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SURFACE TREATED GALVANIZED STEEL SHEET
EXCELLENT IN RESISTANCE TO TAPE PEELING,
MANUFACTURING METHOD THEREOF
AND SURFACE TREATING AGENT

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention concerns a galvanized steel sheet applied with surface treatment and, more in particular, it relates to a galvanized steel sheet formed with a surface treatment layer excellent in the resistance to tape peeling and further excellent in the resistance to tape peeling after alkali degreasing, a manufacturing method thereof and a surface treating agent used for the surface treatment.

2. Description of the Prior Art

As steel sheets used for home electric appliances, building materials and automobiles, galvanized steel sheets have been used generally with a viewpoint of corrosion resistance. However, since zinc-type plating when used alone is insufficient, for attaining corrosion resistance (white rust resistance) and difficult to ensure adhesion with coating materials in a case of use as primer coating, a phosphate treatment or chromate treatment has been applied as a countermeasure. While the phosphate treatment applied as the primer treatment can improve the adhesion with the coating layer considerably, it lacks in versatility since the effect of suppressing the white rust is poor only by the



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phosphate treatment.

Meanwhile, while the chromate treatment has excellent for the effect of suppressing white rust, adhesion with the coating layer is insufficient in the state as it is treated. Then, in order to improve the adhesion and also provide functions such as high corrosion resistance, finger print resistance and lubricity, multi-function products applied with thin film coatings of about 1 μm on chromate treated layers have been developed and used generally mainly in home electric appliances manufacturers.

However, since the chromate treatment uses noxious hexa-valent chromium, it involves a problem of causing public pollution and the chromate treatment has tended to be avoided for circumvented along with the increasing demand for environmental protection. Then, a great deal of surface treatments not using the chromate treatment (non-chromate method) have been proposed and put to practical use.

For example, JP-A No. 8-325760 discloses a surface treating agent for use in zinc-containing metal plated steel sheet using a mixed composition of an aqueous resin and a polyhydric phenol carboxylic acid and a surface treated steel sheet of excellent corrosion resistance formed by roll coating the treating agent to metal plated surfaces. However, since the zinc plated layer is coated directly with an organic layer while omitting the chromate treatment in this technique, the adhesion of the coating layer is not sufficient. Further, while alkali degreasing is conducted

for surface treated galvanized steel sheets for cleaning the surface by removing oils coated the surface during pressing or the like intending for improvement of the adhesion of the coating layer, it involves a problem of deteriorating the corrosion resistance after the alkali degreasing.

As an improvement for such problems, JP-A No. 2000-144448 discloses an organic material coated steel sheet formed by coating an organic layer containing ion exchanged silica on a galvanized steel sheet directly or by way of a primer treatment layer such as lithium silicate or phosphate treated layer thereby improving the corrosion resistance, the corrosion resistance after alkali degreasing, and the adhesion of the coating layer.

Further, JP-A No. 2000-144444 discloses a surface treated steel sheet of excellent corrosion resistance formed with a chemical conversion coating layer of a predetermined thickness, obtained by applying a treatment to a galvanized steel sheet with an acidic treating solution containing silica or silica sol, a phosphoric acid compound, an oxide or a hydroxide of a specified metal at a preferred ratio and then drying the same by heating. However, since pin-holes, etc. are liable to be formed in the layer in a state coated with an inorganic treating agent such as silica sol, phosphate or metal hydroxide and then dried and left as it is, a corrosive liquid might intrude through the pin-holes upon alkali degreasing or the like making it insufficient for corrosion resistance. In view of the above, in this patent

document, an organic resin layer or an organic composite silicate layer is formed on the chemical conversion treated layer to improve the corrosion resistance after alkali degreasing or adhesion of the coating layer.

Meanwhile, JP-A No. 2000-129460 discloses a surface treated steel sheet improved with corrosion resistance and adhesion of the coating layer by forming zinc-based plating as a first layer, an amorphous coating layer formed by coating and drying an aqueous mixed solution of a poly-valent metal primary phosphate and a metal oxide sol as a second layer, and an organic coating layer as a third layer thereby forming a multilayered structure.

