene sorbitan fatty acid ester, a polyoxyethylene sorbitol fatty acid ester, a glycerol fatty acid ester, a polyoxyethylene fatty acid ester, a polyoxyethylene alkylamine, an alkylalkanodeamide, nonylphenol, an alkylnonylphenol, a polyoxyalkylene glycol, an alkylamine oxide, acetylene diol, a polyoxyethylene nonyl phenyl ether, a silicon surfactant such as a polyoxyethylene alkyl phenyl ether-modified silicone, or a fluorinated surfactant having at least one of hydrogen atoms in a hydrophobic group of a hydrocarbon surfactant sub-

stituted by a fluorine atom. Such a nonionic surfactant may be used in combination with another dispersant to further increase the effects.

[0030] Otherwise, the surfactant may be a cationic surfactant such as an alkyltrimethylammonium salt such as lauryl trimethylammonium chloride, cetyltrimethylammonium bromide or stearyltrimethylammonium chloride, an alkyldimethylbenzylammonium salt such as stearyldimethylbenzylammonium chloride, benzalconium chloride or lauryldimethylbenzylammonium chloride, or a phosphoric acid amine salt.

[0031] Or, the surfactant may be an anionic surfactant such as a fatty acid salt, an alkylsulfuric acid ester salt, an alkyl ether sulfuric acid ester salt, an alkylbenzene sulfonate, an alkylnaphthalene sulfonate, an alkylsulfosuccinate, an alkyldiphenylether disulfonate, a polybisphenol sulfonate, an alkyl phosphate, a polyoxyethyl alkylsulfuric acid ester salt, a polyoxyethyl alkylallylsulfuric acid ester salt, an α-olefin sulfonate, a methyltaurine acid salt, a polyasparaginate, an ethercarboxylate, a naphthalene sulfonic acid formalin condensate, or a polyoxyethylene alkyl phosphoric acid ester. These surfactants may be used alone or in combination as a mixture of two or more of them. Among them, it is particularly preferred to employ a polyoxyethylene alkyl phosphoric acid ester. More specifically, as a polyoxyethylene alkyl phosphoric acid ester, Phosphanol RS-610 (manufactured by Toho Chemical Industry Co, Ltd.) or Disperbyk 180 (manufactured by BYK-Chemie Japan KK) may be mentioned as a preferred example, and as a phosphoric acid amine salt, SN-DISPERSANT 2060 (manufactured by San Nopco Limited) may be mentioned as a preferred example.

[0032] The anionic surfactant to be used here, or an anionic resin among the above-mentioned polymer dispersants, may be used as neutralized by ammonia or an amine neutralizing agent. As such an amine neutralizing agent, diethylamine (DEA), triethylamine (TEA), monoethanolamine (META), diethanolamine (DETA), triethanolamine (TETA), dimethylethanolamine (DMEA), diethylethanolamine (DEEA), isopropylethanolamine (IPEA), diisopropanolamine (DIPA), 2-amino-2-methylpropanol (AMP), 2-(dimethylamino)-2-methylpropanol (DMAMP), morpholine (MOR), N-methylmorpholine (NMM) or N-ethylmorpholine (NEM) may, for example, be mentioned.

[0033] Such neutralizing agents may be used alone or in combination as a mixture of two or more of them. Among them, it is particularly preferred to use 2-amino-2-methylpropanol (AMP).

[0034] Or, the surfactant may be an amphoteric surfactant such as an alanine type, an imidazolium betaine type, an aminopropyl betaine type or an aminodipropionate.

[0035] Or, a coupling agent may be mentioned such as a silane type coupling agent, an aluminum type coupling agent, a titanium type coupling agent or a zirconium type coupling agent. These coupling agents may be used alone or in combination as a mixture of two or more of them. Among them, it is particularly preferred to use a silane type coupling agent.

[0036] As a particularly preferred dispersant, a polyoxyethylenealkyl phosphoric acid ester may be used.

[0037] These dispersants may be used alone or in combination as a mixture of two or more of them.

