(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 505 655 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
03.07.2019 Bulletin 2019/27

(21) Application number: **17842888.4**

(22) Date of filing: **22.08.2017**

(51) Int Cl.:
C23C 22/36 *(2006.01)* ***C23C 22/44*** *(2006.01)*
C23C 22/73 *(2006.01)*

(86) International application number:
PCT/CN2017/098430

(87) International publication number:
WO 2018/036465 (01.03.2018 Gazette 2018/09)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
MA MD

(30) Priority: **24.08.2016 CN 201610719583**

(71) Applicant: **Baoshan Iron & Steel Co., Ltd.**
Shanghai 201900 (CN)

(72) Inventors:
- **ZHANG, Jianping**
  Shanghai 201900 (CN)
- **ZHANG, Wenqi**
  Shanghai 201900 (CN)
- **DAI, Yigang**
  Shanghai 201900 (CN)

(74) Representative: **Kuhnen & Wacker**
Patent- und Rechtsanwaltsbüro PartG mbB
Prinz-Ludwig-Straße 40A
85354 Freising (DE)

(54) INORGANIC SURFACE-TREATED GALVANIZED STEEL SHEET, PREPARATION METHOD THEREFOR, AND AQUEOUS INORGANIC SURFACE TREATMENT AGENT THEREOF

(57) An environmentally-friendly inorganic surface-treated galvanized steel sheet, a preparation method therefor and an aqueous inorganic surface treatment agent thereof, capable of satisfying requirements of rapid deep-drawing treatment of progressive dies in the field of micromotors, and providing excellent red rust resistance performance and excellent surface conductivity for parts and components. An aqueous inorganic surface treatment agent comprising a single organic silane cross-linking agent containing hydrophobic groups, a system crosslinking agent, water-soluble nano sol, surface modified high-density polyethylene particles, tetraethyl orthosilicate modified oxidized graphene, a water-soluble fluorinated compound, a water-soluble phosphorous compound and a water-soluble metal salt compound are coated and cured on the surface of a galvanized steel sheet; the obtained inorganic surface-treated galvanized steel sheet has excellent red rust resistance performance, excellent surface conductivity, surface lubricating performance and excellent blackening resistance performance, and can satisfy requirements of rapid deep-drawing treatment and bare service of progressive dies, and the inorganic surface-treated galvanized steel sheet is especially applicable to the field of micromotors.

Printed by Jouve, 75001 PARIS (FR)

Description

Technical Field

[0001] The disclosure pertains to the technical field of surface treatment of galvanized steel sheets. In particular, the disclosure relates to an inorganically surface-treated galvanized steel sheet, a method of preparing the same and an aqueous inorganic surface treatment agent. The inorganically surface-treated galvanized steel sheet and the method of preparing the same can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and impart both excellent red rust resistance and surface electric conductivity to parts.

Background Art

[0002] Galvanized steel sheets are widely used in various fields such as automobiles, home appliances, architectures, etc, and mostly used for parts of automobiles, home appliances, electrical micro-machines, etc. Meanwhile, as the degree of mechanical automation increases, various electrical micro-machines are widely used in automobiles, processing machines or electrical equipment.

[0003] However, due to the special requirements of processing and service of electrical micro-machines, a number of critical issues need attention in storage, transportation, processing and service of galvanized steel sheets for electrical micro-machines.

[0004] In order to prevent generation of white rust due to occurrence of tarnishing in transportation and storage of galvanized steel sheets, coating of rust preventive oil is needed in manufacture of the steel sheets. When stamping processing is performed with progressive dies in the field of electrical micro-machines, the stamping process of rapid deep drawing exasperates the frictional wear between the dies and the metallic sheets. To prevent cracking of the sheets and scratching of surface zinc layers, it’s necessary to add lubricating oil to the dies when parts are stamped, after which the parts are degreased and washed. In the service of an electrical micro-machine, to guarantee the service life, grounding safety and electromagnetic characteristics of the electrical micro-machine, very high requirements are imposed on the red rust resistance and surface electric conductivity of stamped parts. The red rust resistance corresponds to the service life of the electrical micro-machine, and the surface electric conductivity corresponds to the grounding safety and the electromagnetic characteristics of the electrical micro-machine. First of all, the use of the rust preventive oil, lubricating oil and degreasing agent throughout the storage and stamping of the galvanized steel sheets is undesirable for environment and production cost.

[0005] In order to improve corrosion resistance and formability, an existing method mainly involves surface treatment of a galvanized steel sheet by passivation with chromic acid. This method can improve the corrosion resistance of the steel sheet, but has limited improvement in formability and other resistances. It is not able to meet the requirements of rapid deep drawing with progressive dies in the field of electrical micro-machines. Alternatively, after passivation with a chromate salt, the steel sheet may be further coated with an organic resin comprising a solid lubricating aid (usually a low surface energy polymer such as polyolefin and polytetrafluoroethylene), with an aim to balance corrosion resistance and lubrication effect. However, this type of organic skin film usually has a low cohesive energy. When rapid deep-drawing processing is performed with progressive dies in the field of electrical micro-machines, the organic skin film abrades the surfaces of the dies, which easily leads to interlayer separation of the organic skin film, resulting in black chippings or organic skin film peeling on part surfaces. Not only the appearance of the stamped parts is affected, but also the organic skin film chippings that fall off adhere to the parts or dies, entailing frequent cleaning of the dies and affecting the production efficiency of the stamping production line. At the same time, in order to improve the surface electric conductivity of the parts, a conductive aid such as a strong polar compound, a metal powder or a carbon powder are usually added to the skin film. However, these conductive aids are detrimental to the corrosion resistance of the skin film. That is, they will greatly reduce the corrosion resistance of the skin film, and thus affect the service life of the parts. Meanwhile, along with continuous promulgation of environmental protection directives, chromium-containing galvanized steel sheets have gradually been replaced with environmentally friendly products that do not contain chromium.

[0006] At present, chromium-free environmentally friendly products can be roughly classified into an inorganic type and an organic/inorganic composite type according to the type of surface treatment. An inorganic type lubricating skin film is mainly a skin film containing inorganic compounds such as those of silicon, manganese, phosphorus, etc. This type of inorganic skin film has a high cohesive energy, and the inorganic lubricating skin film is less likely to be subjected to interlayer separation or peeling of the skin film due to friction of the dies during a stamping process. Therefore, this type of products can still acquire a good appearance after deep-drawing processing. However, the inorganic type lubricating film cannot significantly improve the corrosion resistance of the galvanized steel sheet, and does not have good surface electric conductivity, so that they cannot be used in areas where relatively high requirements are imposed on grounding safety and electromagnetic characteristics of parts. An organic/inorganic composite type lubricating film is a thin film formed by compounding a resin, a corrosion inhibitor, a silane coupling agent, a silica colloid, and a solid lubricating aid. It exhibits not only excellent lubricity and corrosion resistance, but also good resistances to various chemical media, such as fingerprint resistance, alkali resistance and the like. However, the organic/inorganic composite type lubricating skin film has a relatively high content of the organic resin. The low cohesive energy of the organic resin tends to cause interlayer separation of the organic skin film when rapid deep-drawing processing is performed with progressive dies in the field of electrical micro-machines, which results in black chippings or organic skin film peeling on part surfaces. Not only the appearance of the stamped parts is affected, but also the organic polymer chippings that fall off adhere to the parts or dies, entailing frequent cleaning of the dies and affecting the production efficiency of the stamping production line. At the same time, the organic/inorganic composite type lubricating skin film generally does not have excellent surface electric conductivity, and thus cannot be used in areas where relatively high requirements are imposed on grounding safety and electromagnetic characteristics of parts. Therefore, the chromium-free environmentally friendly products (including inorganic and organic/inorganic composite types) generally used up to now cannot meet the requirements of high-speed deep-drawing characteristics, red rust resistance and surface electric conductivity of materials in the field of electrical micro-machines.

[0007] Chinese Patent Application Publication No. CN 101376859A discloses use of an inorganic treatment agent containing manganese, nickel, phosphate ions and a silane to form a thin transparent inorganic solid film on a surface of a galvanized steel sheet, enabling improvement of stamping formability of the galvanized steel sheet, elimination or alleviation of Zn sticking, pulverization and peeling of the galvanized steel sheet during the stamping forming. Chinese Patent Application Publication No. CN 1177020A (which has been issued as a Chinese Patent) discloses a lubricated steel sheet having a protective film containing silicic acid or a silicate formed on the steel sheet having fine irregularities on its surface, wherein its skin film coverage is about 60%, and the skin film has phosphatability and good lubricity. All of the above patents provide steel sheets with good lubricity, but corrosion resistance thereof is not as good as that of chromium-containing passivated products. Thus, they cannot meet the requirement of red rust resistance of the materials for electrical micro-machines.

[0008] Chinese Patent Application Publication No. CN 101787527A provides a galvanized steel sheet having excellent processability, alkali resistance and solvent resistance, wherein a surface thereof is covered with an organic/inorganic composite protective film comprising an aqueous cationic polyurethane resin, one or more organosilane coupling agents, as well as a corrosion inhibitor and polyoxyethylene particles. The protective film imparts excellent stamping formability, solvent resistance and alkali resistance to the surface of the galvanized steel sheet, and also enables the galvanized steel sheet to have excellent corrosion resistance and coating adhesion. However, in fact, electrical micro-machines have high requirements on surface electric conductivity. The abovementioned organic/inorganic composite protective film does not have excellent surface electric conductivity, and thus cannot be used in areas where relatively high requirements are imposed on grounding safety and electromagnetic characteristics of parts.

[0009] Chinese Patent Application Publication No. CN 101394998A provides a coated steel sheet having excellent bending processability, stamping processability, solvent resistance, chemical resistance, corrosion resistance, and having a good surface appearance and sufficient coating film hardness. However, the steel sheet is a product having a single-layer of thick coating having a film thickness of 2-10 micrometers, and the manufacturing process is a two-step method. First, a chemical conversion skin film containing no chromium is formed, and then a polyester resin is coated. That is, a post-treatment skin film is obtained by two coatings and two bakings. Usually, the second baking requires heating at a steel sheet temperature of 170-250 °C. The coated steel sheet according to this patent is relatively demanding for production equipment, and has no surface electric conductivity, not suitable for use in the field of electrical micro-machines.

Summary

[0010] In view of the above status quo, one object of the present disclosure is to provide an inorganically surface-treated galvanized steel sheet, a preparation method therefor, and an aqueous inorganic surface treatment agent therefor, wherein the inorganically surface-treated galvanized steel sheet and the aqueous inorganic surface treatment agent therefor are chromium-free and thus environmentally friendly. They can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and at the same time, they impart both excellent red rust resistance and surface electric conductivity to parts, so as to meet the requirements of users in the field of electrical micro-machines on environmental friendliness, surface electric conductivity and red rust resistance of galvanized steel sheets, and on rapid stamping processability.

[0011] In order to solve the problems existing in the prior art, it has been found after painstaking research that, by coating a surface of a galvanized steel sheet with a monoorganosiloxane containing a specific hydrophobic group, a plurality of orthosilicates used as a systematic crosslinking agent or a plurality of biorganosiloxanes having a bridging structure, one or more aqueous nanosols, one or more solid lubricating particles, an orthosilicate-modified graphene oxide having a specific structure, a fluorine-containing compound, a phosphoric acid compound, and a metal salt compound, among other components, an inorganically surface-treated galvanized steel sheet is formed, wherein the inorganically surface-treated galvanized steel sheet exhibits excellent stamping processability, can meet the requirements of rapid deep-drawing processing with progressive dies, and imparts both excellent red rust resistance and surface electric conductivity to parts. The object of solving the prior art problems is thus achieved, and the present invention has been accomplished.

[0012] At the same time, the present disclosure also provides an environmentally-friendly aqueous inorganic surface treatment agent for producing the above surface-treated galvanized steel sheet.

[0013] The technical solution of an inorganically surface-treated galvanized steel sheet of the present disclosure is as follows:

> An inorganically surface-treated galvanized steel sheet which is a galvanized steel sheet having a surface coated with a single-layer inorganic skin film having a thickness of 0.3-1.0 μm, wherein
> the inorganic skin film comprises:
>
> > A) one or more hydrophobic monoorganosilane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
> > wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
> > B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
> > wherein the systematic crosslinking agent is one or more of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
> > C) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
> > wherein the water-soluble nanosol has a mass fraction of 20-30%;
> > D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
> > E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
> > wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%.

[0014] The inorganically surface-treated galvanized steel sheet according to the present disclosure, wherein
the inorganic skin film further comprises:

> F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic skin film;
> G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;
> H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

[0015] According to the present disclosure, preferably,
according to the present disclosure, the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) is one or two selected from the group consisting of $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-C_3H_7$ (propyl), $-C_6H_5$ (phenyl), $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl), $-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) or $-C_9F_{19}$ (perfluorononyl);
according to the present disclosure, the reactive group in the hydrophobic monoorganosilane coupling agent is one to three selected from the group consisting of $-OCH_3$ (methoxy), $-OC_2H_5$ (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido or 2,3-epoxypropoxy;
according to the present disclosure,
a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four;
the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

[0016] According to the present disclosure, preferably,
the systematic crosslinking agent (B) may be one or more of an orthosilicate having 4 reactive groups, a titanate having 4 reactive groups or a diorganosilane coupling agent having 6 reactive groups and a bridging structure;
the reactive group in the orthosilicate is any one selected from the group consisting of a methoxy group, an ethoxy group, a propoxy group or a butoxy group;
the reactive group in the titanate is one or more selected from the group consisting of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group or a n-butyl ester group;

the bridging structure of the diorganosilane coupling agent is consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups;

the reactive group of the diorganosilane coupling agent is any one selected from the group consisting of a methoxy group, an ethoxy group or a propoxy group.