Further, JP-A No. 2001-11645 discloses an organic material-coated steel sheet improved with the corrosion resistance, the corrosion resistance after alkali degreasing, and the adhesion of the coating layer by: forming a composite oxide layer comprising fine SiO_2 particles and a phosphate compound of a predetermined thickness as a first layer on the surface of a galvanized steel sheet; and forming thereon, an organic material layer of a predetermined thickness comprising an organic polymer having OH groups or COOH groups as a base resin.

Further, JP-A No. 2003-293151 discloses a non-chromate type surface treated galvanized steel sheet formed with a surface modified layer containing Al, Si, and P each at a predetermined ratio, showing corrosion resistance comparable with that of chromate treated steel sheets.

As described above, various improved techniques for several subjects have been proposed in the non-chromate treatment and various improvements for the performance have been tried. However, according to the recent experience of the present inventors, it has become clear that even the galvanized steel sheets applied with the improved non-chromate treatment involve a serious problem that the resistance to tape peeling is not sufficient.

That is, the surface treated steel sheets are shipped in the state coiled from hoops and users use them as sheared sheets after uncoiling them. In this case, remaining coils after use are sometimes stored by provisionally securing the end of the coil with an adhesive tape. Further, sheared sheets are fabricated into AV product cases or parts by way of steps such as punching, oil coating, pressing and alkali degreasing. In this case, adhesive labels indicating part numbers, sizes, grades, etc. are sometimes appended on the surface of cases or parts for provisional securing. The tape peeling is a phenomenon that the topcoat layer on the galvanized surface is peeled together with the tape from the plated surface when the user peels the adhesive tape or adhesive label. This is a critical issue in view of the quality of the surface treated steel sheet and might cause serious defects of the products.

The tape peeling scarcely occurred in the conventional chromate treated type surface treated steel sheets applied with the thin film coating at the upper layer and,

accordingly, the subject of "improvement in the tape peeling" for preventing tape peeling has not been recognized so far.

By the way, in the course of the study for the improvement of the non-chromate type galvanized steel sheet, conducted by the present inventors, it has become clear that the resistance to the tape peeling is good or poor depending on the case of the non-chromate surface treated steel sheets. Particularly, it has become clear that the tape peeling is liable to occur in a case of storing for a long time while appending the adhesive tape or label on the surface or in a case of storing high temperature and high humidity conditions assuming marine transportation. Then, it has become recognized that "resistance to tape peeling" is one of extremely important product properties.

However, since the problem of "tape peeling" per se is scarcely recognized at present, it cannot be aware of the subject of "improvement of the resistance to tape peeling". Also for the countermeasure, the techniques already disclosed for the non-chromate treated type plated steel sheets described above are still insufficient and, as a matter of fact, no tangible method has yet been developed.

SUMMARY OF THE INVENTION

Under the circumstances, the present invention is directed to non-chromate surface treated galvanized steel sheets and aims at providing a surface treated galvanized steel sheet excellent in the resistances to tape peeling and

to tape peeling after alkali degreasing, a manufacturing method thereof, and a surface treating agent useful for the manufacturing process.

An aspect of the invention solving the problems above resides in a surface treated galvanized steel sheet having at least a surface modified layer and a topcoat layer formed on a zinc-based plated layer in a galvanized steel sheet, wherein the surface modified layer contains from 1 to 30 mg/m² of SiO₂, being converted as Si, from 0.5 to 15 mg/m² of P and from 0.4 to 10 mg/m² of Al.

Another aspect of the invention resides in an SiO₂-containing phosphate type surface treating agent which is useful for obtaining the galvanized steel sheet having the excellent resistance to tape peeling, wherein the concentration of the solid content is from 0.01 to 14.5% (mass% here and hereinafter) and the amount and the compositional ratio (mass ratio) for each of Si, P and Al contained in the treating agent can satisfy the following conditions:

Si: 0.002 - 4.5%

P : 0.0005 - 1.5%

Al: 0.0001 - 0.5%

$1.5 \leq \text{Si/P} \leq 60$, $4.5 \leq \text{Si/Al} \leq 230$

An aspect of the invention resides in a method of manufacturing a surface treated galvanized steel sheet which comprises forming a surface treating agent layer on the surface of a galvanized steel sheet using the surface

treating agent which satisfies the conditions described above, applying water rinsing thereby removing excess P and/or Al from the surface treating agent layer followed by drying to form the surface modified layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Fig. 1 is an FT-IR spectrum for surface modified layer of No. 38 described later.