[0038] The amount of zinc phosphate to be incorporated is usually from 0.5 to 50 wt% in the dispersant. If it is less than 0.5 wt%, the content of zinc phosphate is too small, whereby the effect of the surface conditioning agent obtainable by means of the dispersion will be inadequate. On the other hand, if it exceeds 50 wt%, it tends to be difficult to obtain a uniform fine particle size distribution by pulverization in a wet system, or it tends to be difficult to form a finely dispersed state. It is particularly preferably from 1 to 50 wt%.

[0039] Further, the amount of the dispersant to be incorporated is within a range of from 0.1 to 50 wt%, preferably from 0.5 to 20 wt%, in the dispersion. If the amount is less than 0.1 wt%, the dispersibility may not be sufficient, and if it exceeds 50 wt%, the dispersibility may tend to be poor due to an interaction among excess dispersants, and even if the dispersibility is sufficient, such is economically disadvantageous.

Dispersed state

[0040] By the following method, zinc phosphate is finely dispersed in a dispersion medium. The degree of dispersion at that time is preferably such that the average dispersed diameter is at most 3 μm. Here, D_{50} (volume 50% diameter) is used as the average dispersed diameter or the average particle size.

[0041] A method to obtain a dispersion in which zinc phosphate is finely dispersed with an average particle size of at most 3 μm, is not particularly limited. Preferably, from 0.5 to 50 wt% of zinc phosphate and from 0.1 to 50 wt% of a dispersant are permitted to be present in a dispersing medium, followed by pulverization in a wet system. The method for pulverization in a wet system is not particularly limited, and a common method for pulverization in a wet system may be employed. For example, it is possible to employ a beads mill represented by a disc type or a pin type, a high pressure homogenizer or a medialess dispersing machine represented by a supersonic dispersing machine.

[0042] Further, at the time of pulverization, if pulverization is carried out excessively, dispersant deficiency due to an increase of the specific surface area will result, and excessively dispersed particles tend to undergo coagulation, thus leading to a phenomenon of excessive dispersion wherein the dispersion stability will be impaired by formation of coarse particles. Further, depending upon the blending or dispersing conditions, the dispersibility will be non-uniform, thus leading to coagulation or viscosity increase due to the most dense packing of coarse particles or fine particles,

or leading to a phenomenon such as coagulation of fine particles to one another. To prevent such a phenomenon, it is advisable that D_{90} (volume 90% diameter) is monitored to select the blending and dispersing conditions not to create excessive dispersion. In the present invention, D_{90} is at most 4 μm.

[0043] Here, D_{50} (volume 50% diameter) and D_{90} (volume 90% diameter) are particle sizes at points of 50% and 90%, respectively, in an accumulative curve of particle sizes, when the accumulative curve is obtained based on the particle size distribution in the dispersion, taking the total volume of particles as 100%. Typically, D_{50} and D_{90} can automatically be measured by using a particle size measuring apparatus such as a laser Doppler system particle size analyzer ("Microtrack UPA 150", manufactured by Nikkiso Co., Ltd.).

[0044] By the above method, the average value of dispersed diameters of zinc phosphate in the aqueous medium can be adjusted to be at most 3 μm, whereby an aqueous dispersion which is excellent in stability and which has an excellent performance as a surface conditioning agent, can be obtained. The average value of the dispersed diameters can be usually adjusted to be a desired level within a range of from 0.01 to 3 μm.

[0045] By preparing an aqueous dispersion by the process of the present invention as described above, even zinc phosphate exceeding 3 μm can be dispersed in a liquid with a dispersed diameter of at most 3 μm. The same applies also in the case of zinc phosphate particles having a primary particle size of a few tens μm. This means that even without using zinc phosphate having small primary particle sizes, the primary particle sizes of a pigment can be reduced by carrying out pulverization in a wet system in accordance with the above-described process. According to the above-described process, the average value of the dispersed diameters in the aqueous dispersion can be made to be at most 3 μm, further at most 1 μm, still further at most 0.2 μm.

[0046] With the dispersion of the present invention thus obtained, the average value of the dispersed diameter of zinc phosphate in the liquid can be adjusted within a range of at most 3 μm depending upon the particular purpose, and it is an aqueous dispersion which is excellent in the dispersion stability and which has an excellent performance as a surface conditioning agent.

