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(54) **A composition containing silica sol, its preparation method, and galvanized self-lubricating metal material using the composition**

(57) The present invention provides a composition containing trivalent chromium compound, silica sol, organic carboxylic acid, and water, and having pH of 4-7. The present invention further provides a galvanized self-lubricating metal material comprising a galvanized metal substrate and a self-lubricating coat on the galvanized metal substrate, wherein the self-lubricating coat is produced by curing a self-lubricating composition which is the composition according to the present invention. As the self-lubricating coat is formed by curing the composition containing silica sol in the present invention, the

galvanized self-lubricating metal material in the present invention not only has very high lubricating performance and corrosion resistance, but also dramatically lowers requirement for galvanized metal substrate, and allows use of hot dipped galvanized plate with high surface roughness fluctuation and low cost as substrate. Therefore, the inventive product has improved market competitiveness and economic benefits, and represents development trend of self-lubricating plate.

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Description**Technical Field**

- 5 **[0001]** The present invention relates to a composition containing silica sol, its preparation method, and galvanized self-lubricating metal material using the composition.

Technical Background

- 10 **[0002]** Galvanized self-lubricating steel plate is a galvanized steel plate product with thin organic coat on surface thereof. Owing to the self-lubricating function imparted by the organic coat, the product can prevent rust corrosion during transportation and storage without requiring application of anti-rust oil, which can simplify packing procedure, and lower production and transportation cost. Therefore, galvanized self-lubricating steel plate has attracted extensive attention in the industry.

- 15 **[0003]** Japanese steel enterprises initiated study of galvanized self-lubricating steel plate in mid-1980s, and realized commercial production of galvanized self-lubricating steel plate in 1990s. The enterprises mainly includes Kawasaki Steel Corporation and

- [0004]** Nippon Steel Corporation, etc., the products of which each have their own features. Recently, other steel enterprises abroad also have started research and production of self-lubricating steel plates, and gained rapid development.

- 20 **[0005]** As the self-lubricating film has thin thickness (usually 1-3 micron), the film is required be coated on zinc-electroplated steel plate with low surface roughness to ensure lubrication and anticorrosion performance. Therefore, the self-lubricating steel plates manufactured by Japanese steel enterprises and Korean steel enterprises all adopt zinc-electroplated steel plate as substrate. The composition for forming the self-lubricating coat is usually prepared from
25 resin-silica sol mixture. As hot-dipped galvanized steel plate has high surface roughness, coat with both excellent lubrication and anticorrosion performance can not be achieved when applied on the hot-dipped galvanized steel plate.

- [0006]** As zinc-electroplated steel plate generally has much higher production cost than that of hot dipped galvanized steel plate, hot dipped galvanized steel plate is still most frequently used, especially in appliance industry in developing countries. Therefore, it is necessary to develop a galvanized self-lubricating steel plate using hot dipped galvanized
30 steel plate as substrate. Until now, there has not been any report regarding the galvanized self-lubricating steel plate with hot dipped galvanized steel plate as substrate and the self-lubricating agent thereof.

- [0007]** Another method for surface treatment of galvanized material is to adopt treating agent containing Cr^{6+} such as chromate to form a chromate passivation film on the galvanized steel plate, and form a coated film after heat drying. The method using hexavalent chromium for passivation treatment is well developed, and the formed passivation film
35 has good anticorrosion performance, and has the advantage of easily accessible raw material and low cost. But hexavalent chromium has high toxicity and carcinogenicity, and has severe potential hazard to environment and human health. With increasingly stricter environment protection laws, development of steel surface treatment has attracted more and more attention. Particularly, the EU RoHS Directive enforced on July 1, 2007 mandates that steel plates used in appliance should be free of lead or hexavalent chromium (i.e. non-pollution); to comply with the Directive, enterprises in the world
40 adopts non-pollution surface thin coat treatment technique for galvanized steel plate, such as non-hazard passivation treatment and non-hazard antifingerprint treatment.

- [0008]** Consequently, environment friendly water-borne coatings, particularly inorganic coating, inorganic-organic composite coating, fire-resistant coating, and anti-corrosive coating prepared from inorganic silicon compounds, become more and more popular in steel enterprises. The environment friendly water-borne coatings have the features of good
45 anti-mold performance, high coat hardness, good adhesion, high resistance to water and alkali, good resistance to high temperature and low temperature, good staining resistance, and good color retention, and are applicable to decoration protection of various steel materials. Among the environment friendly water-borne coatings, the inorganic-organic composite coating containing silica sol is most desirable.

- [0009]** The basic component of silica sol is colloidal solution of SiO_2 and the colloidal particle is spherical, with diameter
50 of 6-50nm; as the particle is small, it has good penetration and adhesion, and is suitable for composite coating and functional coating.

- [0010]** Due to the preparation conditions, the colloidal particles in silica sol have different structural compactness, aggregation states and potentials; therefore their solation degrees are different. The solation degree is a parameter for representing silica content in the silica sol; the higher the solation degree, the higher the silica content, or vice versa.
55 Environments for stable existence of silica sols with different solation degrees are different. Generally, system with pH of 8-10 is beneficial for stable existence of alkaline silica sol. At pH of 5-6, alkaline silica sol is most likely to gelate, and usually severe gelation may occur after standing for several hours. In contrast, acidic silica sol often requires acidic environment with pH not more than 2 to exist stably. As acidic silica sol has high acidity, it may cause corrosion to

galvanized plate when applied as protection layer of the steel plate, which can not realize protection function, and thus is not suitable for forming protection layer of galvanized steel plate.

Summary of the Invention

[0011] The object of the present invention is to provide a composition containing silica sol, its preparation method, and galvanized self-lubricating metal material using the composition.

[0012] The present inventors believe that if alkaline silica sol can be made to stably exist in a system having pH of 5-6 and containing trivalent chromium compound, a self-lubricating agent composition containing both silica sol and trivalent chromium compound can be prepared, which can exert significant promotion effect on formation of self-lubricating layer containing trivalent chromium compound on galvanized steel plate. On one hand, the system with pH of 5-6 can react with the galvanized steel plate surface to improve bonding between the galvanized layer and the film layer formed by the surface treating agent. On the other hand, silica sol participates in film formation, and can fully exhibit its characteristics of good adhesion and corrosion resistance. Compared with hexavalent chromium compound, trivalent chromium compound also can form uniform and dense self-lubricating passivation layer on the galvanized metal material surface, has no damage to human health, and complies with environment requirements.

[0013] Therefore, the present invention provides a composition containing trivalent compound, silica sol, organic carboxylic acid, and water, and having pH of 4-7.

[0014] The present invention also provides a method for preparing the composition comprising the steps of:

(1) contacting a hexavalent chromium compound with a reducing agent and a complexing agent in presence of water, wherein the reducing agent is a substance capable of reducing hexavalent chromium into trivalent chromium, and the complexing agent is a substance capable of complexing with trivalent chromium ions; and

(2) mixing the product obtained in the step (1) with an alkaline silica sol, water and an organic carboxylic acid so that the composition is obtained.