[0017] According to the invention, preferably, the aqueous nanosol (C) is an aqueous inorganic oxide sol or a metal oxide sol;

the aqueous nanosol is one or more selected from the group consisting of an aqueous silica sol, an aqueous titanium dioxide sol, an aqueous zirconia sol or an aqueous alumina sol.

[0018] According to the present disclosure, preferably,

the surface-modified high-density polyethylene particles (D) have a particle diameter of between 0.1 and 0.5 μm; and the surface-modifying group is reactive, specifically selected from one or more of an amino group, a hydroxyl group, a carboxyl group, an epoxy group or a urethane group;

[0019] According to the present disclosure, preferably,

the orthosilicate-modified graphene oxide (E) comprises 1-5 sheet layers (thickness being between 0.35 nm and 1.75 nm); the orthosilicate-modified graphene oxide has a sheet diameter of between 2-5 microns, and an aspect ratio (of diameter to thickness) of the graphene is between 1100-14000.

[0020] According to the present disclosure, the orthosilicate in the orthosilicate-modified graphene oxide is one or more selected from the group consisting of methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate or butyl orthosilicate.

[0021] In the orthosilicate-modified graphene oxide, a ratio of the number of carbon atoms to the number of oxygen atoms is <3, and the silicon element has a content of 5-12%.

[0022] According to the present disclosure, preferably,

the water-soluble fluorine-containing compound (F) is a fluorine-containing metal salt or a fluorine-containing acid, particularly one or more selected from the group consisting of sodium fluoride, ammonium fluorotitanate, sodium fluorosilicate, hexafluorotitanic acid, and fluorosilicic acid.

[0023] According to the present disclosure, preferably,

the water-soluble phosphorus-containing compound (G) is a phosphate salt or a phosphorus-containing acid, wherein the water-soluble phosphorus-containing compound is one or more selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, ammonium phosphate, aluminum triphosphate and ammonium polyphosphate.

[0024] According to the present disclosure, preferably,

the water-soluble metal salt compound (H) is one or more of a titanium salt, a cerium salt, a lanthanum salt, a molybdenum salt, a tungsten salt, a cobalt salt, and a zirconium salt.

[0025] Specifically, the titanium salt is one or more selected from the group consisting of ammonium fluorotitanate, hexafluorotitanic acid, titanium orthosulfate, titanium oxysulfate or titanium chloride.

[0026] Specifically, the cerium salt is one or more selected from the group consisting of cerium nitrate, cerium sulfate, a fluorine-containing cerium salt, and a composite salt of cerium and ammonium.

[0027] Specifically, the lanthanum salt may be one or more of lanthanum chloride, lanthanum sulfate, and lanthanum nitrate.

[0028] Specifically, the molybdenum salt is one or more selected from the group consisting of ammonium molybdate, magnesium molybdate or sodium molybdate.

[0029] Specifically, the tungsten salt is one or more selected from the group consisting of ammonium tungstate, magnesium tungstate, ammonium paratungstate or ammonium metatungstate.

[0030] Specifically, the cobalt salt may be an inorganic cobalt salt such as cobalt nitrate, cobalt sulfate or cobalt chloride, or one or more of cobalt naphthenate, cobalt oxalate or cobalt stearate.

[0031] The zirconium salt may be one or more of potassium fluorozirconate, zirconium nitrate, and zirconium sulfate.

[0032] The above inorganically surface-treated galvanized steel prepared according to the disclosure is chromium free and environmentally friendly, can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and imparts both excellent red rust resistance and surface electric conductivity to parts.

[0033] Another object of the present disclosure is to provide a method of preparing an inorganically surface-treated galvanized steel sheet, wherein the steel sheet can meet the rapid deep-drawing processing of the progressive die in the field of electrical micro-machines, and imparts both excellent red rust resistance and surface electric conductivity to parts. The technical solution is as follows:

A method of preparing an inorganically surface-treated galvanized steel sheet, comprising

forming an aqueous inorganic surface treatment agent by dissolving or dispersing components of the aqueous inorganic surface treatment agent in water, applying the aqueous inorganic surface treatment agent on a surface of a galvanized steel sheet by one-pass roll coating, and drying at 60-100 °C, thereby providing an inorganic skin film having a dry film

thickness of 0.3-1.0 microns,
wherein the inorganic skin film comprises:

A) one or more hydrophobic monoorganosilane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
wherein the systematic crosslinking agent is one or more selected from the group consisting of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
C) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
wherein the water-soluble nanosol has a mass fraction of 20-30%;
D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%.

[0034] The method of preparing an inorganically surface-treated galvanized steel sheet according to the present disclosure, wherein
the inorganic skin film further comprises:

F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic skin film;
G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;
H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

[0035] According to the method of producing an inorganically surface-treated galvanized steel sheet according to the present disclosure, preferably,
the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) may be one or two of $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-C_3H_7$ (propyl), $-C_6H_5$ (phenyl), $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl), $-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) or $-C_9F_{19}$ (perfluorononyl); the reactive group in the hydrophobic monoorganosilane coupling agent may be at most three of $-OCH_3$ (methoxy), $-OC_2H_5$ (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido or 2,3-epoxypropoxy; a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four; the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

[0036] According to the present disclosure, preferably,
the systematic crosslinking agent (B) may be one or more of an orthosilicate having 4 reactive groups, a titanate having 4 reactive groups or a diorganosilane coupling agent having 6 reactive groups and a bridging structure; the reactive group in the orthosilicate may be any one of a methoxy group, an ethoxy group, a propoxy group or a butoxy group; the reactive group in the titanate may be one or more of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group or a n-butyl ester group; the bridging structure of the diorganosilane coupling agent is consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups; and the reactive group of the diorganosilane coupling agent may be any one of a methoxy group, an ethoxy group or a propoxy group.

[0037] According to the present disclosure, preferably,
the aqueous nanosol (C) is an aqueous inorganic oxide sol or a metal oxide sol; and the aqueous nanosol is one or more selected from the group consisting of an aqueous silica sol, an aqueous titanium dioxide sol, an aqueous zirconia sol and an aqueous alumina sol.

[0038] According to the present disclosure, preferably,
the surface-modified high-density polyethylene particles (D) have a particle diameter of between 0.1 and 0.5 μm; and the surface-modifying group is reactive, specifically selected from one or more of an amino group, a hydroxyl group, a carboxyl group, an epoxy group or a urethane group.

[0039] According to the present disclosure, preferably,
the orthosilicate-modified graphene oxide (E) comprises 1-5 sheet layers (thickness being between 0.35 nm and 1.75 nm); the orthosilicate-modified graphene oxide has a sheet diameter of between 2-5 microns, and an aspect ratio of the graphene is between 1100-14000.

[0040] According to the present disclosure, the orthosilicate in the orthosilicate-modified graphene oxide is one or more selected from the group consisting of methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate and butyl orthosilicate.

[0041] In the orthosilicate-modified graphene oxide, a ratio of the number of carbon atoms to the number of oxygen atoms is <3, and the silicon element has a content of 5-12%.

[0042] According to the present disclosure, preferably,
the water-soluble fluorine-containing compound (F) is a fluorine-containing metal salt or a fluorine-containing acid, particularly one or more selected from the group consisting of sodium fluoride, ammonium fluorotitanate, sodium fluorosilicate, hexafluorotitanic acid, and fluorosilicic acid.

[0043] According to the present disclosure, preferably,
the water-soluble phosphorus-containing compound (G) is a phosphate salt or a phosphorus-containing acid, wherein the water-soluble phosphorus-containing compound is one or more selected from the group consisting of orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, ammonium phosphate, aluminum triphosphate and ammonium polyphosphate.

[0044] According to the present disclosure, preferably,
the water-soluble metal salt compound (H) is one or more of a titanium salt, a cerium salt, a lanthanum salt, a molybdenum salt, a tungsten salt, a cobalt salt, and a zirconium salt.

[0045] Specifically, the titanium salt is one or more selected from the group consisting of ammonium fluorotitanate, hexafluorotitanic acid, titanium orthosulfate, titanium oxysulfate or titanium chloride.

[0046] Specifically, the cerium salt is one or more selected from the group consisting of cerium nitrate, cerium sulfate, a fluorine-containing cerium salt, and a composite salt of cerium and ammonium.

[0047] Specifically, the lanthanum salt may be one or more of lanthanum chloride, lanthanum sulfate, and lanthanum nitrate.

[0048] Specifically, the molybdenum salt is one or more selected from the group consisting of ammonium molybdate, magnesium molybdate or sodium molybdate.

[0049] Specifically, the tungsten salt is one or more selected from the group consisting of ammonium tungstate, magnesium tungstate, ammonium paratungstate and ammonium metatungstate.

[0050] Specifically, the cobalt salt may be an inorganic cobalt salt such as cobalt nitrate, cobalt sulfate or cobalt chloride, or one or more of cobalt naphthenate, cobalt oxalate or cobalt stearate.

[0051] The zirconium salt may be one or more of potassium fluorozirconate, zirconium nitrate, and zirconium sulfate.

[0052] The above inorganically surface-treated galvanized steel prepared according to the method of the disclosure is environmentally friendly and chromium free, can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and imparts both excellent red rust resistance and surface electric conductivity to parts.

[0053] The disclosure further provides an aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the aqueous inorganic surface treatment agent can be used for the galvanized steel sheet that meets the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and impart both excellent red rust resistance and surface electric conductivity to parts.

[0054] An aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet by coating a surface of the galvanized steel sheet to form an inorganic skin film, wherein
the total solids in an aqueous solution thereof comprise the following components:

A) one or more hydrophobic monoorganosilane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
wherein the systematic crosslinking agent is one or more of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
C) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
wherein the water-soluble nanosol has a mass fraction of 20-30%;
D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%;
F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic

skin film;

G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;

H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

[0055] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) may be one or two of -CH_3 (methyl), -C_2H_5 (ethyl), -C_3H_7 (propyl), -C_6H_5 (phenyl), -CF_3 (perfluoromethyl), -C_2F_5 (perfluoroethyl), -C_3F_7 (perfluoropropyl), -C_5F_{11} (perfluoropentyl), -C_7F_{15} (perfluoroheptyl) or -C_9F_{19} (perfluorononyl); the reactive group in the hydrophobic monoorganosilane coupling agent may be at most three of -OCH_3 (methoxy), -OC_2H_5 (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido or 2,3-epoxypropoxy; a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four; the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

[0056] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the systematic crosslinking agent (B) may be one or more of an orthosilicate having 4 reactive groups, a titanate having 4 reactive groups or a diorganosilane coupling agent having 6 reactive groups and a bridging structure; the reactive group in the orthosilicate may be any one of a methoxy group, an ethoxy group, a propoxy group or a butoxy group; the reactive group in the titanate may be one or more of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group or a n-butyl ester group; the bridging structure of the diorganosilane coupling agent is consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups; the reactive group of the diorganosilane coupling agent may be any one of a methoxy group, an ethoxy group or a propoxy group.

[0057] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the aqueous nanosol (C) is an aqueous inorganic oxide sol or a metal oxide sol; and the aqueous nanosol may be one or more of an aqueous silica sol, an aqueous titanium dioxide sol, an aqueous zirconia sol or an aqueous alumina sol.

[0058] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the surface-modified high-density polyethylene particles (D) have a particle diameter of between 0.1 and 0.5 μm; and the surface-modifying group is reactive, specifically one or more of an amino group, a hydroxyl group, a carboxyl group, an epoxy group or a urethane group.

[0059] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the orthosilicate-modified graphene oxide (E) comprises 1-5 sheet layers (thickness being between 0.35 nm and 1.75 nm); the orthosilicate-modified graphene oxide has a sheet diameter of between 2-5 microns, and an aspect ratio of the graphene is between 1100-14000; the orthosilicate in the orthosilicate-modified graphene oxide may be one or more of methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate or butyl orthosilicate; the ratio of the number of carbon atoms to the number of oxygen atoms is <3, and the silicon element has a content of 5-12%.

[0060] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the water-soluble fluorine-containing compound (F) is a fluorine-containing metal salt or a fluorine-containing acid. For example, the water-soluble fluorine-containing compound may be one or more of sodium fluoride, ammonium fluorotitanate, sodium fluorosilicate, hexafluorotitanic acid, and fluorosilicic acid.

[0061] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the water-soluble phosphorus-containing compound (G) is a phosphate salt or a phosphorus-containing acid. For example, the water-soluble phosphorus-containing compound may be one or more of orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, ammonium phosphate, aluminum triphosphate and ammonium polyphosphate.

[0062] The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet, wherein the water-soluble metal salt compound (H) is one or more of a titanium salt, a cerium salt, a lanthanum salt, a molybdenum salt, a tungsten salt, a cobalt salt, and a zirconium salt. For example, the titanium salt may be one or more of ammonium fluorotitanate, hexafluorotitanic acid, titanium orthosulfate, titanium oxysulfate or titanium chloride; the cerium salt may be cerium nitrate, cerium sulfate, or may be a fluorine-containing cerium salt, or may be one or more of composite salts of cerium and ammonium; the lanthanum salt may be one or more of lanthanum chloride, lanthanum sulfate, and lanthanum nitrate; the molybdenum salt may be one or more of ammonium molybdate, magnesium molybdate or sodium molybdate; the tungsten salt may be one or more of ammonium tungstate, magnesium tungstate, ammonium paratungstate or ammonium metatungstate; the cobalt salt may be an inorganic cobalt salt such as cobalt nitrate, cobalt sulfate or cobalt chloride, or one or more of cobalt naphthenate, cobalt oxalate or cobalt stearate; and the zirconium salt may be one or more of potassium fluorozirconate, zirconium nitrate, and zirconium sulfate.