[0047] By the above-mentioned wet system pulverization method, the proportion of coarse particles shown as particles having particle sizes exceeding D_{90}, can be reduced, whereby it is possible to obtain a dispersion having a sharp distribution of dispersed diameters, wherein D_{90} as the dispersed diameter distribution is at most 4 μm, further, at most 2.6 μm, still further at most 0.3 μm and particles having large dispersed diameters are suppressed. Accordingly, it is considered that zinc phosphate is dispersed with fine dispersed diameters, and the dispersed state is extremely stable. Further, since the proportion of coarse particles is low, zinc phosphate in the liquid can contribute to formation of crystal nuclei efficiently, and since the distribution of dispersed diameters is sharp, and the particle size is uniform, more uniform crystal nuclei will be formed in the surface conditioning treatment step, and uniform zinc phosphate crystals will be formed by the subsequent conversion treatment, whereby the surface state of the resulting conversion treated steel plate will be uniform and excellent, and further, this is a reason for the improvement in the treating properties of a pocket portion of a component having a complicated structure or a steel plate to be hardly conversion treated such as a black-skin steel plate.

[0048] The dispersed diameters of zinc phosphate in the dispersion can be obtained by measuring the particle size distribution by means of a laser Doppler system particle size analyzer.

[0049] The aqueous dispersion of the present invention can be obtained as an aqueous dispersion having a high concentration wherein zinc phosphate is incorporated in an amount of at most 10 wt%, further at least 20 wt%, still further at least 30 wt%. Accordingly, it is possible to readily prepare a surface conditioning agent which can provide high performance.

[0050] As described in the foregoing, an aqueous dispersion having zinc phosphate finely dispersed in an aqueous medium, is preliminarily prepared, and an aqueous medium is optionally added to obtain a surface conditioning agent. In this manner, a constantly finely dispersed state can be accomplished.

[0051] The zinc phosphate surface conditioning agent of the present invention contains from 600 to 20,000 ppm of zinc phosphate. If zinc phosphate is less than 600 ppm, a phosphate which will be crystal nuclei, tends to be inadequate. On the other hand, even if it exceeds 20,000 ppm, no further effect beyond the desired effect can be obtained, and such will be uneconomical. It is particularly preferably from 50 ppm to 1,000 ppm.

Additives

[0052] Further, a thickener may be added as the case requires, in order to further improve the stability. Such a thickener may, for example, be an inorganic thickener such as white clay, talc, clay, diatomaceous earth, calcium carbonate, barium sulfate, titanium oxide, alumina white, silica, kaolin, mica or aluminum hydroxide, an organic thickener such as a polyacrylate, a polyurethane, a polyester, a polyethylene, a polypropylene, a polyvinyl chloride, a polyvinylidene chloride, a polystyrene, a polysiloxane, a thickening polysaccharide, a phenol resin, an epoxy resin or a benzoguanamine resin, or a thickener made of such a polymer. These thickeners may be used alone or in combination of as a mixture of two or more of them. At the time of using a thickener, the type, the amount, etc., may suitably be

selected. Usually, it is added in an amount of from 0.01 to 10 wt%, preferably from 0.1 to 5 wt%, in the dispersion.

[0053] Further, a defoaming agent may be used for the purpose of suppressing foaming during the operation, and an antiseptic or mildew proofing agent may be employed for the antiseptic or mildew proofing purpose of the dispersion. When such an agent is to be used, the type, amount, etc. may suitably be selected.

[0054] The zinc phosphate surface conditioning agent of the present invention has a pH of from 3 to 11. If the pH is less than 3, the pH in the conversion bath in the subsequent step tends to be low, whereby formation of the conversion coating will be hindered. On the other hand, if the pH exceeds 11, the phosphate fine particles tend to be soluble and unstable. Further, such will influence the subsequent step. The pH is preferably from 7 to 10.

[0055] In the present invention, an alkali salt such as soda ash may further be added for the purpose of stabilizing fine particles of zinc phosphate and forming fine conversion coating in the subsequent step of phosphate conversion coating treatment.