Fig. 2 is an FT-IR spectrum for surface modified layer of No. 52 described later.

Fig. 3 shows an FT-IR spectrum for sodium polyacrylate.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

The surface treated galvanized steel sheet according to the invention is based on the premise of having a surface modified layer formed by a non-chromate treating agent. The galvanized steel sheet to which the invention is applied can include steel sheets plated only with zinc, as well as all other zinc alloy plated steel sheets such as zinc-Ni, zinc-Fe, zinc-Al plated steel sheets. Further, also for the plating method, any of molten plating method, electric plating method of vapor deposition plating method can be adapted.

The invention has a most prominent feature in incorporating from 1 to 30 mg/m² of SiO₂ being converted as Si, from 0.5 to 15 mg/m² of P and from 0.4 to 10 mg/m² of Al in the surface modified layer, as a means for improving "resistance to tape peeling" which is a new subject to be

solved raised at first by the present inventors in the field of non-chromate galvanized steel sheets.

"Resistance to tape peeling" in the invention means such a peeling resistance of not causing peeling of the surface treatment layer together with an adhesive label or adhesive tape in a case of appending and leaving them to the surface treated galvanized steel sheet and then peeling the same. The degree of the resistance to tape peeling is different depending on the kind of the adhesive tape used for the tape peeling test, particularly, the adhesion or the kind of the solvent and plasticizer contained therein.

It is considered that the greatest reason for the peeling of the topcoat resin layer or the surface modified layer by the tape peeling is attributable to the diffusion and penetration of the solvent or the plasticizer contained in the adhesive through the surface modified layer and the topcoat layer formed thereon as far as the surface of the zinc-based plated layer and accumulation to the bonding boundary which lowers the bonding strength, and that the resistance to tape peeling may vary considerably depending on the kind and the content of the solvent or the plasticizer contained in the adhesive tape.

However, while the kind and the blending amount of the solvent or the plasticizer blended as the adhesive to usual adhesive tapes may somewhat vary, it is considered that there is no significant difference in the rate of diffusion or penetration thereof particularly to the SiO_2 content. Then

the resistance to tape peeling is evaluated in the invention when selecting and using, as typical examples, a filament tape "part number #9510" manufactured by Surion Tech Co.", and " [Cellophane tape] manufactured by Nichiban Co." as prima-facie evaluation criterion as shown in examples to the described later.

Silica (SiO_2) as the main ingredient in the surface modified layer according to the invention is, for example, silicon oxide incorporated therein being derived from colloidal silica or silicate. Since the silica described above is an inorganic material by nature and has good affinity with the zinc-based plated layer, when it is formed as an underlayer for the topcoat layer, it provides an effect of enhancing the peeling resistant property between the zinc-based plated layer and the topcoat layer.

As has been described above, one of the causes of tape peeling is considered to be lowering of the bonding strength at the interface or boundary between each of the layers caused by the movement of diffusive ingredients such as solvent and plasticizer contained in the adhesive of the adhesive tape or the like. However, it is considered that silica contained as the main ingredient in the surface modified layer of the invention provides excellent barrier effect against the solvent and the plasticizer that diffuse and penetrate from the topcoat layer and provides a function of inhibiting intrusion to the zinc plated surface, or inhibiting diffusion at the topcoat layer or the surface

modified layer boundary. Accordingly, when a surface treatment layer incorporated with an appropriate amount of silica is formed, the resistance to tape peeling is improved outstandingly. Then, as a result of the study made by the present inventors for the quantitative relation to effectively provide the effect of silica for improving the resistance to tape peeling, it was confirmed that the excellent resistance to tape peeling can be provided by controlling the silica content in the surface treatment layer within a range from 1 to 30 mg/m² (2.14 to 64.3 mg/m² of SiO₂) being converted as Si.

In a case where the silica content is less than 1 mg/m² being converted as Si, the function as the barrier layer described above is insufficient and it is difficult to provide a satisfactory resistance to tape peeling. Accordingly, the silica content in the surface modified layer has to be 1 mg/m² or more being converted as Si. The lower limit of the silica content is, preferably, 2 mg/m² and, more preferable 2.5 mg/m².