[0015] The present invention further provides a galvanized self-lubricating metal material, which comprises galvanized metal substrate, and self-lubricating coat on the substrate; wherein the self-lubricating coat is produced by curing a self-lubricating composition which is the composition according to the present invention.

[0016] The composition containing the silica sol in the present invention has the following advantages: (1) the composition can be used for forming self-lubricating protection layer on hot dipped galvanized steel plate, so that requirement for galvanized metal substrate is lowered, that is, hot dipped galvanized steel plate with high surface roughness fluctuation and low cost is useful as substrate to obtain self-lubricating galvanized metal material; (2) by using the composition, it is possible to obtain self-lubricating galvanized metal material free of hexavalent chromium compound harmful to human health and environment and having excellent corrosion resistance and adhesion; and (3) the composition containing silica sol has good stability, generates no precipitation after standing at pH of 4-7 for 180 days or longer, and expands application scope of alkaline silica sol.

[0017] As the self-lubricating coat of the self-lubricating galvanized metal material in the present invention is formed by curing a self-lubricating composition according to the present invention, the obtained self-lubricating galvanized metal material has extremely high lubrication and anti-corrosion performance, contains no hexavalent chromium compound harmful to human health and environment, and complies with environment protection requirement. Additionally, compared with the self-lubricating galvanized metal material produced by Japanese and Korean steel enterprises, the inventive self-lubricating galvanized steel plate has significantly lower requirement for galvanized metal substrate, and can adopt hot dipped galvanized steel plate with high surface roughness fluctuation and low cost as substrate, therefore having improved market competitiveness and economic benefits.

Embodiment

[0018] Although the object of the present invention can be achieved as long as the composition contains trivalent chromium compound, silica sol, water, and organic carboxylic acid, preferably, the molar ratio of the trivalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1-10, the weight ratio of the silica sol calculated as silica to the trivalent chromium compound is 1:0.1-10, and water content is 70-95wt% relative to the total weight of the composition. More preferably, in the composition, the weight ratio of the trivalent chromium compound to the organic carboxylic acid is 1:1.5-5, the weight ratio of the silica sol to the trivalent chromium compound is 1:0.5-5, and water content is 75-90wt% relative to the total weight of the composition. By controlling the contents of the trivalent chromium compound, organic carboxylic acid, silica sol and water within aforementioned scope, pH of the self-lubricating composition can be controlled within 4-7, preferably 5-6, and the composition, is prevented from precipitation after standing at room temperature for 50hr or longer, preferably 200hr or longer. Under the same conditions, as the molar ratio of trivalent

chromium compound and organic carboxylic acid approaches 1:1.5-5, the composition containing silica sol stably exists longer, and the self-lubricating effect becomes better when the composition is applied to the galvanized steel plate.

[0019] The trivalent chromium compound can be various inorganic and/or organic acid salts of trivalent chromium, such as one or more of trivalent chromium oxides or salts, wherein the trivalent chromium salt can be inorganic and/or organic salts of trivalent chromium. Particularly, the trivalent chromium compound can be one or more of chromium nitrate, chromium sulfate, chromium chloride, chromium acetate, chromium oxalate, chromium citrate, chromium gluconate, chromium maleate, chromium succinate, chromium trihydroxyglutarate, and their hydrate.

[0020] The organic carboxylic acid can be one or more of C1-C10 dicarboxylic acid, C1-C10 tricarboxylic acid, and C1-C10 amino acid. Particularly, the organic carboxylic acid can be one or more of oxalic acid, malonic acid, citric acid, tartaric acid, maleic acid, gluconic acid, adipic acid, cyclohexanedicarboxylic acid, sebacic acid, aminoacetic acid, 3-aminopropionic acid, and trihydroxyglutaric acid. For the overall consideration of accessibility of raw material and stability of the composition, the preferred organic carboxylic acid is one or more of oxalic acid, citric acid, tartaric acid, maleic acid, gluconic acid, trihydroxyglutaric acid, and 3-aminopropionic acid.

[0021] The inventors of the present invention have found when the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has a content not less than 20wt% relative to the total weight of the organic carboxylic acids, the stability of the composition can be significantly improved, usually by 5-50hr, under the same conditions. Therefore, the preferred organic carboxylic acid in the present invention is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has a content not less than 20wt% by total weight of the organic carboxylic acid.

[0022] As pH of acidic silica sol is usually not more than 4, which is too acidic, the composition prepared from the acidic silica sol is too acidic, and may lead to excessive corrosion of galvanized layer and blushing of the galvanized steel plate and thus influence appearance. Therefore, alkaline silica sol with pH not less than 9 is used as the raw material of the silica sol in the composition according to the present invention, so that the prepared composition containing the silica sol has pH of 4-7, preferably 5-6. More preferably, the alkaline silica sol has SiO₂ content of 20-60wt% based on its total amount, most preferably 20-45wt%.

[0023] The inventors of the present invention have found that when the trivalent chromium compound is chromium gluconate, or a mixture of chromium gluconate and chromium oxalate and/or chromium citrate, and the chromium gluconate has content of 50-100wt% relative to the total weight of the trivalent chromium compounds; and the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxy glutaric acid, and each of them has content not less than 20wt% relative to the total weight of the organic carboxylic acids, the obtained self-lubricating galvanized metal material has more excellent anti-fingerprint performance. Therefore, in the present invention, preferably, the trivalent chromium compound is chromium gluconate, or a mixture of chromium gluconate and chromium oxalate and/or chromium citrate, and the chromium gluconate has content of 50-100wt% relative to the total weight of the trivalent chromium compounds; and the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxy glutaric acid, each of which has content not less than 20wt% relative to the total weight of the organic carboxylic acids.

[0024] Those skilled in the art know that generally trivalent chromium exists in form of hexahydrated ion, i.e. [Cr(H₂O)₆]³⁺, formed with six water molecules, and can not cooperate with alkaline silica sol to improve self-lubricating performance of galvanized steel plate, i.e. there is no available technique capable of forming self-lubricating coat from composition containing both trivalent chromium ions and alkaline silica sol; while as the inventive composition containing silica sol comprises organic carboxylic acid, and the organic carboxylic acid can complex with trivalent chromium compound so as to make trivalent chromium compound exist not or mainly not in form of [Cr(H₂O)₆]³⁺; therefore the composition is useful as self-lubricating agent for galvanized steel plate to form protection layer containing trivalent chromium.