Surface conditioning treatment

[0056] Surface conditioning treatment of various metal materials can be carried out by using the surface conditioning agent of the present invention as described above.

[0057] The method for the surface conditioning treatment is not limited, and a known method which is commonly used for contacting the surface conditioning agent with a metal surface, may optionally be employed.

[0058] A metal material may be immersed in the zinc phosphate-containing surface conditioning agent of the present invention as described above, and then the zinc phosphate conversion treatment is carried out to produce a zinc phosphate conversion treated steel plate. Typically, a metal material is immersed in a surfaceconditioning bath, followed by a phosphate conversion treatment. The contact time of the surface conditioning agent with the metal surface or the temperature of the surface conditioning agent is also not particularly limited, and a known method may be employed.

[0059] The metallic material to be treated, is also not particularly limited. Namely, the agent is applicable to various materials which are commonly subjected to phosphate conversion treatment, such as iron steel, a zinc-plated steel plate, aluminum or an aluminum alloy, and a magnesium alloy.

[0060] Further, the surface conditioning agent of the present invention may be used for a degreasing and surface treating step, whereby a step of washing with water after the degreasing treatment, can be omitted. In the degreasing and surface conditioning step, a known inorganic alkali builder, organic builder, surfactant, etc. may be added in order to increase the cleaning power. Further, a known chelating agent or a condensed phosphate may, for example, be added.

Conversion treatment step

[0061] A metallic material may be immersed in the zinc phosphate-containing surface conditioning agent of the present invention as described above, followed by zinc phosphate conversion treatment and further by electropainting to produce a painted steel plate.

[0062] The phosphate conversion treating method is not particularly limited, and various known methods, such as dipping treatment, spraying treatment and electrolytic treatment, may be used. A plurality of them may be used in combination. The phosphate coating to be precipitated, is not particularly limited so long as it is a phosphate such as zinc phosphate, iron phosphate, manganese phosphate or zinc calcium phosphate.

[0063] After the phosphate conversion treatment, painting is carried out. As the painting method, electropainting is common. The paint to be used for the painting is not particularly limited. Various paints which are commonly used for painting of phosphate conversion treated steelplates may be mentioned, such as an epoxy melamine paint, a cationic electrodeposition paint, a polyester type intermediate coating paint and a polyester type top coating paint. Further, a known method may be employed such that after the conversion treatment, a cleaning step is carried out prior to painting.

[0064] Now, the present invention will be described in further detail with reference to Examples. However, it should be understood that the present invention is by no means restricted to such specific Examples.

EXAMPLE 1

[0065] A zinc phosphate dispersion was prepared by the following method.

[0066] 100 parts by weight of commercially available zinc phosphate (scaly standard type zinc phosphate, average particle size of 3 μm as measured by a centrifugal type light transmission particle size distribution measuring apparatus, water-soluble content of at most 1% by JIS K-5101, pH of 6.9 by JIS K-5101, oil absorption of 26 ml/100 g by JIS K-5101, density of 3.0 g/ml by JIS K-5101, sieving residue (45 μm) of at most 1% by JIS K-5101, ZnO content of 58% by EDTA method, P_2O_5 content of 33% by a colorimetric analysis) was added to 142.3 parts by weight of water. Then, as a dispersant, 5 parts by weight of "Phosphanol RS-610" (manufactured by Toho Chemical Industry Co, Ltd.) being

a polyoxyethylene alkyl phosphoric acid ester as a commercially available anionic surfactant, was added. Further, as a neutralizing agent, 1 part by weight of AMP, and as a thickener, 0.3 part by weight of Xanthan gum, were added, followed by stirring. After the stirring, wet pulverization was carried out by means of a dynomill pulverizer (alkali glass beads of 1 mm in diameter), and the particle size distribution was measured by means of a laser Doppler system particle size analyzer ("Microtrack UPA 150", manufactured by Nikkiso Co., Ltd.), whereby D_{50} (the average particle size of dispersed particles) and D_{90} were monitored, to obtain a dispersion having a D_{50} of 0.49 μm and a D_{90} of 1.40 μm.