[0063] The inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent according to the present disclosure, wherein

the hydrophobic monoorganosilane coupling agent (A) in the aqueous inorganic surface treatment agent may be one of the above monoorganosilanes or a mixture thereof, and it’s a major film-forming component in the aqueous inorganic surface treatment agent according to the present disclosure. In the present disclosure, the inorganic skin film formed using the hydrophobic monoorganosilane coupling agent (A) as a major component has a strong cohesive energy, and the inorganic skin film has a remarkable cohesive effect. When a rapid deep-drawing processing is performed with progressive dies in the field of electrical micro-machines, the inorganic skin film having a strong cohesive energy can maintain the integrity of the skin film when it is abraded violently by the dies, and interlayer separation or peeling of the inorganic skin film is prevented, thus ensuring that the parts should still have a good appearance after stamped several times by the progressive dies. At the same time, the frequency of cleaning the dies on the stamping production line is also reduced, and the production efficiency of the stamping production line is improved. However, the hydrophobic monoorganosilane coupling agent (A) in the present disclosure is notably hydrophobic per se, but the reactive group contained in the monoorganosiloxane may react with water to form a hydrophilic group having excellent hydrophilic property, such as a hydroxyl group, a carboxyl group or an amino group; or may be capable of reacting with the systematic crosslinking agent in the aqueous inorganic surface treatment agent, thereby entering an aqueous system. Therefore, the hydrophobic monoorganosilane coupling agent (A) can be dissolved or dispersed steadily in the aqueous system.

[0064] The inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent according to the present disclosure, wherein

in order for the resulting inorganic skin film to have excellent corrosion resistance, it’s necessary for the inorganic skin film to have a high degree of crosslinking. As the major film-forming component in the inorganic skin film, the hydrophobic monoorganosilane coupling agent (A) needs to be cross-linkable with other components in the skin film, such as the systematic crosslinking agent (B) and the aqueous nanosol (C), thereby increasing the crosslinking density of the skin film. Therefore, in order to ensure excellent reactivity of the hydrophobic monoorganosilane coupling agent (A) used in the present disclosure, the hydrophobic monoorganosilane coupling agent (A) must comprise two or more reactive groups. The reactive group may be one or more of $-OCH_3$ (methoxy) and $-OC_2H_5$ (ethoxy) which can react with water first to form a hydroxyl group that can then further react with other components (B and C); or may be one or more of an epoxy group, an amino group, a hydroxyl group, a carboxyl group, an amido group, and a 2,3-epoxypropoxy group which can react with other components (B and C) directly; or may be one or more of a vinyl group and a propenyl group which are self-polymerizable.

[0065] In order to ensure a clean surface of a part after rapid deep-drawing with progressive dies and no broken inorganic skin film or zinc powder adhering to the surface of the part, the surface of the part is required to have a "non-stick" characteristic. Accordingly, when it comes to a surface of a steel sheet, only an inorganic skin film is likely to provide such a "non-stick" characteristic. After painstaking research and many attempts, it has been found that, after introduction of a hydrophobic group into a conventional monoorganosilane coupling agent to form a hydrophobic monoorganosilane coupling agent (A), the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) can migrate to the surface of a skin film during curing of the skin film, forming an extremely thin hydrophobic layer on the surface of the inorganic skin film, thereby reducing the surface polarity and Gibbs free energy of the inorganic skin film, and reducing adhesion of zinc powder, impurities and broken skin film to the inorganic skin film, so as to endow the surface of the inorganic skin film with the "non-stick" characteristic which ensures a clean surface of a part after rapid deep-drawing with progressive dies and no broken inorganic skin film or zinc powder adhering to the surface of the part.

[0066] Based on overall consideration, according to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the hydrophobic monoorganosilane coupling agent (A) in the present disclosure should have both a reactive group and a hydrophobic group, and a sum of the number of the reactive group and the number of the hydrophobic group should be 4. In order to ensure that the hydrophobic monoorganosilane coupling agent (A) in the present disclosure have sufficient reactivity to achieve a certain crosslinking density after baking and curing, the number of the reactive group is required to be greater than or equal to two (i.e., may be two or three). Therefore, the number of the hydrophobic group capable of providing the "non-stick" characteristic to the hydrophobic monoorganosilane coupling agent (A) is (4 - the number of the reactive group), indicating that the number of the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) in the present disclosure may be one or two. The hydrophobic group in the above hydrophobic monoorganosilane coupling agent (A) may be a short-chain hydrocarbyl group such as $-CH_3$(methyl), $-C_2H_5$(ethyl), $-C_3H_7$(propyl) or $-C_6H_5$(phenyl); or may be a fluorine-containing hydrophobic group such as $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl), $-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) or $-C_9F_{19}$ (perfluorononyl). The hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) in the present disclosure may be any one or two of the above groups.

[0067] In summary, according to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the hydrophobic monoorganosilane coupling agent (A) in the present disclosure should have both a reactive group (two or three) and a hydrophobic group (one or two) in its structure, and a sum of the number of the reactive group and the number of the hydrophobic group is 4. For example, those that may be exemplified include a trimethoxymethylsilane coupling agent, a triethoxymethylsilane coupling agent, a tripropoxymethylsilane coupling agent, a trimethoxyethylsilane coupling agent, a triethoxyethylsilane coupling agent, a tripropoxyethylsilane coupling agent, a trimethoxypropylsilane coupling agent, a triethoxypropylsilane coupling agent, a tripropoxypropylsilane coupling agent, a 3-aminopropyl-ethoxymethylsilane coupling agent, a N-(2-aminoethyl)-aminopropylmethyldimethoxysilane coupling agent, a 1H, 1H, 2H, 2H-perfluorodecyltrimethoxysilane coupling agent, a 1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane coupling agent, a 1H, 1H, 2H, 2H-perfluorooctyltrimethoxysilane coupling agent, a 1H, 1H, 2H, 2H-perfluorooctyltriethoxysilane coupling agent, methylphenyldiethoxysilane, diphenyldiethoxysilane, fluoromethyltrimethoxysilane, fluoromethyltriethoxysilane, fluoromethylethoxydimethoxysilane, fluoroethyltrimethoxysilane, fluoroethyltriethoxysilane, 3-fluoropropylmethyldimethoxysilane, 3-fluoropropylmethyldiethoxysilane, 3-fluoropropyltriethoxysilane, etc. Any one or two or more of the above silane coupling agents may be used as the hydrophobic monoorganosilane coupling agent (A).

[0068] The hydrophobic monoorganosilane coupling agent (A) in the present disclosure is 40-60 parts by weight of the inorganic skin film. If it is less than 40 parts, the corrosion resistance and "non-stick" characteristic of the inorganic skin film will be poor, wherein poor corrosion resistance of the inorganic skin film may affect the red rust resistance of stamped parts; and poor "non-stick" characteristic may lead to adhesion of a lot of impurities to the part surface after stamping, affecting the appearance of the stamped parts. If it is more than 60 parts, the ductility of the inorganic skin film will be deteriorated, and the inorganic skin film is liable to crack and peel off during a forming process, resulting in decreased stamping formability of the skin film.

[0069] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the systematic crosslinking agent (B) used in the present disclosure comprises a large number of reactive groups which can be chemically bonded to a metal substrate and the other components in the inorganic skin film. This can not only improve adhesion between the inorganic skin film and the metal substrate, but also enhance the crosslinking density of the inorganic skin film to achieve the purpose of enhancing the corrosion resistance and stamping formability of the inorganic skin film, so that stamped parts have excellent red rust resistance and surface appearance.

[0070] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the systematic crosslinking agent (B) in the present disclosure may be one or more of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure; the orthosilicate comprises 4 reactive groups, wherein the reactive group may be any one of a methoxy group, an ethoxy group, a propoxy group or a n-butoxy group; the titanate comprises four reactive groups, wherein the reactive group may be one or more of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group or a n-butyl ester group; and the diorganosilane coupling agent means that two silane structures exist in the same molecular structure, wherein one molecule comprises 6 reactive groups, and the number of reactive groups is larger than that of a conventional monoorganosilane coupling agent. The diorganosilane coupling agent in the present disclosure comprises a bridging structure consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups, wherein the reactive group of the diorganosilane coupling agent may be any one of a methoxy group, an ethoxy group or a propoxy group.

[0071] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the orthosilicate used in the systematic crosslinking agent (B) in the present disclosure may be one or more of methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate, butyl orthosilicate or isopropyl orthosilicate; the titanate used in the systematic crosslinking agent (B) in the present disclosure may be one or more of tetraisopropyl orthotitanate, isopropyl tris(dioctylphosphoryloxy) titanate, isopropyl trioleyl titanate, tetraisopropyl bis(dioctylphosphate) titanate, bis(dioctyloxypyrophosphate) ethylene titanate, isopropyl tris(dodecylbenzenesulfonyl) titanate, tetra-tert-butyl orthotitanate or diisopropyl bis(triethanolamine) titanate; and the diorganosilane coupling agent used in the systematic crosslinking agent (B) in the present disclosure may be one or more of 1,2-bistrimethoxysilylethane, 1,2-bisethylmethoxysilylethane, bis-(γ-triethoxysilylpropyl) tetrasulfide, bis-[γ-(triethoxysilyl)propyl] disulfide, bis-(γ-trimethoxysilylpropyl) amine. The systematic crosslinking agent (B) used in the present disclosure may be any one or more of the above-mentioned orthosilicates, titanates and diorganosilane coupling agents.

[0072] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the systematic crosslinking agent (B) in the present disclosure is 10-30 parts by weight of the inorganic skin film. If it is less than 10 parts, the crosslinking density of the inorganic skin film will be lowered greatly, thereby affecting the corrosion resistance of the inorganic skin film, and ultimately, the red rust resistance of stamped parts will be poor. If it is higher than 30 parts, because compatibility of a selected systematic crosslinking agent with water is not very good, the systematic crosslinking agent in a high amount will affect stability of the aqueous inorganic surface treatment agent, which will result in obvious stratification of the treatment agent after standing for a long time, leading to large decrease in the overall performance of the aqueous inorganic surface treatment agent.

[0073] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and

the aqueous inorganic surface treatment agent in the present disclosure,
the water-soluble nanosol (C) used in the present disclosure is preferably a water-soluble colloid having a particle diameter of 5 - 50 nm, and it may be a type of aqueous inorganic oxide or metal oxide sol. Specifically, it may be one or more of a silica sol, an aqueous titania sol, an aqueous zirconia sol or an aqueous alumina sol. The crosslinking density of the inorganic skin film can be further increased by a large number of reactive groups in the aqueous nanosol, thereby enhancing the corrosion resistance of the inorganic skin film. At the same time, fine particles formed by baking and curing the aqueous nanosol have high hardness, which can effectively improve scratch resistance of the inorganic skin film and avoid surface scratches on stamped parts.

[0074] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,
the water-soluble nanosol (C) used in the present disclosure may be an aqueous silica sol, such as SNOWTEX-40, SNOWTEX-50, SNOWTEX-C, SNOWTEX-N, SNOWTEX-O, SNOWTEX-OL, SNOWTEX-ZL and SNOWTEX-UP from Nissan Chemical; LUDOX-AM, LUDOX-AS, LUDOX-CL, LUDOX-DF, LUDOX-HS, LUDOX-LS, LUDOX-SK, LUDOX-SM, LUDOX-TM and LUDOX-TMA from Grace, the USA; ADELITE AT-20N or ADELITE AT-20A from Asahi Denka, Japan; the water-soluble nanosol (C) used in the present disclosure may also be an aqueous titanium dioxide sol, such as MTI-2080 from Shenzhen Yoshida Chemical; EFUT- GY01, EFUT-GY02, EFUT-GY03 from Shanghai Yifu, etc; the water-soluble nanosol (C) used in the present disclosure may also be an aqueous zirconia sol, such as VK-RJ80 from Xuancheng Jingrui, GT-360 from Yizhen Technology, UG03W, UG-R10W and UR-R30W from Suzhou Yougao, etc; and the water-soluble nanosol (C) used in the present disclosure may be an aqueous alumina sol, such as SH-33 from Qingdao Shankehaitai, LA-20 from Ji'nan Fujing, EFUAL-Y10C, EFUAL-Y10S, EFUAL-Y20C, EFUAL-Y20S, EFUAL-Y30C and EFUAL-Y30S from Shanghai Yifu, etc. The aqueous nanosol (C) used in the present disclosure may be any one or more of the above aqueous silica sols, aqueous titania sols, aqueous zirconia sols or aqueous alumina sols.

[0075] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,
the aqueous nanosol (C) in the present disclosure is 5-15 parts by weight of the inorganic skin film. If it is less than 5 parts, the surface hardness of the inorganic skin film will be lowered greatly, thereby affecting the scratch resistance of the inorganic skin film, such that the inorganic skin film will be easily damaged during a stamping forming process. If it is more than 15 parts, there will be too many nanoparticles in the inorganic skin film, and thus the ductility of the skin film will be deteriorated, resulting in decreased stamping formability of the skin film.