[0025] Besides aforementioned components, the inventive composition containing silica sol may further comprise various other components not affecting the properties of the composition, such as one or more of high temperature resistant additive, water resistant additive, dye, pigment, and dispersant. On basis of the total weight of the composition, the content of the other components is not more than 20wt%, preferably not more than 10wt%. The high temperature resistant additive can be polyurethane acrylate. The polyurethane acrylate can be any conventional polyurethane acrylate, the molecular weight of which may vary within a large scope. Preferably the weight, average molecular weight of the polyurethane acrylate is 700-1,500, more preferably 800-1,200.

[0026] The polyurethane acrylate satisfying the aforementioned molecular weight requirement can be commercially available, such as polyurethane acrylate produced by Tianjin Tianjiao Chemical Co. Ltd., and the polyurethane acrylate SM6201 produced by Jiangsu Sanmu Group Corporation. The polyurethane acrylate also can be prepared according to routine method, such as precrosslinking method. The precrosslinking method may comprise grafting polyurethane on backbone of (meth)acrylate polymer containing hydroxyl, or grafting (meth)acrylate monomer containing hydroxyl on polyurethane backbone via emulsion polymerization. The (meth)acrylate polymer containing hydroxyl can be obtained by polymerizing (meth)acrylate monomers containing hydroxyl. The preparation method of polyurethane acrylate may refer to "Study on Preparation and Properties of Polyurethane Acrylate", Chen Yihong, etc., Journal of Xiamen University

(Natural Science), Vol. 45, 3, p370-374; "Study on Synthesis Technology of Polyether Type Aromatic Polyurethane Acrylate", Yu Zongping, Shanghai Coatings, Vol. 43, 01/02, p28-29; "Synthesis and characterization of polyurethane-methacrylate macromonomer and its copolymer", Fang Shaoming, etc., Modern Plastics Processing and Applications, 2005, Vol. 17, 4, p1-3. These literatures are incorporated herein as whole by reference.

[0027] The composition can be characterized by IR analysis to judge whether organic carboxylic acid and silica sol exist by identifying presence of -COOH and -Si-O-; and presence of trivalent chromium can be determined by continuous spectrophotometry (Xu wenlong, Electroplating & Pollution Control, 1992, Vol. 12, 3, p29-31). The test proves that the composition according to the present invention contains a large amount of organic carboxylic acid, trivalent chromium compound, and silica sol.

[0028] The composition containing silica sol in the present invention can be prepared by any method as long as it allows trivalent chromium compound to complex with the organic carboxylic acid so that trivalent chromium compound does not or substantially not in form of $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$.

[0029] For example, according to an embodiment of the present invention, the method for preparing the composition comprises uniformly mixing alkaline silica sol, trivalent chromium compound or aqueous solution containing trivalent chromium compound, water, and organic carboxylic acid.

[0030] The temperature and time for mixing alkaline silica sol, trivalent chromium compound or aqueous solution containing trivalent chromium compound, water, and organic carboxylic acid may be respectively 10-50°C, and 10-50min.

[0031] The kind and amount of the silica sol, trivalent chromium compound, water, and organic carboxylic acid to be used have been in details described above.

[0032] According to another preferred embodiment, the method for preparing the composition comprises the steps of:

(1) contacting a hexavalent chromium compound with a reducing agent and a complexing agent in presence of water, wherein the reducing agent is a substance capable of reducing hexavalent chromium into trivalent chromium, and the complexing agent is a substance capable of complexing with trivalent chromium ions; and

(2) mixing the product obtained in the step (1) with an alkaline silica sol, water and an organic carboxylic acid so that the composition is obtained.

[0033] The ratio of the hexavalent chromium compound to the reducing agent can be a value close to stoichiometric ratio. For different reducing agents, the molar ratio of the hexavalent chromium compound to the reducing agent can be varied. The preferred molar ratio of the hexavalent chromium compound to the total amount of the reducing agent and the complexing agent can be 1: 0.3 to 1: 4, and the weight ratio of the reducing agent to the complexing agent can be 1: 0.1 to 1: 10; the molar ratio of the hexavalent chromium compound to the organic carboxylic acid calculated as carboxyl group can be 1: 1.5 to 1: 5; the weight ratio of the alkaline silica sol calculated as SiO_2 to the hexavalent chromium compound can be 1: 1 to 1: 5. In the step (1), the water amount can be 1-5 times of the total weight of the hexavalent chromium compound, reducing agent, and complexing agent; and in the step (2), the water amount makes the water content of the self-lubricating composition within 70-95wt%, preferably 75-90wt%.

[0034] The organic reducing agent can be organic substance containing hydroxyl and/or aldehyde group, such as one or more of C1-C10 alcohol, C1-C10 aldehyde, C1-C10 compound containing hydroxyl and/or aldehyde group. The C1-C10 alcohol can be one or more of methanol, ethanol, n-propanol, isopropanol, n-butanol, isobutanol, t-butanol, n-pentanol, isopentanol, t-pentanol, neopentyl alcohol, n-hexanol, cyclohexanol, heptanol, ethylene glycol, glycerol, and pentaerythritol. The C1-C10 aldehyde can be one or more of formaldehyde, acetaldehyde, and propionaldehyde. The C1-C10 compound containing hydroxyl and/or aldehyde group can be one or more of formic acid, oxalic acid, tartaric acid, malonic acid, citric acid, trihydroxyglutarate, and maleic acid. The inorganic reducing agent may be selected from one or more of alkali metal iodide, ferrous salt, and alkali metal sulfite. The ferrous salt can be one or more of ferrous chloride, ferrous sulfate, ferrous nitrate, ferrous phosphate, ferrous acetate, and ferrous oxalate. The alkali metal iodide can be potassium iodide and/or sodium iodide. The alkali metal sulfite can be potassium sulfite and/or sodium sulfite. Preferably, the organic reducing agent can be one or more of methanol, ethanol, propanol, formic acid, oxalic acid, tartaric acid, citric acid, gluconic acid, potassium iodide, sodium iodide, sodium sulfite, trihydroxyglutarate, and maleic acid.

[0035] According to the present invention, the complexing agent can be any compound capable of forming complexing ion with trivalent chromium ion, such as one or more of halogen compound, C1-C10 organic monocarboxylic acid, C1-C10 dicarboxylic acid, C1-C10 tricarboxylic acid, and C1-C10 amino acid. Particularly, the halogen compound can be one or more of potassium fluoride, sodium fluoride, sodium bromide, and potassium bromide. The C1-C10 organic monocarboxylic acid, dicarboxylic acid, tricarboxylic acid and amino acid can be one or more of formic acid, acetic acid, n-propionic acid, isopropionic acid, n-butyric acid, isobutyric acid, t-butyric acid, n-valeric acid, pivalic acid, hexanoic acid, heptylic acid, cyclohexyl formic acid, tartaric acid, gluconic acid, oxalic acid, 1,2-malonic acid, 1,3-malonic acid, 1,2-succinic acid, 1,3-succinic acid, 2,3-succinic acid, 1,4-succinic acid, trihydroxyglutaric acid, maleic acid, fumaric acid, citric acid, butyl 1,2,3-tricarboxylic acid, 3-aminopropionic acid, and aminoacetic acid. Preferably, the complexing

agent can be one or more of potassium fluoride, oxalic acid, citric acid, maleic acid, gluconic acid, trihydroxyglutaric acid, aminoacetic acid and 3-aminopropionic acid.