[0067] After dispersing, in order to stabilize the dispersion, 0.6 part by weight of xanthan gum was further added as a thickener, followed by stirring.

EXAMPLE 2

[0068] A zinc phosphate dispersion was prepared by the following method.

[0069] 100 parts by weight of commercially available zinc phosphate (commercially available silicate-modified zinc phosphate, average particle size of from 4 to 5 μm as measured by a centrifugal type light transmission particle size distribution measuring apparatus, water-soluble content of 1.9% by JIS K-5101, pH of 9.4 by JIS K-5101, ZnO content of 40% by EDTA method, P_2O_5 content of 24% by a colorimetric analysis, CaO content of 9% by EDTA method, SiO_2 content of 10% by weight method) was mixed to 142.3 parts by weight of water. Then, as a dispersant, 5 parts by weight of "Phosphanol RS-610" (manufactured by Toho Chemical Industry Co, Ltd.) being a polyoxyethylene alkyl phosphoric acid ester as a commercially available anionic surfactant, was added. Further, as a neutralizing agent, 1 part by weight of AMP, and as a thickener, 0.3 part by weight of xanthan gum, were added, followed by stirring. After the stirring, wet system pulverization was carried out by means of a dynomill pulverizer (alkali glass beads of 1 mm in diameter), and the particle size distribution was measured by means of a laser Doppler system particle size analyzer ("Microtrack UPA 150", manufactured by Nikkiso Co., Ltd.), whereby D_{50} and D_{90} were monitored, to obtain a dispersion having a D_{50} of 0.49 μm and a D_{90} of 1.36 μm.

[0070] After dispersing, in order to stabilize the dispersion, 0.6 part by weight of xanthan gum was further added as a thickener, followed by stirring.

COMPARATIVE EXAMPLE 1

[0071] 100 parts by weight of the same commercially available zinc phosphate as used in Example 1, was mixed to 142.3 parts by weight of water. Then, as a dispersant, 5 parts by weight of "Phosphanol RS-610" (manufactured by Toho Chemical Industry Co, Ltd.) being a polyoxyethylene alkyl phosphoric acid ester as a commercially available anionic surfactant, was added. Further, as a neutralizing agent, 1 part by weight of AMP, and as a thickener, 0.3 part by weight of xanthan gum, were added, followed by stirring. After the stirring, wet system pulverization was carried out by means of a dynomill pulverizer (alkali glass beads of 1 mm in diameter). In the pulverization step, no monitoring of the average particle size and D_{90} was carried out.

[0072] After dispersing, in order to stabilize the dispersion, 0.6 part by weight of xanthan gum was further added, followed by stirring to obtain a dispersion.

[0073] This dispersion was subjected to particle size distribution measurement by means of a laser Doppler system particle size analyzer ("Microtrack UPA 150", manufactured by Nikkiso Co., Ltd.), whereby D_{50} (average diameter of dispersed particles) was 4 μm, and D_{90} was 5 μm.

COMPARATIVE EXAMPLE 2

[0074] A surface conditioning agent "Surf Dine 5N-10" (powder), manufactured by Nippon Paint Co., Ltd., was employed.

Evaluation tests

[0075] Water was added to each of the zinc phosphate dispersions obtained in Examples 1 and 2 to a predetermined concentration (as identified in item "Surface treating agent" in Table 1, as degree of dilution based on the dispersion), followed by stirring thoroughly to prepare a bath. Using the obtained surface conditioning liquid, evaluation was carried out by the following methods, and the results are shown in Table 1. Also with respect to the surface conditioning agent of Comparative Example 2, water was added thereto to bring it to a predetermined concentration, followed by stirring thoroughly to prepare a bath. Using the obtained surface conditioning liquid, evaluation was carried out in the same manner, and the results are shown in table 1.

Evaluation methods

1. Stability of the surface conditioning liquid

The surface conditioning liquids of Examples 1 and 2 were set in a constant temperature vessel of 50°C, and an accelerated test for stability with time was carried out, whereby even upon expiration of one month, no precipitation or no viscosity increase was observed, and also no change in the particle size distribution was observed. Thus, these surface conditioning liquids were found to be excellent in stability.