[0076] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,
the surface-modified high-density polyethylene particles (D) used in the present disclosure are commercially available solid lubricating particles. This kind of lubricating aid is characterized by low surface energy, high lubricity and high surface hardness. It can form a hard lubricating layer on the surface of the inorganic skin film, which can not only improve scratch resistance of the inorganic skin film, but also enhance surface smoothness of the inorganic skin film, thereby achieving the purpose of improving the stamping formability of the inorganic skin film, so that the inorganic skin film can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines. In the field of electrical micro-machines, progressive die stamping usually exceeds 10 passes, and each pass of stamping causes frictional wear to the inorganic skin film in the present disclosure. To ensure the appearance and corrosion resistance of stamped parts, the inorganic skin film in the present disclosure is required to have strong scratch resistance and be able to ensure integrity and excellent appearance of the skin film during the multi-pass stamping process. After painstaking research and attempts, it has been found that if it is necessary to ensure that the inorganic skin film in the present disclosure should have the above properties, it is necessary to precisely control the distribution of the composite lubricating particles used in the present disclosure in the inorganic skin film, so that a small amount of the solid lubricating particles can gather in the surface of the inorganic skin film, and the solid lubricating particles can also be dispersed uniformly inside the inorganic skin film. Thus, the inorganic skin film exhibits excellent scratch resistance across the entire thickness, thereby ensuring that the inorganic skin film can meet the requirements of multi-pass progressive die stamping.

[0077] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,
the surface-modified high-density polyethylene particles (D) used in the present disclosure are solid lubricating particles having a reactive group grafted on a particle surface. Specifically, the reactive group may be one or more of an amino group, a hydroxyl group, a carboxyl group, an epoxy group or a urethane group, wherein the hydroxyl group and the carboxyl group can be obtained by immersing the high-density polyethylene particles in a strong oxidative solution; the amino group and the urethane group can be obtained by grafting ethylenediamine, hexamethylenediamine or ethyl urethane to the surface of the high-density polyethylene particles; and the epoxy group can be obtained by grafting glycidyl methacrylate or allyl glycidyl ether to the surface of the high-density polyethylene particles. The above reactive groups can react with the organosilane coupling agent in the treatment solution to form a covalent bond, which can not

only enhance the bonding strength between the high-density polyethylene particles and the inorganic skin film, but also confine the high-density polyethylene particles, thereby ensuring that the high-density polyethylene particles can be uniformly dispersed in the inorganic skin film, provide excellent anti-wear property across the entire thickness of the inorganic skin film, and improve the stamping processability and scratch resistance of the inorganic skin film. At the same time, the chemical bonding between the high-density polyethylene particles and the skin film can delay penetration of a corrosive medium along the surface of the high-density polyethylene particles into the skin film, and alleviate the negative influence of the addition of the high-density polyethylene particles on the corrosion resistance of the inorganic skin film.

[0078] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the surface-modified high-density polyethylene particles (D) used in the present disclosure have a particle diameter in the range of 0.1-0.5 μm. If the particle diameter is less than 0.1 μm, the surface-modified high-density polyethylene particles (D) in the inorganic skin film will not have the effect of enhancing the scratch resistance of the inorganic skin film. If the particle diameter is higher than 0.5 μm, the surface-modified high-density polyethylene particles (D) will be too large, and most of the particles will be exposed on the surface of the skin film. When subjected to stamping friction, large particles will be easily detached. As a result, the stamping processability of the skin film will be lowered drastically.

[0079] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the surface-modified high-density polyethylene particles (D) used in the present disclosure are 10-25 parts by weight of the inorganic skin film. If the content is less than 10 parts, the surface of the inorganic skin film will not have sufficient lubricity and scratch resistance. If the content is more than 25 parts, too many surface-modified high-density polyethylene particles (D) will be present in the inorganic skin film, and the corrosive medium may penetrate into the inorganic skin film along the interface of the surface-modified high-density polyethylene particles (D), thereby reducing the corrosion resistance of the inorganic skin film.

[0080] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the inorganically surface-treated galvanized steel sheet of the present disclosure needs to have good surface electric conductivity, and be able to discharge the static electricity generated during the actual operation of a stamped and formed part through the surface thereof, thereby preventing accumulation of a large amount of electrostatic charge on the surface of the part. Otherwise, the safety and electromagnetic characteristics of the part will be affected, and thus normal use of the part will be affected. After painstaking research and attempts, it has been found that advantage of the excellent electric conductivity of a graphene sheet may be taken to significantly improve the surface electric conductivity of the inorganically surface-treated galvanized steel sheet in the present disclosure by adding an appropriate amount of graphene sheets to the inorganic skin film of the galvanized steel sheet.

[0081] Further, the abovementioned graphene sheets need to be stably present in the aqueous inorganic surface treatment agent for a long period of time without agglomeration, precipitation, or segregation. However, due to the large van der Waals force between the graphene sheets, the graphene sheets are particularly prone to agglomeration, and cannot be easily dispersed in the aqueous inorganic surface treatment agent uniformly. Therefore, it is necessary to modify the surface of the graphene sheets. By introducing other substances to destroy the surface van der Waals force, the graphene sheets are separated from each other, so that they can be stably present in the aqueous inorganic surface treatment agent for a long period of time. In order for the graphene sheets to be stably present in the aqueous inorganic surface treatment agent of the present disclosure for a long period of time, the substance used to modify the graphene surface needs to be further defined. In view of the fact that the main components of the aqueous inorganic surface treatment agent of the present disclosure are mostly silicon-containing substances, such as a hydrophobic monoorganosilane coupling agent (A), a systematic crosslinking agent (B) and a water-soluble nanosol (C), etc, the present disclosure utilizes an orthosilicate as a modifying substance and propanol as a solvent to modify the surface of the graphene sheets with an aim to further improve dispersibility of the graphene sheets, and improve compatibility between the graphene sheets and the aqueous inorganic surface treatment agent.

[0082] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the graphene sheet used in the present disclosure has a layered structure, and may be mono-layered or multilayered. When the graphene is multilayered, the number of sheet layers is preferably 5 or less (a sheet layer has a thickness of between 0.35 and 1.75 nm). Further, the graphene sheet used in the present disclosure has a sheet diameter of 2-5 μm and a graphene aspect ratio of 1100-14000. By controlling the number of graphene oxide layers to 5 or less and the sheet diameter to 2-5 μm, graphene can maintain excellent electric conductivity and easily form a conductive network in the inorganic skin film, thereby improving the surface electric conductivity of the inorganic skin film.

[0083] The surface of the graphene sheet used in the present disclosure is modified with an orthosilicate, and a method known to date for preparation of a surface-modified graphene sheet can be used. For example, first, a graphite oxide may be immersed in a strong oxidative solution (such as a mixed solution of concentrated sulfuric acid/potassium permanganate, a mixed solution of concentrated sulfuric acid/concentrated nitric acid) at 70-80 °C and ultrasonically dispersed for 1 hour, and then filtered and washed with a large amount of deionized water to neutral to obtain a graphene oxide sheet; further, the graphene oxide sheet is mixed with an orthosilicate and propanol under agitation at 100 °C for 24 h, and then filtered to obtain an orthosilicate-modified graphene oxide; secondly, the orthosilicate-modified graphene oxide is diluted with propanol to a mass fraction of 1-5%.

[0084] The orthosilicate used for the orthosilicate-modified graphene oxide used in the present disclosure may be one or more of methyl orthosilicate, ethyl orthosilicate, propyl orthosilicate or butyl orthosilicate. In the orthosilicate-modified graphene oxide according to the disclosure, the ratio of the number of carbon atoms to the number of oxygen atoms is <3, and the silicon element has a content of 5-12%.

[0085] The orthosilicate-modified graphene oxide according to the present disclosure comprises a surface-grafted orthosilicate, which can not only increase the dispersion stability coefficient of the graphene oxide in the aqueous inorganic surface treatment agent system and prevent agglomeration or precipitation thereof, but also promote chemical bonding reactions of the graphene oxide with the hydrophobic monoorganosilane coupling agent (A), the systematic crosslinking agent (B) and the water-soluble nanosol (C) in the system, so that the graphene oxide is more likely to form a conductive network in the inorganic skin film, and enhance the effect of the graphene oxide in increasing the surface electric conductivity of the inorganic skin film. Further, the graphene oxide having a layered structure is uniformly dispersed inside the inorganic skin film. When a corrosive medium attempts to penetrate into the inorganic skin film, the sheet layers of the graphene oxide can extend the permeation path of the corrosive medium, thereby providing excellent physical protection and thus greatly improving the corrosion resistance of the skin film. At the same time, the atoms in the graphene oxide sheet are linked by carbon-carbon covalent bond. Hence, the graphene oxide sheet has excellent mechanical properties, and has good resistance to wear and damage caused by external objects. Therefore, it has a function in improving the scratch resistance of the inorganic skin film.

[0086] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,
the orthosilicate-modified graphene oxide used in the present disclosure is 0.05-0.5 parts by weight of the inorganic skin film based on graphene oxide. If the content is less than 0.05 parts, that is, when too little graphene oxide is used, the graphene oxide will have no obvious effect in improving the surface electric conductivity of the inorganic skin film. If the content is higher than 0.5 parts, that is, when too much graphene oxide is used, the inorganic skin film will become dark under the influence of the graphene oxide, and its appearance will be affected. At the same time, when too much graphene oxide is used, it's prone to agglomeration, which will decrease the surface quality of the inorganic skin film.

[0087] The fluorine-containing compound used in the present disclosure is water-soluble, and may be a fluorine-containing metal salt or a fluorine-containing acid. For example, the fluorine-containing compound may be one or more of sodium fluoride, ammonium fluorotitanate, sodium fluorosilicate, hexafluorotitanic acid, and fluorosilicic acid. The mass fraction of the fluorine-containing compound in the inorganic skin film is 1-4 parts based on the fluorine element in the fluorine-containing compound. If the mass fraction of the fluorine element is less than 1 part, that is, when too little fluorine-containing compound is used, the corrosion resistance of the inorganic skin film may decrease. If the mass fraction of the fluorine element is more than 4 parts, that is, when too much fluorine-containing compound is used, the aqueous inorganic surface treatment agent may become less stable.

[0088] The phosphorus-containing compound used in the present disclosure is water-soluble, and may be a phosphate salt or a phosphorus-containing acid. For example, the phosphorus-containing compound may be one or more of orthophosphoric acid, pyrophosphoric acid, triphosphoric acid, trimetaphosphoric acid, ammonium phosphate, aluminum triphosphate and ammonium polyphosphate. The mass fraction of the phosphorus-containing compound in the inorganic skin film is 0.5-4 parts based on the phosphorus element in the phosphorus-containing compound. If the mass fraction of the phosphorus element is less than 0.5 parts, that is, when too little phosphorus-containing compound is used, the addition thereof will have no effect, and the corrosion resistance of the inorganic skin film may decrease. If the mass fraction of the phosphorus element is more than 4 parts, that is, when too much phosphorus-containing compound is used, the inorganic skin film may become less adhesive.

[0089] The metal salt compound used in the present disclosure is a water-soluble salt, and may be one or more of a titanium salt, a cerium salt, a lanthanum salt, a molybdenum salt, a tungsten salt, a cobalt salt, and a zirconium salt. For example, the titanium salt may be one or more of ammonium fluorotitanate, hexafluorotitanic acid, titanium orthosulfate, titanium oxysulfate or titanium chloride; the cerium salt may be cerium nitrate, cerium sulfate, or may be a fluorine-containing cerium salt, or may be one or more of composite salts of cerium and ammonium; the lanthanum salt may be one or more of lanthanum chloride, lanthanum sulfate, and lanthanum nitrate; the molybdenum salt may be one or more of ammonium molybdate, magnesium molybdate or sodium molybdate; the tungsten salt may be one or more of ammonium tungstate, magnesium tungstate, ammonium paratungstate or ammonium metatungstate; the cobalt salt may be an inorganic cobalt salt such as cobalt nitrate, cobalt sulfate or cobalt chloride, or one or more of cobalt naphthenate, cobalt oxalate or cobalt stearate; and the zirconium salt may be one or more of potassium fluorozirconate, zirconium nitrate, and zirconium sulfate. The metal salt compound can react with a zinc coating on a surface of the galvanized steel sheet and hydroxyl groups of the other components in the aqueous inorganic surface treatment agent to form metallic bonds having a high bond energy, thereby forming a thin layer of metal salt conversion film having a dense structure on the surface of the zinc coating. The metal salt conversion film physically prevents direct contact between the steel sheet and a corrosive medium, reduces the possibility of corrosion of the steel sheet, and thus significantly improves the ability of the steel sheet to resist expansion of under-film corrosion. The mass fraction of the metal salt compound in the skin film is 0.1-2.5 parts based on the metal element. If the mass fraction of the rare earth elements is less than 0.1 part, that is, when too little metal salt compound is used, the addition thereof will have no effect, and the corrosion resistance and adhesion of the inorganic skin film may be lowered. If the mass fraction of the rare earth elements is more than 2.5 parts, that is, when too much metal salt-containing compound is contained, the aqueous inorganic surface treatment agent will become less stable, and the quality of the inorganically surface-treated galvanized steel sheet may be affected.

[0090] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the disclosure provides a method of manufacturing an environmentally-friendly, inorganically surface-treated galvanized steel sheet which can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines and imparts excellent red rust resistance and surface electric conductivity to parts. The steel sheet is dried at a temperature of 60-120°C. If the temperature is lower than 60°C, crosslinking reactions in the inorganic skin film will not proceed sufficiently, which may lead to degradation of various properties of the inorganic skin film. If the temperature is higher than 120 °C, the properties of some components in the aqueous inorganic surface treatment agent may change, and the film-forming effect may be affected.