[0036] Preferably, the reducing agent is gluconic acid or mixture of gluconic acid and trihydroxyglutaric acid and/or methanol, and the content of gluconic acid is 50-100wt% of the total weight of the reducing agent; the complexing agent is citric acid or mixture of citric acid and trihydroxyglutaric acid and/or maleic acid, and the content of citric acid is 60-100wt% of the total weight of the complexing agent; the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, and each of them has content no less than 20wt% of the total weight of the organic carboxylic acid.

[0037] Particularly, from aforementioned description of the organic carboxylic acid, reducing agent, and complexing agent, it can be observed that certain substance, such as citric acid, can be used as either organic carboxylic acid or complexing agent, or even as reducing agent. In this case, the total amount of the substance should be sum of content of each substance satisfying requirement, for example, citric acid can be used as reducing agent as well as complexing agent, and thus the usage amount of citric acid is the sum of the amount of the reducing agent and the completing agent during preparation of trivalent chromium compound. Although the object of the present invention can be achieved as long as the total amount of the substance in the self-lubricating composition can be satisfied, preferably, particularly when hexavalent chromium compound is used as starting material, the substance may be added according to usage amount required for each step, and the self-lubricating composition obtained in such manner has better adhesion with the galvanized steel substrate after being cured.

[0038] In the present invention, the hexavalent chromium compound can be any compound capable of providing chromium ions, such as chromic anhydride and/or hexavalent chromate. The hexavalent chromate can be potassium bichromate and/or sodium bichromate. To avoid introduction of other impurity cations, the preferred hexavalent chromium compound in the present invention is chromic anhydride or mixture of chromic anhydride and potassium chromate and/or sodium chromate. More preferably, the chromic anhydride has content of 50-90wt% in the hexavalent chromium compound.

[0039] The water can be routine industrial tape water, deionized water or distilled water. In the preparation process of the composition containing silica sol, the water amount in each step may be varied within a large range, as long as each water soluble reactant can be fully dissolved; but for ensuring that the obtained self-lubricating composition can be coated on the galvanized metal substrate, the preferred water content in the composition is 70-95wt%, preferably 75-90wt%; therefore the water content in the self-lubricating composition can be regulated via water addition or evaporation.

[0040] The hexavalent chromium compound can be contacted with the reducing agent at ambient temperature, such as 10-50°C, for a period sufficient to allow the reaction to be fully carried out. Generally, the contact time of hexavalent chromium compound and the reducing agent may be 0.5-5 hr, preferably 30-200 min; or the obtained aqueous solution does not bubble, or turns into pale greenish purple, which indicates the reaction is complete. To contact sufficiently, the contacting is preferably carried out under stirring.

[0041] In the step (2), the mixing temperature may be 10-50°C, and the mixing time may be 10-50mins. To speed up mixing well, the mixing is preferably carried out under stirring. The kind and amount of the silica sol, water, and organic carboxylic acid to be used have been in details described above.

[0042] The obtained product can be characterized by methods well known for those skilled in the arts to judge whether the product contains trivalent chromium compound, for example, it can be determined by continuous spectrophotometry (Xu wenlong, Electroplating & Pollution Control, 1992, Vol. 12, 3, p29-31) that whether the product contains trivalent chromium compound and the starting material hexavalent chromium compound is completely reacted (content lower than 0.01g/l indicates the reaction is complete).

[0043] Within the scope of not adversely affecting the performances of the properties of the composition, other component such as one or more of high temperature resistant additive, water resistant additive, dye, pigment, and dispersant can be added to the composition. The kind and amount of the other component have also been in details described above.

[0044] According to the galvanized metal material in the present invention, the galvanized metal substrate can be any metal material with surface plated with zinc, for example, galvanized steel plate substrate such as hot dipped galvanized steel substrate and zinc-electroplated steel substrate. When the hot dipped galvanized steel plate is adopted as substrate, the advantage of the present invention can be fully exhibited. Therefore, the present invention preferably adopts galvanized steel substrate as the galvanized metal substrate, and more preferably the galvanized steel substrate is hot dipped galvanized steel substrate with surface roughness not less than 0.2, such as 0.4-1.5.

[0045] In the present invention, the reactors for preparing and accommodating trivalent chromium compound and self-lubricating composition are preferably enameled reactor or plastic reactor, such as plastic tank. As steel material will react with the obtained composition, when steel reactor is adopted for preparation, on one hand the reactor will be corroded, and on the other hand impurities will be introduced to the composition. Therefore, it is desirable that steel reactor, such as stainless steel reactor and common carbon steel reactor, should be avoided.

[0046] The self-lubricating galvanized metal material in the present invention can be obtained by any coating methods,

such as continuous coating, or intermittent coating. The continuous coating method usually adopts roll coater generally comprising two rollers mutually cooperating at the same linear velocity, wherein one of the rollers is a pickup roller used for picking up the self-lubricating composition, and the other roller is a coating roller used for coating the self-lubricating composition on the galvanized steel substrate. The galvanized steel substrate is usually conveyed by belt, and a unit for curing the self-lubricating agent coated on the galvanized steel substrate is arranged above the belt, by either heat curing or UV curing. The roller coater with the aforementioned structure or function can be commercially available.

[0047] For achieving hot dipped galvanized self-lubricating metal material with better adhesion of self-lubricating coat and better self-lubricating performance, the process parameters of the roll coater can be varied depending to the surface roughness of the hot dipped galvanized steel plate. For example, for non skin-passed galvanized steel plate, the ratio of the velocities of the front and back sides of the roller coater set to the velocity of the roller coater set (i.e., the velocity of the belt), i.e., the relative velocity is preferably 150%/70%-150%/90%, with pressure of 50-60 kgf/cm². When the velocity of the roller coater set is relatively high, the pressure is preferably close to lower limit of the aforementioned range; and when the velocity of the roller coater set is relatively low, the pressure is preferably close to higher limit of the aforementioned range. The meanings of the velocities of the front and back sides of the roller coater set are well known to those skilled in the arts; for example, the aforementioned "150%/70%" refers to that the linear velocity of the pickup roller is 150% (i.e. 1.5 times) of the conveying belt velocity of the galvanized steel substrate, and the linear velocity of the coating roller is 70% (i.e. 0.7 time) of the conveying belt velocity of the galvanized steel substrate.