Then, as the silica-content increases, the function as the barrier layer is enhanced but as the silica content increases excessively, the resistance to tape peeling rather tends to lower. That is, it is considered that silica in the surface treatment layer is present as agglomerates of fine particles in a state where the amount thereof is small but the fine particles may become a multi-layered lamination state as the amount of silica increases. Since the bonding

strength is not always strong between each of the fine silica particle layers in the multi-layered lamination state, the tape peeling force exerts in the direction of peeling the fine silica particle layers in the multi-layered lamination state thereby causing interlayer peeling for the fine silica particle layers. For suppressing the interlayer peeling caused by shear fracture of the surface modified layer per se, as much as possible, the silica content in the surface modified layer should be retained to 30 mg/m² or less being converted as Si. In a case where the silica content in the surface modified layer exceeds the upper limit value, the resistance to tape peeling apparently shows a lowering tendency. Further, excessive increase in the silica content in the surface modified layer is also wasteful with an economical point of view, the upper limit is preferably 15 mg/m², more preferably, 10 mg/m² and, most preferably 8 mg/m² being converted as Si in view of the above.

In the silica containing surface modified layer of the invention, P and Al are also contained. In preparing the surface modified layer, it is preferred to etch the surface of the zinc-based plated layer and deposit fine silica particles derived from colloidal silica or the like on the surface of the properly roughened plated layer. The etching ingredient usable herein is, for example, nitric acid, sulfuric acid, hydrochloric acid and phosphoric acid. It is particularly preferred to use, as the surface modifying agent, an acidic aqueous solution comprising an aluminum salt, for

example, phosphate, hydrogen phosphate, phosphite or hydrogen phosphite (hereinafter simply referred to as aluminum phosphate compound) as an etching ingredient to which an appropriate amount of colloidal silica is dispersed. Therefore, P and Al are contained in the resultant surface modified layer.

When the acidic aqueous solution containing colloidal silica and the aluminum phosphate compound is used as the surface treating agent, the surface of the zinc-based plated layer is etched by the acidic aqueous solution, during which a reaction layer (surface modified layer) mainly comprising AlPO_4 or $\text{Al}_2(\text{HPO}_4)_3$, which is less soluble (less soluble to water or an aqueous alkaline solution) among aluminum phosphate, is formed to the surface of the zinc-based plated layer. Aluminum phosphate and fine silica particles are composited and integrated when the fine silica particles are deposited and taken into the reaction layer. Further, a dense reaction layer is formed with respect to the zinc-based plated layer roughened by etching and bonding with the topcoat layer formed on the reaction layer is also dense and strong, so that the resistance to tape peeling is improved remarkably. Further, as will be described later, when an aqueous solution of an organic resin is incorporated to the acidic aqueous solution, the deposited state of fine silica particles in the obtained surface modifying agent can be made stronger.

Since the reaction layer in which aluminum phosphate

mainly comprising less soluble AlPO_4 or $\text{Al}_3(\text{HPO}_4)_3$ and fine silica particles are composited and integrated has more excellent alkali resistance than the surface modified layer obtained by using, for example, nitric acid as an etching agent, it can provides excellent performance also in the resistance to tape peeling after alkali degreasing. However, in a case of forming the silica-containing surface modified layer by using the aluminum phosphate compound described above as the etching ingredient, it has been found that the alkali resistance or the resistance to the tape peeling after alkali degreasing is different depending on the content of each of P and Al contained in the surface modified layer. Particularly, it has been recognized that the resistance to tape peeling after alkali degreasing tends to be lowered as the thickness of the surface modified layer increases and the amount of aluminum phosphate in the layer increases.

In a case where the surface modified layer is thin, since the surface modified layer and the zinc-based plated layer are close to each other, zinc is leached by the etching of the zinc-based plated layer and H^+ in the treating agent is reduced into H_2 gas, so that pH near the surface modified layer close to the zinc-based plated layer increases and tends to become alkaline. In an atmosphere where pH increases greatly, a great deal of AlPO_4 or $\text{Al}_2(\text{HPO}_4)_3$ are formed to form a reaction layer in which the less soluble aluminum phosphate and fine silica particles are composited and integrated to remarkably improve the resistance to tape

peeling and the resistance to tape peeling after alkali degreasing. However, as the thickness of the surface modified layer increases, since the surface of the surface modified layer under formation and the zinc-based plated layer recede from each other, the effect of pH along with leaching of zinc is less exerted and the atmosphere near the surface of the surface modified layer becomes acidic inherent to the surface treating agent, so that $\text{Al}_2(\text{HPO}_4)_3$, more soluble to water (more liable to suffer from alkali attack) tends to be formed more than less soluble AlPO_4 or $\text{Al}_2(\text{HPO}_4)_3$. It is considered that when the water soluble $\text{Al}_2(\text{HPO}_4)_3$ is present in a greater amount to the uppermost surface of the surface modified layer, since the water soluble ingredient is leached from the surface modified layer upon undergoing alkali attack, and the alkali resistance of the surface modifying agent is deteriorated and the resistance to tape peeling after alkali degreasing is lowered.