[0091] According to the inorganically surface-treated galvanized steel sheet, the method of preparing the same, and the aqueous inorganic surface treatment agent in the present disclosure,

the aqueous inorganic surface treatment agent in the disclosure is applied on a surface of a galvanized steel sheet, and a dry film thickness thereof is between 0.3 and 1 micrometer. If the thickness is less than 0.3 micrometers, the inorganic skin film will be rather thin, which may lead to degradation of the stamping processability and red rust resistance of the inorganic skin film. If the thickness of the inorganic skin film exceeds 1 micrometer, surface treatment cost per unit area will be increased.

[0092] The method of heating and drying the aqueous inorganic surface treatment agent applied on the surface of the galvanized steel sheet is not particularly limited, and may be hot air heating, induction heating, infrared heating or the like. The size, shape, and the like of the galvanized steel sheet are not particularly limited in the present disclosure. The galvanized steel sheet useful in the present disclosure may be a steel sheet electroplated with pure zinc, a hot-dip pure zinc coated steel sheet, a hot-dip zinc-aluminum coated steel sheet, or an alloyed hot-dip galvanized steel sheet.

[0093] In an open environment, the aqueous inorganic surface treatment agent of the present disclosure can form an inorganic skin film on a surface of a galvanized steel sheet after coating and low temperature rapid curing (less than 100 °C). The galvanized steel sheet coated with the inorganic skin film needs to meet the requirements of rapid deep-drawing processing with progressive dies, such as no die blocking, part appearance, dimensional precision and surface cleanness, and also has excellent red rust resistance of a part, surface electric conductivity and non-sticking of the skin film. Specifically, stamping without die blocking requires that a part can be detached from a die naturally under gravity after rapid stamping (the stamping mold will be damaged if the stamped part is stuck to a die at a certain station of a progressive die stamping process and cannot be detached naturally), so that the naturally detached part can automatically arrive at the next stamping station under the guidance of tapping. As the appearance of a stamped part is concerned, the surface of the stamped part is required to be free of surface defects such as blackening, brightening, scratches, black spots or streaks due to stamping. At the same time, the surface of the stamped part is clean, with no broken skin film or zinc powder adhered to the surface. Red rust resistance of a part is mainly utilized to evaluate the corrosion resistance of the part by observing appearance of red rust on the surface of the stamped part. Excellent red rust resistance ensures that the material can be used nakedly with no need of post-coating. Surface electric conductivity mainly means that the surface of a galvanized steel sheet coated with the inorganic skin film should have certain electric conductivity, thereby ensuring grounding safety and electromagnetic characteristics of the formed part.

[0094] The disclosure has the following beneficial effects in comparison with the prior art:

1) The present disclosure uses a hydrophobic monoorganosilane coupling agent having both a hydrophobic group and a reactive group as a main film-forming component, such that an inorganic skin film further possesses hydrophobicity and low surface energy properties in addition to excellent red rust resistance. Hence, a "non-stick" characteristic of the inorganic skin film is achieved, thereby enabling a part to maintain excellent surface cleanness after rapid deep-drawing processing with progressive dies.

2) The disclosure utilizes a systematic crosslinking agent with a plurality of reactive groups and a water-soluble nanosol, thereby further enhancing the crosslinking degree of the inorganic skin film in three dimensions, so that

the red rust resistance, hardness and scratch resistance of the inorganic skin film are increased greatly.

3)The reactive group in the surface-modified high-density polyethylene particles of the present disclosure can react with various main components in a treatment solution to form covalent bond linkages, which can not only increase the bonding strength between the high-density polyethylene particles and the inorganic skin film, but also confine the high-density polyethylene particles to ensure that the high-density polyethylene particles can be uniformly dispersed in the inorganic skin film, provide excellent anti-wear property across the entire thickness of the inorganic skin film, and improve the stamping processability and scratch resistance of the inorganic skin film.

4) The disclosure uses a graphene oxide with a layered structure comprising 5 or less layers, and grafts an orthosilicate on a surface thereof, so as to improve dispersion stability of the graphene oxide in the aqueous inorganic surface treatment agent system, and enhance chemical bonding reactions of the graphene oxide with the hydrophobic monoorganosilane coupling agent (A), the systematic crosslinking agent (B) and the water-soluble nanosol (C) in the aqueous inorganic surface treatment system. Therefore, the graphene oxide is more likely to form a conductive network in the inorganic skin film, and enhance the effect of the graphene oxide in increasing the surface electric conductivity of the inorganic skin film.

5) The aqueous inorganic surface treatment agent of the present disclosure is chromium-free. So, it is an environmentally-friendly surface treatment agent. After surface treatment of a galvanized steel sheet with the aqueous inorganic surface treatment agent, the galvanized steel sheet can meet the requirements of rapid deep-drawing processing with progressive dies in the field of electrical micro-machines, and impart both excellent red rust resistance and surface electric conductivity to parts.

Detailed Description

[0095] The disclosure will be further illustrated with reference to the following specific Examples. However, the scope of the disclosure is not limited to these Examples. In the following Examples and Comparative Examples, the galvanizing materials, surface cleaning processes and aqueous inorganic surface treatment agents that are used are described as follows.

Examples

(1) Substrates

[0096] The types of substrates used are shown in Table 1. For substrates to be coated with inorganic skin films, mild steel having a thickness of 0.5 mm was used. The substrates in Table 1 were spray cleaned using an aqueous solution of an alkaline degreaser having a mass fraction of 2% (trade name: FC-364S, manufactured by Shanghai Parkerizing). Aqueous solution temperature: 50 °C; spray time: 60 seconds. Then, they were washed with industrial pure water to remove the alkaline component remaining on the surface, and dried with a blower for use.

Table 1: Substrates

No.	Sample Type	Note
S1	Steel sheet electroplated with pure zinc	Coating weight 20/20 g/m^2
S2	Hot-dip pure zinc coated steel sheet	Coating weight 60/60 g/m^2
S3	Hot-dip zinc-aluminum coated steel sheet	Al in the coating: 5wt%; coating weight 60/60 g/m^2
S4	Alloyed hot-dip galvanized steel sheet	Fe in the coating: 10wt%; coating weight 45/45 g/m^2

(2) Aqueous inorganic surface treatment agents

[0097] An aqueous inorganic surface treatment agent for forming an inorganic skin film was formulated by using a hydrophobic monoorganosilane coupling agent (Table 2), a systematic crosslinking agent (Table 3), a water-soluble nanosol (Table 4), and surface-modified high-density polyethylene particles (Table 5), an orthosilicate-modified graphene oxide (Table 6), a water-soluble fluorine-containing compound (Table 7), a water-soluble phosphorus-containing compound (Table 8) and a water-soluble metal salt compound (Table 9) in blending amounts shown in Table 10, and samples were prepared in accordance with the sample types and sample preparation conditions shown in Table 10.

Table 2: Monoorganosilane coupling agents

No.	Monoorganosilane coupling agent
A1	Trimethoxymethylsilane coupling agent
A2	Triethoxymethylsilane coupling agent
A3	Tripropoxymethylsilane coupling agent
A4	Trimethoxyethylsilane coupling agent
A5	Triethoxyethylsilane coupling agent
A6	Trimethoxypropylsilane coupling agent
A7	Triethoxypropylsilane coupling agent
A8	3-aminopropyl-ethoxy-methylsilane coupling agent
A9	N-(2-aminoethyl)-aminopropylmethyldimethoxysilane coupling
A10	1H,1H,2H,2H-perfluorodecyltrimethoxysilane coupling agent
A11	1H,1H,2H,2H-perfluorodecyltriethoxysilane coupling agent
A12	1H,1H,2H,2H-perfluorooctyltrimethoxysilane coupling agent
A13	1H,1H,2H,2H-perfluorooctyltriethoxysilane coupling agent
A14	Methylphenyldiethoxysilane
A15	Fluoromethylethoxydimethoxysilane
A16	Fluoroethyltriethoxysilane
A17	3-fluoropropylmethyldiethoxysilane

Table 3: Systematic crosslinking agents

No.	Systematic crosslinking agent
B1	Ethyl orthosilicate
B2	Propyl orthosilicate
B3	Butyl orthosilicate
B4	Tetraisopropyl orthotitanate
B5	Isopropyl tris(dioctylphosphoryloxy) titanate
B6	Isopropyltris(dodecylbenzenesulfonyl) titanate
B7	1,2-bisethylmethoxysilylethane
B8	Bis-(γ-triethoxysilylpropyl)tetrasulfide
B9	Bis-(γ-trimethoxysilylpropyl)amine

Table 4: Water-soluble nanosols

No.	Water-soluble nanosol
C1	Water-soluble nanosilica sol SNOWTEX-O
C2	Water-soluble nanosilica sol SNOWTEX-40
C3	Water-soluble nanosilica sol LUDOX-AS
C4	Water-soluble nanosilica sol ADELITE AT-20N
C5	Water-soluble titanium dioxide sol EFUT-GY01

(continued)

No.	Water-soluble nanosol
C6	Water-soluble zirconia sol UG-R10W
C7	Water-soluble zirconia sol VK-RJ80
C8	Water-soluble alumina sol EFUAL-Y10C

Table 5: Surface-modified high density polyethylene particles

No.	Surface-modified high density polyethylene particles
D1	Amino-surface-modified high-density polyethylene particles: particle size 0.1 μm
D2	Amino-surface-modified high-density polyethylene particles: particle size 0.3 μm
D3	Amino-surface-modified high-density polyethylene particles: particle size 0.5 μm
D4	Carboxyl-surface-modified high-density polyethylene particles: particle size 0.1 μm
D5	Carboxyl-surface-modified high-density polyethylene particles: particle size 0.3 μm
D6	Carboxyl-surface-modified high-density polyethylene particles: particle size 0.5 μm

Table 6: Orthosilicate-modified graphene oxides

No.	Orthosilicate-modified graphene oxide
E1	Methyl orthosilicate-modified graphene oxide: 1-3 layers, sheet diameter 2-3 microns
E2	Methyl orthosilicate-modified graphene oxide: 4-5 layers, sheet diameter 2-5 microns
E3	Ethyl orthosilicate-modified graphene oxide: 1-3 layers, sheet diameter 2-3 microns
E4	Ethyl orthosilicate-modified graphene oxide: 4-5 layers, sheet diameter 2-5 microns
E5	Propyl orthosilicate-modified graphene oxide: 1-3 layers, sheet diameter 2-3 microns
E6	Propyl orthosilicate-modified graphene oxide: 4-5 layers, sheet diameter 2-5 microns

Table 7: Water-soluble fluorine-containing compounds

No.	Water-soluble fluorine-containing compound
F1	Sodium fluoride
F2	Ammonium fluorotitanate
F3	Sodium fluorosilicate
F4	Hexafluorotitanic acid

Table 8: Water-soluble phosphorus-containing compounds

No.	Water-soluble phosphorus-containing compound
G1	Orthophosphoric acid
G2	Triphosphoric acid
G3	Ammonium phosphate
G4	Polyammonium phosphate

Table 9: Water-soluble metal salts

No.	Water-soluble metal salt
H1	Titanium oxysulfate
H2	Cerium nitrate
H3	Lanthanum nitrate
H4	Ammonium molybdate
H5	Ammonium paratungstate
H6	Cobalt nitrate
H7	Potassium fluorozirconate

Table 10: Aqueous inorganic surface treatment agents

No.	Substrate	Hydrophobic monoorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Ex. 1	S1	A1	50	B1	15	C1	7	D1	15	E2	0.05	F1	1.5	G1	1.5	H1	1.2	0.6	100°C
Ex. 2	S1	A2	50	B1	16	C1	8	D1	15	E2	0.1	F1	1.5	G1	1.7	H1	1.2	0.6	100°C
Ex. 3	S1	A3	50	B1	17	C1	9	D1	15	E2	0.15	F1	1.5	G1	2	H1	1.2	0.6	100°C
Ex. 4	S1	A4	50	B1	18	C1	10	D1	15	E2	0.2	F1	1.5	G1	2.2	H1	1.2	0.6	100°C
Ex. 5	S1	A5	50	B1	15	C1	11	D1	15	E2	0.25	F1	1.5	G1	2.5	H1	1.2	0.6	100°C
Ex. 6	S1	A6	50	B1	16	C1	12	D2	15	E2	0.3	F1	1.5	G1	2.7	H1	1.2	0.6	100°C
Ex. 7	S1	A7	50	B1	17	C1	7	D2	15	E2	0.35	F1	2.5	G1	3	H1	1.2	0.6	100°C
Ex. 8	S1	A8	50	B1	18	C1	8	D2	15	E2	0.4	F1	2.5	G1	3.2	H1	1.2	0.6	100°C
Ex. 9	S1	A9	50	B1	19	C1	9	D2	15	E2	0.45	F1	2.5	G1	3.5	H1	1.2	0.6	100°C
Ex. 10	S1	A10	50	B1	20	C1	10	D2	15	E2	0.5	F1	2.5	G1	3.2	H1	1.2	0.6	100°C
Ex. 11	S1	A11	50	B1	21	C1	11	D3	15	E5	0.4	F1	2.5	G1	3	H1	1.2	0.6	100°C
Ex. 12	S1	A12	50	B1	22	C1	12	D3	15	E5	0.35	F1	2.5	G1	2.7	H1	1.2	0.6	100°C
Ex. 13	S1	A13	50	B1	23	C1	7	D3	15	E5	0.3	F1	3.5	G1	3.5	H1	1.2	0.6	100°C
Ex. 14	S1	A14	50	B1	24	C1	8	D3	15	E5	0.25	F1	3.5	G1	2.2	H1	1.2	0.6	100°C
Ex. 15	S1	A15	50	B1	25	C1	9	D3	15	E5	0.2	F1	3.5	G1	2	H1	1.2	0.6	100°C
Ex. 16	S1	A16	50	B1	26	C1	10	D4	15	E5	0.15	F1	3.5	G1	1.7	H1	1.2	0.6	100°C
Ex. 17	S1	A17	50	B1	27	C1	11	D4	15	E5	0.1	F1	3.5	G1	1.5	H1	1.2	0.6	100°C
Ex. 18	S1	A2	40	B1	15	C1	15	D4	13	E5	0.1	F1	3.5	G2	1	H1	1	0.3	60°C
Ex. 19	S1	A2	50	B4	20	C5	8	D4	17	E5	0.3	F2	1	G2	2	H2	2	0.6	70°C
Ex. 20	S1	A2	60	B9	25	C7	5	D4	21	E5	0.5	F3	1.5	G2	3	H3	1.5	1.0	80°C
Ex. 21	S1	A5	40	B1	15	C1	15	D5	13	E1	0.1	F1	2	G2	1	H4	1	0.3	90°C