[0048] For skin-passed galvanized steel plate, the ratio of the velocities of the front and back sides of the roller coater set to the velocity of the roller coater set (i.e., the velocity of the belt), i.e., the relative velocity is preferably 140%/70%-100%/50%, with pressure of 70-100 kgf/cm². Depending on types (i.e. DX51D, DX52D, DX53D, and DX54D), the galvanized steel plates have different surface roughness due to its skin-pass reduction amount, and running time of the skin-pass roll; the settings of the velocity and pressure of the front and back sides of the roll coater set are different from each other; for roughness Ra within 1.2-1.4, the relative velocity is set at a value close to upper limit, and pressure is set at a value close to lower limit; for roughness Ra within 0.8-1.2, the relative velocity is set at a medium value, and pressure is set at a medium value; and for surface roughness Ra within 0.45-0.8, the relative velocity is set at a value close to lower limit, and pressure is set at a value close to upper limit.

[0049] For obtaining hot dipped galvanized plate having self-lubricating coat with further improved corrosion resistance, fingerprint resistance, conductivity, and lubrication performance, the curing temperature is required to ensure that the thin self-lubricating coat can be fully crosslinked and cured; different induction temperature, hot air curing temperature and hot air cooling temperatures are set according to different relative velocities and pressures of the roller coater sets; the regulation is mainly based on the difference of relative velocities, and fine tuning is based on pressure parameters. The example is as below:

When the relative velocity of the coater roller is 150%/70%-150%/90%, the induction heating is preferably set at 1-30-140.°C, the hot air curing temperature can be set at 160-180°C, 150°C, 130°C, and 110°C, upper air tunnel cooling blower has open degree of 80%, and lower air tunnel cooling blower has open degree of 70%.

When the relative velocity of the coater roller is 140%/70%-130%/70%, the induction heating is preferably set at 110-120°C, the hot air curing temperature can be set at 150-160°C, 130°C, 110°C, and 110°C, upper air tunnel cooling blower has open degree of 60%, and lower air tunnel cooling blower has open degree of 50%.

When the relative velocity of the coater roller is 120%/60%-100%/50%, the induction heating is preferably set at 80-100°C, the hot air curing temperature can be set at 150°C, 110°C, 110°C, and 110°C, upper air tunnel cooling blower has open degree of 50%, and lower air tunnel cooling blower has open degree of 50%.

By controlling the parameters of the roller coater within the aforementioned scope, the amount of the self-lubricating coat on the substrate can be controlled within 200-3,000mg/m², the curing temperature is 50-180°C, and the curing time is 10-100 seconds.

The self-lubricating galvanized metal material in the present invention has qualification rate of 100%; the material has corrosion area of 0% after salt fog test for 120hr, which is much better than the international standard for similar product (corrosion area not more than 5% after salt fog test for 72hr), fingerprint resistance ΔE of 0.78, which is lower than the requirement of ΔE not more than 3, and dynamic friction coefficient of 0.13, which is lower than highest available level 0.34.

Compared with global self-lubricating production process, the invention has the advantage of significantly improved production efficiency, lower cost, and better product quality stability, whose performance is significantly more outstanding than that of similar product in the world. By using the self-lubricating plate to complement domestic market, the invention is important for ensuring competitiveness of the galvanized plates for domestic appliance in the field, improving economic benefits, and providing solid technical basis for export of self-lubricating plates.

The present invention will be described in further detail through the following examples. However, it can be understood by those skilled in the art that this invention is not intended to limit to these examples.

Example 1

[0050] Preparation of the composition containing silica sol comprises: charging deionized water 300kg into 3,000L enameled reactor at 20°C, then further charging chromium citrate 10kg, turning on the stirrer of the reactor, stirring to make the chromium citrate completely dissolved in water, adding citric acid 3kg at stirring to make citric acid rapidly dissolved, then charging 12kg of alkaline silica sol containing 40wt% of silica, and stirring for 5min to give a composition containing silica sol with pH of 6. Through IR spectrogram analysis, it is determined that the composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr³⁺, indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 200 days at room temperature.

[0051] The obtained composition containing silica sol is coated on surface of DX52D+AZ hot dipped galvanized strip steel having thickness ≤0.6mm by Stein vertical roller coater (France) at coating conditions as below:

Relative velocity of coating roller: 100-120%, set value 110%;
 Relative velocity of pickup roller: 50-70%, set value 60%;
 Upper roller pressure: 80kg/cm²;
 Lower roller pressure: 70kg/cm²;
 Set temperature of the inductor: daytime 80-100°C, night 100-120°C;
 Hot air temperature: 150°C (the temperatures for the stages 1-4 are sequentially 150°C, 110°C, 110°C, and 110°C);
 Temperature of strip steel to the top diversion roller: ≤60°C;
 Strip steel coiling temperature: ≤15°C;
 Open degree of the upper air tunnel: 50%;
 Open degree of the lower air tunnel: 50%;
 Open degree of the air blower: all cooling air blowers are open at open degree of 50%;
 A hot dipped galvanized self-lubricating strip steel with dry coat adhesion quantity of 500mg/cm² is obtained.

Comparison example 1

[0052] The galvanized self-lubricating metal material is produced according to the method similar to example 1, except that no citric acid is added during preparation of the composition containing silica sol to obtain a reference composition containing silica sol. When the reference composition containing silica sol is used for production of self-lubricating galvanized metal material, serious precipitation occurs after the composition stands for 2hr; therefore production of galvanized self-lubricating metal material can not be continued. Galvanized steel plate with the aforementioned self-lubricating coat is cut to give reference galvanized self-lubricating steel plate for subsequent performance test.

Example 2

[0053] Preparation of the composition containing silica sol comprises: charging deionized water 500kg into 3,000L enameled reactor at 25°C, then further charging chromium gluconate 50kg, starting the stirrer of the reactor, stirring to make the chromium gluconate completely dissolved in water, adding maleic acid 20kg at stirring to make maleic acid rapidly dissolved, then charging 25kg of alkaline silica sol containing 30wt% of silica, and stirring for 3min to give the inventive composition containing silica sol with pH of 4. Through IR spectrogram analysis, it is determined that the composition containing the silica sol contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr³⁺, indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition does not gelate or precipitate after standing for 300 days at room temperature.

[0054] The obtained composition containing silica sol is coated on surface of DX52D+AZ hot dipped galvanized strip steel having thickness 0.6-1.2mm by the same roller coater as example 1 at coating conditions as below:

Relative velocity of coating roller: 130-140%, set value 140%;
 Relative velocity of pickup roller: 80-100%, set value 90%;
 Upper roller pressure: 80kg/cm²;
 Lower roller pressure: 70kg/cm²;
 Set temperature of the inductor: daytime 110-120°C, night 130-140°C;
 Hot air temperature: 160°C (the temperatures for the stages 1-4 are sequentially 160°C, 130°C, 110°C, and 110°C);
 Temperature of strip steel to the top diversion roller: ≤65°C;
 Strip steel coiling temperature: ≤45°C;

Open degree of the upper air tunnel: 60%;
 Open degree of the lower air tunnel: 50%;
 Open degree of the air blower: all cooling air blowers are open at open degree of 50%;
 A hot dipped galvanized self-lubricating strip steel with dry coat adhesion quantity of 1,500mg/cm² is obtained.