2. Conversion property of the zinc phosphate coating

[0076] Each of a preliminarily degreased cold drawn steel plate (SPC) (70 mm × 150 mm × 0.8 mm) and an aluminum steel plate (A6063S) (70 mm × 150 mm × 0.8 mm) was treated by dipping in the surface conditioning liquid at room temperature for 30 seconds, and then, after removing the liquid, immediately subjected to conversion treatment at 43°C for two minutes by a dipping method using a zinc phosphate treating liquid ("Surf Dine SD6000", manufactured by Nippon Paint Co., Ltd.), followed by washing with water, washing with pure water and drying, to obtain a test plate. The zinc phosphate conversion coating of each test plate thus obtained was observed (1500 magnifications) by SEM (JSM5600, manufactured by Nippon Denshi K.K.). The crystal size is shown in Table

1. It is evident that those of Examples 1 and 2 are very dense crystals. The results of evaluation of the surface state by visual observation are shown as "Appearance" in Table 1. ⓞ indicates that the appearance is uniform, and no rust is observed; ○ indicates that slight irregularities are observed, but no rust is observed; and × indicates that irregularities are distinct, and rusting is also observed.

3. Weight of conversion coating (C/W)

[0077] The weight of the obtained test plate is represented by ① (g), and the weight after peeling the conversion coating from the test plate by the following method is represented by ② (g). Their difference (① -②) (g) was divided by the surface area of the test plate to obtain this value. The results are shown in Table 1.

(1) Peeling method for the SPC test plate The test plate was dipped for five minutes in a solution containing 50 g/l of chromium trioxide, heated to 75°C, whereby the conversion coating was peeled.

(2) Aluminum test plate The test plate was dipped in a 30% nitric acid aqueous solution at room temperature for one minute, whereby the conversion coating was peeled.

Table 1

	Examples				Comparative Examples			
	1		2		1		2	
Surface treating agent	0.3% solution of 1		0.3% solution of 2		0.3% solution of 1		0.1% solution of 2	
Treated metal	SPC	Al	SPC	Al	SPC	Al	SPC	Al
C/W (g/m^3)	1.79	1.59	1.71	1.72	3.25	0.73	2.07	1.52
Appearance	◎	◎	◎	◎	×	×	◎	○
Crystal size (μm)	2 to 3	3 to 5	2 to 3	3 to 5	15 to 20	15 to 20	3 to 5	5 to 7

[0078] With the above-described construction, the zinc phosphate-containing surface conditioning agent of the present invention has good stability in a liquid state as compared with conventional surface conditioning agents, whereby in the next step i.e. the zinc phosphate conversion coating step, a uniform dense zinc phosphate conversion coating free from irregularities, can be obtained.

[0079] The entire disclosure of Japanese Patent Application No. 2002-172373 filed on June 13, 2002 including specification, claims and summary is incorporated herein by reference in its entirety.

Claims

1. A zinc phosphate-containing surface conditioning agent to be used for surface conditioning as pretreatment for zinc phosphate conversion coating of a metallic material, which contains from 500 to 20,000 ppm of zinc phosphate and which has a pH of from 3 to 11, wherein said zinc phosphate has an average particle size of at most 3 μm and D_{90} of at most 4 μm.

2. A process for producing a phosphate conversiontreated steel plate, which comprises immersing a metallic material in the zinc phosphate-containing surface conditioning agent as defined in Claim 1, followed by phosphate conversion treatment.

3. A process for producing a painted steel plate, which comprises immersing a metallic material in the zinc phosphate-containing surface conditioning agent as defined in Claim 1, followed by phosphate conversion treatment and further by painting.

4. A zinc phosphate dispersion to be used for preparation of a zinc phosphate-containing surface conditioning agent to be used for surface conditioning as pretreatment for zinc phosphate conversion coating of a metallic material, which contains from 0.5 to 50 wt% of zinc phosphate and which has a pH of from 3 to 11, wherein said zinc phosphate has an average particle size of at most 3 μm and D_{90} of at most 4 μm.

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 03 01 3178

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The present search report has been drawn up for all claims

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MUNICH	7 November 2003	Brisson, O

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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