(continued)

No.	Substrate	Hydrophobic mono-organosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Ex. 22	S1	A5	50	B4	20	C5	8	D5	17	E1	0.3	F2	2.5	G2	2	H5	2	0.6	100°C
Ex. 23	S1	A5	60	B9	25	C7	5	D5	21	E1	0.5	F3	3	G2	3	H6	1.5	1.0	120°C
Ex. 24	S1	A8	40	B1	15	C1	15	D5	13	E1	0.1	F1	3.5	G2	1	H7	1	0.3	60°C
Ex. 25	S1	A8	50	B4	20	C5	8	D5	17	E1	0.3	F2	4	G2	2	H1	2	0.6	70°C
Ex. 26	S1	A8	60	B9	25	C7	5	D6	21	E2	0.5	F3	1	G2	3	H2	1.5	1.0	80°C
Ex. 27	S1	A9	40	B1	15	C1	15	D6	13	E2	0.1	F1	1.5	G2	1	H3	1	0.3	90°C
Ex. 28	S1	A9	50	B4	20	C5	8	D6	17	E2	0.3	F2	2	G2	2	H4	2	0.6	100°C
Ex. 29	S1	A9	60	B9	25	C7	5	D6	21	E2	0.5	F3	2.5	G2	3	H5	1.5	1.0	120°C
Ex. 30	S1	A10	40	B1	15	C1	15	D6	13	E2	0.1	F1	3	G2	1	H6	1	0.3	60°C
Ex. 31	S1	A10	50	B4	20	C5	8	D1	17	E4	0.3	F2	3.5	G2	2	H7	2	0.6	70°C
Ex. 32	S1	A10	60	B9	25	C7	5	D1	21	E4	0.5	F3	4	G2	3	H1	1.5	1.0	80°C
Ex. 33	S1	A11	40	B1	15	C1	15	D1	13	E4	0.1	F1	1	G2	1	H2	1	0.3	90°C
Ex. 34	S1	A11	50	B4	20	C5	8	D1	17	E4	0.3	F2	1.3	G2	2	H3	2	0.6	100°C
Ex. 35	S1	A11	60	B9	25	C7	5	D1	21	E4	0.5	F3	1.5	G2	3	H4	1.5	1.0	120°C
Ex. 36	S1	A13	40	B1	15	C1	15	D1	13	E6	0.1	F1	1.7	G2	1	H5	1	0.3	60°C
Ex. 37	S1	A13	50	B4	20	C5	8	D1	17	E6	0.3	F2	1.9	G2	2	H6	2	0.6	70°C
Ex. 38	S1	A13	60	B9	25	C7	5	D1	21	E6	0.5	F3	2.2	G2	3	H7	1.5	1.0	80°C
Ex. 39	S1	A15	40	B1	15	C1	15	D1	13	E6	0.1	F1	2.5	G2	1	H1	1	0.3	90°C
Ex. 40	S1	A15	50	B4	20	C5	8	D1	17	E6	0.3	F2	2.7	G2	2	H2	2	0.6	100°C
Ex.41	S1	A15	60	B9	25	C7	5	D4	21	E3	0.5	F3	3	G3	3	H3	1.5	1.0	120°C
Ex. 42	S1	A16	40	B1	15	C1	15	D4	13	E3	0.1	F1	3.2	G3	1	H4	1	0.3	100°C

(continued)

No.	Substrate	Hydrophobic monoorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Ex. 43	S1	A16	50	B4	20	C5	8	D4	17	E3	0.3	F2	3.5	G3	2	H5	2	0.6	100°C
Ex. 44	S1	A16	60	B9	25	C7	5	D4	21	E3	0.5	F3	3.7	G3	3	H6	1.5	1.0	100°C
Ex. 45	S1	A2	40	B1	30	C2	15	D4	10	E3	0.05	F2	1	G3	0.5	H7	0.1	0.6	100°C
Ex. 46	S1	A2	43	B1	28	C2	14	D4	12	E3	0.07	F2	4	G3	0.8	H2	0.4	0.6	100°C
Ex. 47	S1	A2	45	B1	26	C2	13	D4	14	E3	0.1	F2	1.4	G3	1.1	H2	0.7	0.6	100°C
Ex. 48	S1	A2	47	B1	24	C2	12	D4	16	E3	0.13	F2	3.7	G3	1.5	H2	1	0.6	100°C
Ex. 49	S1	A2	50	B1	22	C2	11	D4	18	E3	0.15	F2	1.8	G3	1.8	H2	1.3	0.6	100°C
Ex. 50	S1	A2	52	B7	20	C4	10	D4	19	E3	0.17	F2	3.3	G3	2.1	H3	1.6	0.6	100°C
Ex. 51	S1	A2	55	B7	17	C4	9	D2	20	E3	0.2	F2	2.2	G3	2.4	H3	1.9	0.6	100°C
Ex. 52	S1	A2	56	B7	15	C4	8	D2	21	E3	0.23	F2	3	G3	2.7	H3	2.1	0.6	100°C
Ex. 53	S1	A2	58	B7	13	C4	7	D2	23	E3	0.25	F2	2.5	G3	3	H3	2.3	0.6	100°C
Ex. 54	S1	A2	60	B7	10	C4	6	D2	25	E3	0.27	F2	2.7	G3	3.5	H3	2.5	0.6	100°C
Ex. 55	S1	A11	41	B4	11	C3	5	D2	25	E3	0.15	F2	3.8	G3	1	H4	0.1	0.6	100°C
Ex. 56	S1	A11	43	B4	12	C3	6	D2	24	E3	0.18	F2	2.7	G3	1.3	H4	0.4	0.6	100°C
Ex. 57	S1	A11	44	B4	14	C3	7	D2	22	E3	0.23	F2	1.9	G3	1.7	H4	0.7	0.6	100°C
Ex. 58	S1	A11	46	B4	16	C3	8	D2	20	E3	0.27	F2	3.5	G3	2	H4	1	0.6	100°C
Ex. 59	S1	A11	48	B4	18	C3	9	D2	18	E3	0.3	F2	2.4	G3	2.3	H4	1.3	0.6	100°C
Ex. 60	S1	A11	52	B9	20	C6	10	D2	17	E3	0.32	F2	1.6	G3	2.7	H5	1.6	0.6	100°C
Ex. 61	S1	A11	54	B9	22	C6	11	D5	16	E3	0.35	F2	3.3	G1	3	H5	1.9	0.6	100°C
Ex. 62	S1	A11	56	B9	24	C6	12	D5	14	E3	0.37	F2	2.3	G2	3.3	H5	2.1	0.6	100°C
Ex. 63	S1	A11	58	B9	26	C6	13	D5	12	E3	0.4	F2	1.4	G3	3.6	H5	2.3	0.6	100°C

(continued)

No.	Substrate	Hydrophobic mo-noorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Ex. 64	S1	A11	60	B9	28	C6	14	D5	10	E3	0.44	F2	3.1	G4	4	H5	2.5	0.6	100°C
Ex. 65	S1	A16	40	B2	21	C8	15	D5	18	E3	0.3	F4	2.1	G1	3.7	H6	0.1	0.6	100°C
Ex. 66	S1	A16	43	B2	23	C8	13	D5	17	E3	0.25	F4	1.1	G2	3.4	H6	0.4	0.6	100°C
Ex. 67	S1	A16	45	B2	25	C8	12	D5	16	E3	0.2	F4	2.1	G3	3.1	H6	0.7	0.6	100C
Ex. 68	S1	A16	47	B2	27	C8	11	D5	15	E3	0.17	F4	2.2	G4	1.8	H6	1	0.6	100°C
Ex. 69	S1	A16	50	B2	29	C8	10	D5	14	E3	0.15	F4	2.5	G1	1.5	H6	1.3	0.6	100°C
Ex. 70	S1	A16	52	B5	19	C1	9	D5	19	E3	0.14	F4	3.1	G2	1.2	H7	1.6	0.6	100°C
Ex. 71	S1	A16	55	B5	18	C1	8	D1	20	E4	0.12	F4	2.7	G3	2.9	H7	1.9	0.6	100°C
Ex. 72	S1	A16	56	B5	16	C1	7	D1	21	E4	0.1	F4	2.7	G4	2.6	H7	2.1	0.6	100°C
Ex. 73	S1	A16	58	B5	14	C1	6	D1	22	E4	0.07	F4	2.7	G1	2.3	H7	2.3	0.6	100°C
Ex. 74	S1	A16	60	B5	12	C1	5	D1	23	E4	0.05	F4	2.7	G2	2	H7	2.5	0.6	100°C
Ex. 75	S1	A17	40	B6	14	C1	7	D1	10	E4	0.1	F1	2.7	G3	1.5	H7	1.4	0.6	100°C
Ex. 76	S1	A17	45	B6	16	C1	7.5	D1	11	E4	0.2	F1	2.7	G4	1.9	H2	1.1	0.6	100°C
Ex. 77	S1	A17	50	B6	18	C1	8	D1	12	E4	0.3	F1	2.7	G1	2.9	H2	1.1	0.6	100°C
Ex. 78	S1	A17	55	B6	20	C1	8.5	D1	13	E4	0.4	F1	2.7	G2	2.4	H2	1.1	0.6	100°C
Ex. 79	S1	A17	60	B6	22	Cl	9	D1	14	E4	0.5	F1	2.7	G3	3.3	H2	1.1	0.6	100°C
Ex. 80	S1	A8	45	B4	19	C1	9.5	D1	15	E4	0.15	F1	2.7	G4	4	H2	1.1	0.6	100°C
Ex. 81	S1	A9	47	B4	21	C1	10	D1	16	E4	0.25	F1	2.7	G1	3.5	H2	1.1	0.6	100°C
Ex. 82	S1	A12	49	B4	23	C1	7.5	D1	17	E4	0.35	F1	2.7	G2	3.1	H2	1.1	0.6	100°C
Ex. 83	S1	A14	50	B4	25	C1	8	D1	20	E4	0.45	F1	2.7	G3	2.8	H2	1.1	0.6	100°C
Ex. 84	S1	A15	52	B4	27	C1	8.5	D1	21	E4	0.4	F1	2.7	G4	2.5	H2	1.1	0.6	100°C

(continued)

No.	Substrate	Hydrophobic mononoorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Ex. 85	S1	A16	55	B4	29	C1	9	D1	23	E4	0.35	F1	2.7	G1	1.5	H2	1.1	0.6	100°C
Ex. 86	S2	A2	47	B1	19	C1	9.5	D4	25	E4	0.3	F1	2.7	G2	2.2	H2	1.1	0.6	100°C
Ex. 87	S2	A8	49	B1	17	C1	10	D4	20	E4	0.25	F1	2.7	G3	3.2	H2	1.1	0.6	100°C
Ex. 88	S2	A10	50	B1	15	C1	7.5	D4	19	E4	0.2	F1	2.7	G4	1.2	H2	1.1	0.6	100°C
Ex. 89	S2	A11	52	B1	13	C1	8	D4	18	E4	0.15	F1	2.7	G1	1.6	H2	1.1	0.6	100°C
Ex. 90	S2	A15	55	B1	11	C1	8.5	D4	17	E4	0.1	F1	2.7	G2	3.6	H2	1.1	0.6	100°C
Ex. 91	S3	A2	47	B1	18	C1	9	D4	16	E4	0.15	F1	2.7	G3	2.6	H2	1.1	0.6	100°C
Ex. 92	S3	A8	49	B1	20	C1	9.5	D4	15	E4	0.2	F1	2.7	G4	1.8	H2	1.1	0.6	100°C
Ex. 93	S3	A10	50	B1	22	C1	10	D4	14	E4	0.25	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 94	S3	A11	52	B1	24	C1	7.5	D4	13	E4	0.3	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 95	S3	A15	55	B1	26	C1	8	D4	12	E4	0.35	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 96	S4	A2	47	B1	17	C1	8.5	D4	11	E4	0.4	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 97	S4	A8	49	B1	16	C1	9	D4	10	E4	0.45	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 98	S4	A10	50	B1	15	C1	9.5	D4	15	E4	0.5	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 99	S4	A11	52	B1	14	C1	10	D4	20	E4	0.4	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Ex. 100	S4	A15	55	B1	13	C1	7.5	D4	25	E4	0.3	F1	2.7	G1	2.2	H2	1.1	0.6	100°C
Comp. Ex. 1	S1	A2	40	-	-	C1	6	D1	15	E3	0.1	F1	1.5	G1	3.5	H1	1.5	0.4	100'C
Comp. Ex. 2	S1	A8	45	B1	16	-	-	D1	20	E3	0.2	F1	2	G1	3	H1	1.5	0.4	100°C