Example 3

[0055] Preparation of the composition containing silica sol comprises: charging deionized water 500kg into 3,000L enameled reactor, then further charging chromium gluconate 50kg, starting the stirrer of the reactor, stirring to make the chromium gluconate completely dissolved in water, adding formic acid 20kg at stirring to make formic acid rapidly dissolved, then charging 20kg of alkaline silica sol containing 20wt% of silica, and stirring well to give the inventive composition containing silica sol. Through IR spectrogram analysis, it is determined that the composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr³⁺, indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 280 days at room temperature.

[0056] The obtained composition containing silica sol is coated on surface of DX52D+AZ hot dipped galvanized strip steel having thickness ≥ 1.2 mm by the same roller coater as example 1 at coating conditions as below:

Relative velocity of coating roller: 140-160%, set value 150%;
 Relative velocity of pickup roller: 70-90%, set value 90%;
 Upper roller pressure: 70kg/cm²;
 Lower roller pressure: 60kg/cm²;
 Set temperature of the inductor: 140-150°C;
 Hot air temperature: 180°C(the temperatures for the stages 1-4 are sequentially 180°C, 150°C, 130°C, and 110°C);
 Temperature of strip steel to the diversion roller: $\leq 65^\circ\text{C}$;
 Strip steel coiling temperature: $\leq 50^\circ\text{C}$;
 Open degree of the upper air tunnel: 80%;
 Open degree of the lower air tunnel: 70%;
 Open degree of the air blower: all cooling air blowers are open at open degree of 50%;
 A hot dipped galvanized self-lubricating strip steel with dry coat adhesion quantity of 2,500mg/cm² is obtained.

Example 4

[0057] Galvanized self-lubricating metal material is prepared according to the same method as in example 3, except that the composition containing silica sol is prepared by: charging deionized water 500kg into 3,000L enameled reactor, then further charging chromium gluconate 30kg and chromium citrate 20kg, starting the stirrer of the reactor, stirring to make chromium gluconate and chromium citrate completely dissolved in water, adding fumaric acid 10kg and 2,3,4-trihydroxyglutaric acid 10kg at stirring to make fumaric acid and 2,3,4-trihydroxyglutaric acid rapidly dissolved, then charging 25kg of alkaline silica sol containing 20wt% of silica, and stirring well to give the inventive composition containing silica sol. Through IR spectrogram analysis, it is determined that the composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr³⁺, indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 320 days at room temperature.

Example 5

[0058] Galvanized self-lubricating metal material is prepared according to the same method as in example 3, except that the composition containing silica sol is prepared as below:

(1) Charging deionized water 300kg into 3,000L enameled reactor, then further charging chromic anhydride 50kg, starting the stirrer of the reactor, and stirring for 10min to make chromic anhydride fully dissolved; adding 2,3,4-trihydroxyglutaric acid 100kg, starting the stirrer rapidly to rapidly dissolve 2,3,4-trihydroxyglutaric acid, wherein the reaction is determined to be complete after the solution does not generate bubble any longer;
 (2) Adding deionized water 500kg and maleic acid 120kg into the reaction system obtained in (1) at 25°C, adding 125kg of alkaline silica sol containing 30wt% of silica after maleic acid being completely dissolved, and stirring well to obtain a composition containing silica sol with pH of 5. Through IR spectrogram analysis, it is determined that the

composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr^{3+} , indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 300 days at room temperature.

Example 6

[0059] Galvanized self-lubricating metal material is prepared according to the same method as in example 3, except that the composition containing silica sol is prepared as below:

(1) Charging deionized water 300kg into 3,000L enameled reactor, then further charging sodium bichromate 50kg, starting the stirrer of the reactor, and stirring for 10min to make sodium chromate fully dissolved; adding trihydroxyglutaric acid 20kg, gluconic acid 30kg, and methanol 10kg, starting the stirrer rapidly to rapidly dissolve gluconic acid, trihydroxyglutaric acid, and methanol, wherein the reaction is determined to be complete after the solution generates no bubble;

(2) Adding deionized water 500kg and citric acid 50kg into the reaction system obtained in (1) at 25°C, adding 50kg of alkaline silica sol containing 30wt% of silica after citric acid being completely dissolved, and stirring well to obtain a composition containing silica sol with pH of 5. Through IR spectrogram analysis, it is determined that the composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr^{3+} , indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 320 days at room temperature.

Example 7

[0060] Galvanized self-lubricating metal material is prepared according to the same method as in example 3, except that the composition containing silica sol is prepared as below:

(1) charging methanol 20kg into maleic acid 20kg while stirring, and mixing well to obtain methanol-maleic acid mixture;

(2) charging deionized water 100kg into 2,000L plastic tank, then further charging chromic anhydride 20kg, stirring by PTFE-made stirrer for 10min to make chromic anhydride fully dissolved, adding the aforementioned methanol-maleic acid mixture obtained in (1) at room temperature of 25 °C while stirring, adding deionized water 500kg and 2,3,4-trihydroxyglutaric acid 20kg into the reaction system after the reaction system turns into pale green purple color (the time is about 2hr from addition of the methanol-maleic acid mixture), adding 25kg of alkaline silica sol containing 20wt% of silica after 2,3,4-trihydroxyglutaric acid being completely dissolved, and stirring well to obtain a composition containing silica sol with pH of 5.5. Through IR spectrogram analysis, it is determined that the composition contains a large amount of - COOH and Si-O-; and through spectrophotometry, it is determined that the composition contains a large amount of Cr^{3+} , indicating that the composition contains a large amount of organic carboxylic acid, silica sol, and trivalent chromium compound. The composition containing silica sol does not gelate or precipitate after standing for 300 days at room temperature.

Examples 8-14

[0061] Examples 8-14 are for testing performance of the self-lubricating layers of the galvanized self-lubricating metal materials prepared in the examples 1-7, and the result is shown in Table 1.

(1) Test of anticorrosion performance

[0062] Corrosion test is carried out according to the method and conditions specified in Chinese National Standard GB/T10125-1997 "Corrosion tests in artificial atmospheres Salt spray tests", then the corrosion results are evaluated according to Chinese National Standard GB142335-90 "Rating of test specimens having coatings anodic to the substrate after being subjected to corrosion tests".

(2) Test of adhesion

[0063] Square grid (100 squares, 1mm x 1mm) is scribed on coated surface by scribe, then transparent tape (model 600 from 3M, US) is flatly adhered on the grid without any void, and vertically stripped off at the most rapid speed. It is

observed whether the coat is stripped off at scribing edge. The strip-off amount of the coat within 0-5% is defined as 5B, the strip-off amount of the coat within 5-10% is defined as 4B, the strip-off amount of the coat within 10-20% is defined as 3B, the strip-off amount of the coat within 20-30% is defined as 2B, the strip-off amount of the coat within 30-50% is defined as B, and the strip-off amount of the coat above 50% is defined as 0B.

(3) Test of antifingerprint performance ΔE

[0064] Colorimeter is adopted to measure values of ΔL , Δa , and Δb of the self-lubricating steel plate before and after coating of white vaseline, ΔE is calculated according to the equation $\Delta E = (\Delta L^2 + \Delta a^2 + \Delta b^2)^{1/2}$, and antifingerprint performance is determined according to ΔE value. ΔE less than 3 indicates desirable antifingerprint performance.

(4) Test of dynamic friction coefficient

[0065] M-2000 friction and wear tester is used for testing dynamic friction coefficient of the self-lubricating coat on the galvanized self-lubricating steel plate. The dynamic coefficient within 0.4-0.8 indicates the coat has desirable lubrication performance.

Comparison example 2

[0066] This comparison example is used for testing performance of the galvanized steel plate treated in the comparison example 1.

[0067] The anticorrosion resistance, adhesion, antifingerprint performance and dynamic friction coefficient of the galvanized metal material prepared in the comparison example 1 are tested according to the same methods in the examples 8-14. And the result is shown in Table 1.

Table 1

Example No.	Corrosion resistance	Adhesion	Antifingerprint performance	Dynamic friction coefficient
Example 8	0	5B	0.78	0.13
Comparison Example 2	0	2B	5	0.96
Example 9	0	5B	0.96	0.15
Example 10	0	4B	0.89	0.24
Example 11	0	5B	0.49	0.10
Example 12	0	5B	1.02	0.26
Example 13	0	5B	0.40	0.15
Example 14	0	5B	0.40	0.16
Requirement	-	4B	$\nless 3$	0.34 (current highest level)

[0068] It can be observed from the testing results in the Table 1 that, the galvanized self-lubricating metal material produced by using the composition containing silica sol in the present invention has significantly improved antifingerprint performance, corrosion resistance, and adhesion, and significantly lowered dynamic friction coefficient, indicating that the galvanized metal material provided in the present invention has coat formed on surface thereof with good corrosion resistance and self-lubricating performance, and the coat has good adhesion (above 4B).

[0069] Moreover, it can be observed from the results in Table 1 that, during preparation of the galvanized self-lubricating steel plate in the Example 4, a mixture of chromium gluconate and chromium citrate is used as trivalent chromium compound, and content of chromium gluconate is 50-100wt% of the total weight of the trivalent chromium compound; a mixture of maleic acid and 2,3,4-trihydroxyglutonic acid is adopted as organic carboxylic acid, and each of them has content not lower than 20wt% of the total weight of the organic carboxylic acid; therefore, it has more outstanding antifingerprint performance (the result of Example 11).

Claims

1. A composition, containing a trivalent chromium compound, a silica sol, an organic carboxylic acid, and water, and having pH of 4-7.
2. The composition according to claim 1, wherein the molar ratio of the trivalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1-10, the weight ratio of the silica sol calculated as silica to the trivalent chromium compound is 1:0.1-10, and water content is 70-95wt% relative to the total weight of the composition.
3. The composition according to claim 2, wherein the molar ratio of the trivalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1.5-5, the weight ratio of the silica sol calculated as silica to the trivalent chromium compound is 1:0.5-5, and water content is 75-90wt% relative to the total weight of the composition.
4. The composition according to any of claims 1-3, wherein the trivalent chromium compound is organic and/or inorganic acid salt of chromium; the organic carboxylic acid is one or more of C1-C10 dicarboxylic acid, C1-C10 tricarboxylic acid, and C1-C10 amino acid; in the silica sol, SiO₂ content is 20-60wt%.
5. The composition according to claim 4, wherein the trivalent chromium compound is one or more of chromium nitrate, chromium sulfate, chromium chloride, chromium acetate, chromium oxalate, chromium citrate, chromium gluconate, chromium succinate, chromium maleate, chromium trihydroxyglutarate, and hydrate thereof; the organic carboxylic acid is one or more of oxalic acid, citric acid, tartaric acid, maleic acid, gluconic acid, aminoacetic acid, 3-aminopropionic acid, and 2,3,4-trihydroxyglutaric acid.
6. The composition according to claim 5, wherein the trivalent chromium compound is chromium gluconate, or mixture of chromium gluconate and chromium oxalate and/or chromium citrate, and the chromium gluconate has content of 50-100wt% relative to the total weight of the trivalent chromium compound; the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has content not less than 20wt% relative to the total weight of the organic carboxylic acids.
7. A preparation method for the composition of claim 1, comprising the steps of:
 - (1) contacting a hexavalent chromium compound with a reducing agent and a complexing agent in presence of water, wherein the reducing agent is a substance capable of reducing hexavalent chromium into trivalent chromium, and the complexing agent is a substance capable of complexing with trivalent chromium ions; and
 - (2) mixing the product obtained in the step (1) with an alkaline silica sol, water and an organic carboxylic acid so that the composition is obtained.
8. The preparation method according to claim 7, wherein the molar ratio of the hexavalent chromium compound to the total amount of the reducing agent and the complexing agent is 1:0.3-4, and the weight ratio of the reducing agent to the complexing agent is 1:0.1-10; the molar ratio of the hexavalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1.5-5; the weight ratio of the alkaline silica sol calculated as SiO₂ to the hexavalent chromium compound is 1:1-5; in step (1), the amount of water is 1-5 times of the total weight of the hexavalent chromium compound, the reducing agent, and the complexing agent; and, in step (2), the amount of water makes the water content of the composition within 70-95wt%.
9. The preparation method according to claim 7 or 8, wherein the reducing agent is organic reducing agent and/or inorganic reducing agent, the organic reducing agent is an organic compound containing hydroxyl and/or aldehyde group, the inorganic reducing agent is one or more selected from alkali metal iodide, ferrous salt, and alkali metal sulfite; the complexing agent is one or more of halogen compound, C1-C10 dicarboxylic acid, C1-C10 tricarboxylic acid, and C1-C10 amino acid; the hexavalent chromium compound is one or more of bichromate and chromic anhydride; and the organic carboxylic acid is one or more of oxalic acid, tartaric acid, citric acid, maleic acid, gluconic acid, aminoacetic acid, 3-aminopropionic acid, and 2,3,4-trihydroxyglutaric acid.
10. The preparation method according to claim 9, wherein the reducing agent is one or more of methanol, ethanol, propanol, formic acid, oxalic acid, tartaric acid, citric acid, gluconic acid, potassium iodide, sodium iodide, sodium sulfite, trihydroxyglutaric acid, and maleic acid; the complexing agent is one or more of potassium fluoride, oxalic acid, citric acid, maleic acid, tartaric acid, gluconic acid, trihydroxyglutaric acid, aminoacetic acid, and 3-aminopropionic acid.

pionic acid; the organic carboxylic acid is one or more of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid; and the hexavalent chromium compound is one or more of sodium bichromate, potassium gluconate, and chromic anhydride.