(continued)

No.	Substrate	Hydrophobic monoorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Comp. Ex. 3	S1	A10	50	B3	18	C2	8	-	-	E3	0.3	F1	2.5	G1	2.5	H1	1.5	0.5	100°C
Comp. Ex. 4	S1	A11	55	B4	20	C3	10	D1	25	-	-	F1	3	G1	2	H1	1.5	0.5	100°C
Comp. Ex. 5	S1	A15	60	B7	22	C4	12	D1	10	E3	0.4	-	-	G1	1.5	H1	1.5	0.6	100°C
Comp. Ex. 6	S1	A2	40	-	-	C5	6	D5	17	E4	0.4	F2	1.5	G3	1	H2	2	0.6	100°C
Comp. Ex. 7	S1	A8	45	B1	16	-	-	D5	18	E4	0.3	F2	2	G3	2	H2	2	0.7	100°C
Comp. Ex. 8	S1	A10	50	B3	18	C6	8	-	-	E4	0.2	F2	2.5	G3	3	H2	2	0.7	100°C
Comp. Ex. 9	S1	A11	55	B4	20	C7	10	D5	21	-	-	F2	3	G3	4	H2	2	0.8	100°C
Comp. Ex. 10	S1	A15	60	B7	22	C8	12	D5	22	E4	0.1	F2	3.5	-	-	H2	2	0.8	100°C
Comp. Ex. 11	S1	A2	40	B1	25	C1	15	D1	15	E1	0.2	F1	2.5	G1	2	H1	1.2	0.2	100°C
Comp. Ex. 12	S1	A8	45	B1	22	C1	12	D2	17	E2	0.2	F2	2.5	G2	2	H2	1.2	0.5	50°C
Comp. Ex. 13	S1	A10	50	B3	19	C2	9	D3	19	E3	0.2	F3	2.5	G3	2	H3	1.2	1.5	100°C
Comp. Ex. 14	S1	A11	55	B4	17	C3	7	D4	21	E4	0.2	F4	2.5	G1	2	H4	1.2	0.7	150°C

(continued)

No.	Substrate	Hydrophobic monoorganosilane coupling agent (A)		Systematic cross-linking agent (B)		Water-soluble na- nosol (C)		Surface-modified high density polyethylene particles (D)		Orthosilicate-modified graphene oxide (E)		Water-soluble fluorine-containing compound (F)		Water-soluble phosphorus-containing compound (G)		Water-soluble metal salt (H)		Coating weight g/m^2	PMT °C
		Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight	Type	Parts by weight		Parts by weight		
Comp. Ex. 15	S1	A15	60	B7	15	C4	5	D5	23	E5	0.2	F1	2.5	G3	2	H5	1.2	1.2	100°C

(3) Evaluation tests

[0098] After coated with the aqueous inorganic surface treatment agents for the test sample sheets in the above Examples 1-100 and Comparative Examples 1-15, the test sample sheets were sampled and tested according to the following testing methods, and the tested data for evaluating the various properties thereof were obtained and listed in Table 11. The tests for evaluating the various property parameters thereof are described as follows:

1) Corrosion resistance of flat sheets:
A salt spray test was performed on a flat sheet. The test standard was ASTMB117, and the test time was 120 hours. The evaluation criteria were:

◎ : White rust area ratio was less than 5%
○ : White rust area ratio was greater than 5% and less than 10%
Δ : White rust area ratio was greater than 10% and less than 50%
× : White rust area ratio was greater than 50%

2) Corrosion resistance after forming:
8 mm cupping was performed using an Erichson cupping instrument, and a salt spray test was performed on the cupped portion. The test standard was ASTM B117, and the test time was 72 hours. The evaluation criteria were:

◎ : White rust area ratio on the cupped portion was less than 5%
○ : White rust area ratio on the cupped portion was greater than 5% and less than 10%
Δ : White rust area ratio on the cupped portion was greater than 10% and less than 50%
× : White rust area ratio on the cupped portion was greater than 50%

3) Resistance to red rust corrosion:
A salt spray test was performed on a flat sheet. The test standard was ASTMB 117, and the time when red rust began to appear was recorded. The evaluation criteria were:

◎ : The time when red rust began to appear on S1 steel sheets was more than 240 hours; the time when red rust began to appear on S2-S4 steel sheets was more than 288 hours
○ : The time when red rust began to appear on S1 steel sheets was more than 196 hours but less than 240 hours; the time when red rust began to appear on S2-S4 steel sheets was more than 240 hours but less than 288 hours
Δ : The time when red rust began to appear on S1 steel sheets was more than 168 hours but less than 196 hours; the time when red rust began to appear on S2-S4 steel sheets was more than 196 hours but less than 240 hours
× : The time when red rust began to appear on S1 steel sheets was less than 168 hours; the time when red rust began to appear on S2-S4 steel sheets was less than 196 hours

4) Stamping formability:
A drawbead method was used to prepare samples. Experimental conditions: fixed under-bead pressure 3KN, indenter diameter 9.6mm, drawing speed 200mm/min, evaluation criteria:

◎ : The appearance had no change.
○ : The appearance had a small amount of black spots.
Δ : The appearance had a relatively large amount of obvious black streaks.
× : The appearance was completely blackened.

5) "Non-stick" property of skin film surfaces:
A drawbead method was used to prepare samples. Experimental conditions: fixed under-bead pressure 7 KN, indenter diameter 9.6 mm, and drawing speed 200 mm/min. After the drawing test was completed, the surfaces of the sample sheets were blown with a hair dryer for 5 seconds, and then the cleanness of the surfaces of the sample sheets was observed. Evaluation criteria:

◎ : No skin film chippings or zinc powder adhered to the surface
○ : A trace amount of skin film chippings and zinc powder adhered to the surface
Δ : Some skin film chippings and zinc powder adhered to the surface

× : A large amount of skin film chippings and zinc powder adhered to the surface

6) Wear resistance:
A rubber abrasion method was utilized with a load of 500g, a stroke distance of 20mm and a speed of 300mm/min. The abrasion was repeated for 50 times. Evaluation criteria:

◎ : No change in the skin film
○ : A small amount of scratches on the skin film
Δ : A plurality of scratches on the skin film
× : The skin film fell off completely

7) Surface electric conductivity:
Surface resistance values of the upper and lower surfaces were measured using a four-needle method, wherein 10 points were measured on the upper and lower surfaces. An average surface resistance value at the 20 points was calculated. Evaluation criteria:

◎ : The average surface resistance value was less than 0.1 milliohms.
○ : The average surface resistance value was greater than 0.1 milliohms and less than 0.5 milliohms.
Δ : The average surface resistance value was greater than 0.5 milliohms and less than 1 milliohm.
× : The average surface resistance value was greater than 1 milliohm.

8) Coatability:
The surface-treated galvanized steel sheets were coated under the following conditions, and then the coating adhesion test was carried out. The test conditions were as follows:

Ink (Japan Seiko Ink), 14# bar coating, baking conditions: baking at 120 °C for 20 minutes;
After application of the above two coatings, an art knife was used to scribe 100 small lattices in a surface of a coating film, wherein the lattice size was 1 mm^2, and the depth should reach the surface of the steel sheet by cutting through the paint film layer. After peeling off with a glass cloth tape, the number of the residual lattices of the paint film was counted. A larger number of residual lattices indicated better coatability of the steel sheet for the ink.

Table 11: Various properties of the test sample sheets

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Ex. 1	○	○	○	◎	○	◎	○	◎
Ex. 2	○	○	○	◎	○	◎	○	◎
Ex. 3	○	○	○	◎	○	◎	○	◎
Ex. 4	◎	◎	◎	◎	○	◎	◎	◎
Ex. 5	◎	◎	◎	◎	◎	◎	◎	◎
Ex. 6	◎	◎	◎	◎	○	◎	◎	◎
Ex. 7	○	○	○	◎	○	◎	◎	◎
Ex. 8	○	○	○	◎	○	◎	◎	◎
Ex. 9	○	○	○	◎	○	◎	◎	◎
Ex. 10	◎	◎	◎	◎	◎	○	◎	○
Ex. 11	◎	◎	◎	◎	◎	○	◎	○
Ex. 12	◎	◎	◎	◎	◎	○	◎	○
Ex. 13	◎	◎	◎	◎	◎	○	◎	○
Ex. 14	◎	◎	◎	◎	◎	○	◎	◎
Ex. 15	◎	◎	◎	◎	◎	○	◎	◎
Ex. 16	◎	◎	◎	◎	◎	○	○	◎
Ex. 17	◎	◎	◎	◎	◎	○	○	◎
Ex. 18	○	○	○	◎	○	◎	○	◎
Ex. 19	◎	◎	◎	◎	○	◎	◎	◎
Ex. 20	◎	◎	◎	○	○	◎	◎	◎
Ex. 21	○	○	○	◎	○	◎	○	◎
Ex. 22	◎	◎	◎	◎	○	◎	◎	◎
Ex. 23	◎	◎	◎	○	○	◎	◎	◎
Ex. 24	○	○	○	◎	○	◎	○	◎

(continued)

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Ex. 25	◎	◎	◎	◎	○	◎	◎	◎
Ex. 26	◎	◎	◎	○	○	◎	◎	◎
Ex. 27	○	○	○	◎	○	◎	○	◎
Ex. 28	◎	◎	◎	◎	○	◎	◎	◎
Ex. 29	◎	◎	◎	○	○	◎	◎	◎
Ex. 30	○	○	○	◎	◎	◎	○	○
Ex. 31	◎	◎	◎	◎	◎	◎	◎	△
Ex. 32	◎	◎	◎	○	◎	○	◎	○
Ex. 33	○	○	○	◎	◎	◎	○	○
Ex. 34	◎	◎	◎	◎	◎	◎	◎	△
Ex. 35	◎	◎	◎	○	◎	○	◎	○
Ex. 36	○	○	○	◎	◎	◎	○	○
Ex. 37	◎	◎	◎	◎	◎	◎	◎	△
Ex. 38	◎	◎	◎	○	◎	○	◎	○
Ex. 39	○	○	○	◎	◎	◎	○	○
Ex. 40	◎	◎	◎	◎	◎	◎	◎	△
Ex. 41	◎	◎	◎	○	◎	○	◎	○
Ex. 42	○	○	○	◎	◎	◎	○	○
Ex. 43	◎	◎	◎	◎	◎	◎	◎	△
Ex. 44	◎	◎	◎	○	◎	○	◎	○
Ex. 45	◎	◎	◎	○	○	◎	△	◎
Ex. 46	◎	◎	◎	○	○	◎	△	◎
Ex. 47	◎	◎	◎	◎	○	◎	○	◎
Ex. 48	◎	◎	◎	◎	○	◎	○	◎

(continued)

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Ex. 49	◎	◎	◎	◎	○	◎	○	◎
Ex. 50	◎	◎	◎	◎	○	◎	○	◎
Ex. 51	◎	◎	◎	◎	○	◎	◎	◎
Ex. 52	○	○	○	◎	○	◎	◎	◎
Ex. 53	○	○	○	◎	○	◎	◎	◎
Ex. 54	○	○	○	◎	○	◎	◎	◎
Ex. 55	○	○	○	◎	◎	◎	○	Δ
Ex. 56	○	○	○	◎	◎	◎	○	Δ
Ex. 57	◎	◎	◎	◎	◎	◎	◎	○
Ex. 58	◎	◎	◎	◎	◎	◎	◎	○
Ex. 59	◎	◎	◎	◎	◎	○	◎	○
Ex. 60	◎	◎	◎	◎	◎	○	◎	○
Ex. 61	◎	◎	◎	◎	◎	○	◎	○
Ex. 62	◎	◎	◎	◎	◎	○	◎	○
Ex. 63	◎	◎	◎	○	◎	○	◎	○
Ex. 64	◎	◎	◎	○	◎	○	◎	○
Ex. 65	◎	◎	◎	◎	◎	○	◎	Δ
Ex. 66	◎	◎	◎	◎	◎	○	◎	Δ
Ex. 67	◎	◎	◎	◎	◎	○	◎	○
Ex. 68	◎	◎	◎	◎	◎	○	○	○
Ex. 69	◎	◎	◎	◎	◎	○	○	○
Ex. 70	◎	◎	◎	◎	◎	○	○	○
Ex. 71	◎	◎	◎	◎	◎	◎	○	○
Ex. 72	◎	◎	◎	◎	◎	◎	○	○

(continued)

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Ex. 73	○	○	○	◎	◎	◎	Δ	○
Ex. 74	○	○	○	◎	◎	◎	Δ	○
Ex. 75	○	○	○	○	◎	○	○	○
Ex. 76	◎	◎	◎	○	◎	○	◎	○
Ex. 77	◎	◎	◎	○	◎	○	◎	○
Ex. 78	◎	◎	◎	◎	◎	○	◎	○
Ex. 79	◎	◎	◎	◎	◎	○	◎	○
Ex. 80	◎	◎	◎	◎	○	◎	◎	◎
Ex. 81	◎	◎	◎	◎	○	◎	◎	◎
Ex. 82	◎	◎	◎	◎	◎	○	◎	○
Ex. 83	◎	◎	◎	◎	◎	◎	◎	○
Ex. 84	◎	◎	◎	◎	◎	◎	◎	○
Ex. 85	◎	◎	◎	◎	○	◎	◎	Δ
Ex. 86	◎	◎	◎	◎	○	◎	◎	◎
Ex. 87	○	○	○	◎	◎	◎	◎	◎
Ex. 88	○	○	○	◎	◎	○	◎	○
Ex. 89	○	○	○	◎	◎	○	○	○
Ex. 90	○	○	○	◎	○	○	○	○
Ex. 91	◎	◎	◎	◎	○	◎	◎	◎
Ex. 92	◎	◎	◎	◎	◎	◎	◎	◎
Ex. 93	◎	◎	◎	◎	◎	○	◎	○
Ex. 94	◎	◎	◎	◎	◎	○	◎	○
Ex. 95	◎	◎	◎	○	◎	○	◎	○
Ex. 96	◎	◎	◎	○	○	◎	◎	◎