11. The preparation method according to claim 10, wherein the reducing agent is gluconic acid or mixture of gluconic acid and trihydroxyglutaric acid and/or methanol, and the gluconic acid content is 50-100wt% relative to the total weight of the reducing agent; the complexing agent is citric acid or mixture of citric acid and trihydroxyglutaric acid and/or maleic acid, and citric acid content is 60-100wt% relative to the total weight of the complexing agent; and the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has content not less than 20wt% relative to the total weight of the organic carboxylic acid.
12. The preparation method according to claim 7, wherein in the step (1), the contacting is performed at temperature of 10-50°C for 30-200min; in the step (2), the mixing is performed at temperature of 10-50°C for 10-50min.
13. A galvanized self-lubricating metal material, comprising a galvanized metal substrate and a self-lubricating coat on the substrate, wherein the self-lubricating coat is produced by curing a self-lubricating composition which is the composition according to any of claims 1-6.
14. The galvanized self-lubricating metal material according to claim 13, wherein the amount of the self-lubricating coat on the substrate is 200-3,000mg/m², and the curing is performed at temperature of 50-180°C for 10-100 seconds.
15. The galvanized self-lubricating metal material according to claim 13, wherein the galvanized metal substrate is hot dipped galvanized steel substrate.

Amended claims in accordance with Rule 137(2) EPC.

1. A composition, wherein the raw material of the composition contains a trivalent chromium compound, a silica sol, an organic carboxylic acid, and water, the composition has pH of 4-7, and the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has content not less than 20wt% relative to the total weight of the organic carboxylic acids.

2. The composition according to claim 1, wherein the molar ratio of the trivalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1-10, the weight ratio of the silica sol calculated as silica to the trivalent chromium compound is 1:0.1-10, and water content is 70-95wt% relative to the total weight of the composition.

3. The composition according to claim 2, wherein the molar ratio of the trivalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1.5-5, the weight ratio of the silica sol calculated as silica to the trivalent chromium compound is 1:0.5-5, and water content is 75-90wt% relative to the total weight of the composition.

4. The composition according to any of claims 1-3, wherein the trivalent chromium compound is organic and/or inorganic acid salt of chromium; in the silica sol, SiO₂ content is 20-60wt%.

5. The composition according to claim 4, wherein the trivalent chromium compound is one or more of chromium nitrate, chromium sulfate, chromium chloride, chromium acetate, chromium oxalate, chromium citrate, chromium gluconate, chromium succinate, chromium maleate, chromium trihydroxyglutarate, and hydrate thereof.

6. The composition according to claim 5, wherein the trivalent chromium compound is chromium gluconate, or mixture of chromium gluconate and chromium oxalate and/or chromium citrate, and the chromium gluconate has content of 50-100wt% relative to the total weight of the trivalent chromium compound.

7. A preparation method for the composition of claim 1, comprising the steps of:

- (1) contacting a hexavalent chromium compound with a reducing agent and a complexing agent in presence of water, wherein the reducing agent is a substance capable of reducing hexavalent chromium into trivalent chromium, and the complexing agent is a substance capable of complexing with trivalent chromium ions; and
- (2) mixing the product obtained in the step (1) with an alkaline silica sol, water and an organic carboxylic acid

so that the composition is obtained, wherein the organic carboxylic acid is a mixture of at least two of citric acid, maleic acid, and 2,3,4-trihydroxyglutaric acid, each of which has content not less than 20wt% relative to the total weight of the organic carboxylic acid.

8. The preparation method according to claim 7, wherein the molar ratio of the hexavalent chromium compound to the total amount of the reducing agent and the complexing agent is 1:0.3-4, and the weight ratio of the reducing agent to the complexing agent is 1:0.1-10; the molar ratio of the hexavalent chromium compound to the organic carboxylic acid calculated as carboxyl group is 1:1.5-5; the weight ratio of the alkaline silica sol calculated as SiO_2 to the hexavalent chromium compound is 1:1-5; in step (1), the amount of water is 1-5 times of the total weight of the hexavalent chromium compound, the reducing agent, and the complexing agent; and, in step (2), the amount of water makes the water content of the composition within 70-95wt%.

9. The preparation method according to claim 7 or 8, wherein the reducing agent is organic reducing agent and/or inorganic reducing agent, the organic reducing agent is an organic compound containing hydroxyl and/or aldehyde group, the inorganic reducing agent is one or more selected from alkali metal iodide, ferrous salt, and alkali metal sulfite; the complexing agent is one or more of halogen compound, C1-C10 dicarboxylic acid, C1-C10 tricarboxylic acid, and C1-C10 amino acid; and the hexavalent chromium compound is one or more of bichromate and chromic anhydride.

10. The preparation method according to claim 9, wherein the reducing agent is one or more of methanol, ethanol, propanol, formic acid, oxalic acid, tartaric acid, citric acid, gluconic acid, potassium iodide, sodium iodide, sodium sulfite, trihydroxyglutaric acid, and maleic acid; the complexing agent is one or more of potassium fluoride, oxalic acid, citric acid, maleic acid, tartaric acid, gluconic acid, trihydroxyglutaric acid, aminoacetic acid, and 3-aminopropionic acid; and the hexavalent chromium compound is one or more of sodium bichromate, potassium gluconate, and chromic anhydride.

11. The preparation method according to claim 10, wherein the reducing agent is gluconic acid or mixture of gluconic acid and trihydroxyglutaric acid and/or methanol, and the gluconic acid content is 50-100wt% relative to the total weight of the reducing agent; the complexing agent is citric acid or mixture of citric acid and trihydroxyglutaric acid and/or maleic acid, and citric acid content is 60-100wt% relative to the total weight of the complexing agent.

12. The preparation method according to claim 7, wherein in the step (1), the contacting is performed at temperature of 10-50°C for 30-200min; in the step (2), the mixing is performed at temperature of 10-50°C for 10-50min.

13. A galvanized self-lubricating metal material, comprising a galvanized metal substrate and a self-lubricating coat on the substrate, wherein the self-lubricating coat is produced by curing a self-lubricating composition which is the composition according to any of claims 1-6.

14. The galvanized self-lubricating metal material according to claim 13, wherein the amount of the self-lubricating coat on the substrate is 200-3,000mg/m², and the curing is performed at temperature of 50-180°C for 10-100 seconds.

15. The galvanized self-lubricating metal material according to claim 13, wherein the galvanized metal substrate is hot dipped galvanized steel substrate.



EUROPEAN SEARCH REPORT

Application Number
EP 09 00 2302

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