(continued)

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Ex. 97	◎	◎	◎	○	○	◎	◎	◎
Ex. 98	◎	◎	◎	◎	◎	◎	◎	○
Ex. 99	◎	◎	◎	◎	◎	◎	◎	Δ
Ex. 100	◎	◎	◎	◎	◎	◎	◎	Δ
Comp. Ex. 1	Δ	Δ	Δ	◎	○	◎	○	◎
Comp. Ex. 2	Δ	Δ	Δ	◎	○	◎	◎	○
Comp. Ex. 3	◎	◎	◎	×	◎	×	◎	◎
Comp. Ex. 4	○	○	○	○	◎	○	×	Δ
Comp. Ex. 5	○	○	Δ	○	◎	○	◎	◎
Comp. Ex. 6	Δ	Δ	Δ	○	○	○	◎	◎
Comp. Ex. 7	○	○	Δ	○	○	Δ	○	○
Comp. Ex. 8	◎	◎	◎	×	○	×	◎	○
Comp. Ex. 9	Δ	Δ	Δ	◎	◎	◎	×	○
Comp. Ex. 10	Δ	Δ	Δ	◎	◎	◎	○	○
Comp. Ex. 11	Δ	Δ	×	×	○	×	◎	◎

(continued)

No.	Corrosion resistance of flat sheet	Corrosion resistance after forming	Red rust resistance	Stamping formability:	"Non-stick" property of surface	Wear resistance:	Surface electric conductivity:	Coatability
Comp. Ex. 12	Δ	Δ	×	×	○	×	○	Δ
Comp. Ex. 13	◎	◎	◎	○	◎	○	×	Δ
Comp. Ex. 14	Δ	Δ	Δ	Δ	◎	Δ	Δ	Δ
Comp. Ex. 15	○	○	◎	○	◎	◎	×	Δ

[0099] Table 11 lists the tested various property parameters of the test sample sheets coated with the aqueous inorganic surface treatment agents in Examples 1-100 and Comparative Examples 1-15.

[0100] As can be seen from Table 11, after the test sample sheets coated with the aqueous inorganic surface treatment agents in Example 1-100 were tested, an overwhelming majority of the Examples each showed an evaluation result of "◎" or "○", except for a small number of Examples that showed "Δ" in a certain evaluation result, indicating that the galvanized steel sheets coated with the aqueous inorganic surface treatment agent of the present disclosure all have excellent red rust resistance, surface electric conductivity, surface lubricating property and resistance to blackening caused by stamping, and can meet the requirements of rapid deep-drawing processing with progressive dies and bare service.

[0101] As can be seen from Tables 10 and 11 in combination, in contrast to Example 1-100, the corrosion resistance of the inorganic skin films in Comparative Example 1, Comparative Example 2, Comparative Example 6 and Comparative Example 7 was poor due to the low crosslinking density of the inorganic skin films caused by the absence of the systematic crosslinking agent (C) or the water-soluble nanosol (C) in the aqueous inorganic surface treatment agents.

[0102] The aqueous inorganic surface treatment agents in Comparative Example 3 and Comparative Example 8 did not contain surface-modified high-density polyethylene particles (D). Therefore, the stamping formability and wear resistance of the inorganic skin films of the galvanized steel sheets coated with these aqueous inorganic surface treatment agents were poor.

[0103] The aqueous inorganic surface treatment agents in Comparative Example 4 and Comparative Example 9 did not contain an orthosilicate-modified graphene oxide (E), and a conductive network could not be formed in the inorganic skin films. Therefore, the electric conductivity of the galvanized steel sheets coated with these aqueous inorganic surface treatment agents was poor. In addition, since the inorganic skin film thicknesses of Comparative Example 13 and Comparative Example 15 were relatively large, the surface electric conductivity was also poor.

[0104] The aqueous inorganic surface treatment agents in Comparative Example 5 and Comparative Example 10 did not contain the water-soluble fluorine-containing compound (F) or the water-soluble phosphorus-containing compound (G), so that the corrosion resistance of the inorganic skin films was poor.

[0105] The thickness of the inorganic skin film in Comparative Example 11 was small, resulting in poor overall performance. In Comparative Example 12, the baking and curing temperature was low, resulting in an inorganic skin film that was not completely cured, so that the inorganic skin film was inferior in overall performance.

[0106] It is to be noted that there are listed above only specific examples of the invention. Obviously, the present disclosure is not limited to the above examples. Instead, there exist many similar variations. All variations derived directly or envisioned from the present disclosure by those skilled in the art should be all included in the protection scope of the present disclosure.

Claims

1. An inorganically surface-treated galvanized steel sheet, wherein the inorganically surface-treated galvanized steel sheet is a galvanized steel sheet having a surface coated with a single-layer inorganic skin film having a thickness of 0.3-1.0 μm, wherein the inorganic skin film comprises:

    A) one or more hydrophobic monoorganosilane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
    wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
    B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
    wherein the systematic crosslinking agent is one or more of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
    C) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
    wherein the water-soluble nanosol has a mass fraction of 20-30%;
    D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
    E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
    wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%.

2. The inorganically surface-treated galvanized steel sheet according to claim 1, wherein the inorganic skin film further comprises:

F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic skin film;
G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;
H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

3. The inorganically surface-treated galvanized steel sheet according to claim 1, wherein the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) is one or two selected from the group consisting of $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-C_3H_7$ (propyl), $-C_6H_5$ (phenyl), $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl), $-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) and $-C_9F_{19}$ (perfluorononyl).

4. The inorganically surface-treated galvanized steel sheet according to claim 1, wherein the reactive group in the hydrophobic monoorganosilane coupling agent is one to three selected from the group consisting of -OCH3 (methoxy), -OC2H5 (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido and 2,3-epoxypropoxy.

5. The inorganically surface-treated galvanized steel sheet according to claim 1, wherein a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four;
the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

6. A method of preparing the inorganically surface-treated galvanized steel sheet of any one of claims 1-5, wherein forming an aqueous inorganic surface treatment agent by dissolving or dispersing components of the aqueous inorganic surface treatment agent in water, applying the aqueous inorganic surface treatment agent on a surface of a galvanized steel sheet by one-pass roll coating, and drying at 60-100 °C, thereby providing an inorganic skin film having a dry film thickness of 0.3-1.0 microns,
wherein the inorganic skin film comprises:

A) one or more hydrophobic monoorganic silane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
wherein the systematic crosslinking agent is one or more selected from an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
C) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
wherein the water-soluble nanosol has a mass fraction of 20-30%;
D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%.

7. The method of preparing the inorganically surface-treated galvanized steel sheet according to claim 6, wherein the inorganic skin film further comprises:

F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic skin film;
G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;
H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

8. The method of preparing the inorganically surface-treated galvanized steel sheet according to claim 6, preferably the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) is one or two of $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-C_3H_7$ (propyl), $-C_6H_5$ (phenyl), $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl),

$-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) or $-C_9F_{19}$ (perfluorononyl); the reactive group in the hydrophobic monoorganosilane coupling agent is at most three of $-OCH_3$ (methoxy), $-OC_2H_5$ (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido or 2,3-epoxypropoxy; a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four; the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

9. The method of preparing the inorganically surface-treated galvanized steel sheet according to claim 6, wherein the systematic cross-linking agent (B) is one or more of an orthosilicate having 4 reactive groups, a titanate having 4 reactive groups or a diorganosilane coupling agent having 6 reactive groups and a bridging structure; the reactive group in the orthosilicate is any one of a methoxy group, an ethoxy group, a propoxy group or a butoxy group; the reactive group in the titanate is one or more of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group or a n-butyl ester group; the bridging structure of the diorganosilane coupling agent is consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups; the reactive group of the diorganosilane coupling agent is any one of a methoxy group, an ethoxy group or a propoxy group.

10. An aqueous inorganic surface treatment agent for surface treatment of a galvanized steel sheet by coating a surface of the galvanized steel sheet to form an inorganic skin film by the method of any one of claims 6-9, wherein total solids in an aqueous solution thereof comprise the following components:

A) one or more hydrophobic monoorganosilane coupling agents in an amount of 40-60 parts by weight of the inorganic skin film;
wherein the hydrophobic monoorganosilane coupling agent comprises X hydrophobic groups (X is 1 or 2) and 4-X reactive groups;
B) a systematic crosslinking agent in an amount of 10-30 parts by weight of the inorganic skin film;
wherein the systematic crosslinking agent is one or more of an orthosilicate, a titanate or a diorganosilane coupling agent having a bridging structure;
D) a water-soluble nanosol in an amount of 5-15 parts by weight of the inorganic skin film;
wherein the water-soluble nanosol has a mass fraction of 20-30%;
D) surface-modified high-density polyethylene particles in an amount of 10-25 parts by weight of the inorganic skin film;
E) an orthosilicate-modified graphene oxide, wherein the graphene oxide is 0.05-0.5 parts by weight of the inorganic skin film;
wherein the orthosilicate-modified graphene oxide is a dark brown n-propanol suspension, wherein the orthosilicate-modified graphene oxide has a mass fraction of 1-5%;
F) a water-soluble fluorine-containing compound, wherein fluorine element is 1-4 parts by weight of the inorganic skin film;
G) a water-soluble phosphorus-containing compound, wherein phosphorus element is 0.5-4 parts by weight of the inorganic skin film;
H) a water-soluble metal salt compound, wherein metal element is 0.1-2.5 parts by weight of the inorganic skin film.

11. The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel plate according to claim 10, wherein the hydrophobic group in the hydrophobic monoorganosilane coupling agent (A) is one or two of $-CH_3$ (methyl), $-C_2H_5$ (ethyl), $-C_3H_7$ (propyl), $-C_6H_5$ (phenyl), $-CF_3$ (perfluoromethyl), $-C_2F_5$ (perfluoroethyl), $-C_3F_7$ (perfluoropropyl), $-C_5F_{11}$ (perfluoropentyl), $-C_7F_{15}$ (perfluoroheptyl) or $-C_9F_{19}$ (perfluorononyl); the reactive group in the hydrophobic monoorganosilane coupling agent is at most three of -OCH3 (methoxy), $-OC_2H_5$ (ethoxy), vinyl, propenyl, epoxy, amino, hydroxyl, carboxyl, amido or 2,3-epoxypropoxy; a sum of the number of the hydrophobic groups and the number of the reactive groups in the hydrophobic monoorganosilane coupling agent is equal to four; the hydrophobic monoorganosilane coupling agent is 40-60 parts by weight, preferably 45-55 parts by weight of the inorganic skin film.

12. The aqueous inorganic surface treatment agent for surface treatment of a galvanized steel plate according to claim 10, wherein the systematic cross-linking agent (B) is one or more selected from the group consisting of an orthosilicate having 4 reactive groups, a titanate having 4 reactive groups and a diorganosilane coupling agent having 6 reactive groups and a bridging structure; the reactive group in the orthosilicate is any one selected from the group consisting of a methoxy group, an ethoxy group, a propoxy group and a butoxy group; the reactive group in the titanate is one or more selected from the group consisting of an isopropyl ester group, a phosphoryloxy group, a benzenesulfonyloxy group and a n-butyl ester group; the bridging structure of the diorganosilane coupling agent is consisting of 2-4 methylene groups, amino groups or 2-4 mercapto groups; the reactive group of the diorganosilane coupling agent is any one selected from the group consisting of a methoxy group, an ethoxy group and a propoxy group.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/CN2017/098430

A. CLASSIFICATION OF SUBJECT MATTER

C23C 22/36 (2006.01) i; C23C 22/44 (2006.01) i; C23C 22/73 (2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C 22/-

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

CNPAT, CNKI, EPODOC, WPI: 镀锌钢，硅烷，纳米，溶胶，聚乙烯，氧化石墨烯，galvanized steel, silicane, na-no, sol, polyethylene, graphene oxide

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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A	CN 1360644 A (UNIVERSITY OF CINCINNATI), 24 July 2002 (24.07.2002), entire document	1-12
A	CN 101899657 A (SHANGHAI FENGYE SURFACE TREATMENT AGENT CO., LTD.), 01 December 2010 (01.12.2010), entire document	1-12
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A	CN 104629603 A (UNIVERSITY OF SHANGHAI FOR SCIENCE AND TECHNOLOGY), 20 May 2015 (20.05.2015), entire document	1-12

☐ Further documents are listed in the continuation of Box C. ☒ See patent family annex.

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Date of the actual completion of the international search 17 November 2017	Date of mailing of the international search report 28 November 2017
Name and mailing address of the ISA State Intellectual Property Office of the P. R. China No. 6, Xitucheng Road, Jimenqiao Haidian District, Beijing 100088, China Facsimile No. (86-10) 62019451	Authorized officer LI, Yakun Telephone No. (86-10) 62084093

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Information on patent family members

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