However, in the invention, stable excellent resistance to tape peeling and resistance to tape peeling after alkali degreasing can be obtained by defining the thickness of the surface modified layer to a predetermined range and defining the amount for each of P and Al in the layer to a predetermined range. Accordingly, it is necessary in the invention to control the content of P in a range from 0.5 to 15 mg/m^2 and the content of Al in a range of from 4.0 to 10 mg/m^2 in the surface modified layer. In a case where the content of P is less than 0.5 mg/m^2 or the content of Al is

less than 0.4 mg/m^2 , etching effect is insufficient and a dense reaction layer is less formed and, in addition, the effect of improving the resistance to tape peeling by promotion of the deposition of fine silica particles can not sometime be provided effectively. A more preferred lower limit for the content of P is 0.6 mg/m^2 and a more preferred lower limit for the content of Al is 0.5 mg/m^2 . On the contrary, when the content of P or the content of Al increases excessively, $\text{Al}(\text{H}_2\text{PO}_4)_3$ of insufficient alkali resistance is incorporated in the surface modified layer as described above and tends to be leached from the surface modified layer undergoing alkali attack. A preferred upper limit for the content of P is 9 mg/m^2 and, further preferred upper limit thereof is 7.2 mg/m^2 , and a most preferred upper limit is 5 mg/m^2 . A preferred upper limit for the content of Al is 8 mg/m^2 , a more preferred upper limit thereof is 6.3 mg/m^2 and the most preferred upper limit thereof is 4.4 mg/m^2 .

Further, in a case where the content for each of Si, P and Al contained in the surface modified layer can satisfy the following relations (1) and (2):

$$0.5 \leq \text{Si/P} \leq 20 \quad (1)$$

$$0.7 \leq \text{P/Al} \leq 6 \quad (2),$$

further excellent resistance to tape peeling and resistance to tape peeling after alkali degreasing can be ensured.

When Si/P is less than 0.5, since the ratio of SiO_2 in the surface modified layer tends to be insufficient relatively, the resistance to tape peeling tends to be

lowered. On the other hand, when the ratio exceeds 20, since the amount of aluminum phosphate is insufficient compared with the content of silica, the effect obtained by the less soluble AlPO_4 or $\text{Al}_2(\text{HPO}_4)_3$ becomes less effective. With the view point described above, a more preferred lower limit for the ratio of Si/P in the surface modified layer is 1 and a more preferred upper limit is 15 and a further preferred upper limit is 10.

In a case where P/Al in the relation (2) is less than 0.7, the resistance to tape peeling tends to be lowered due to etching insufficiency derived from the insufficiency of the phosphoric acid. On the other hand, when the ratio increases excessively exceeding 6, the amount of less soluble AlPO_4 or $\text{Al}_2(\text{HPO}_4)_3$ formed after the etching treatment decreases making it insufficient for the formation of the dense reaction layer and the effect for improving the resistance to tape peeling after alkali degreasing is reduced. Accordingly, it is possible to promote the formation of less soluble aluminum phosphate while ensuring an appropriate etching effect, thereby forming a sufficient amount of the reaction layer by controlling P/Al to 0.7 or more and 6 or less. A more preferred lower limit for P/Al is 1 and a more preferred upper limit thereof is 4.

Si/P or P/Al can be controlled by controlling the content of silica, silicate, phosphoric acid ingredient and the Al ingredient in the surface treating agent, or conducting water rinsing upon forming the surface modified

layer and rinsing and removing excess phosphoric acid ingredient or Al ingredient as to be described later. Further, the amount for Si, P and Al in the surface modified layer can be recognized respectively, for example, by fluoro X-ray analysis.

When P and Al are incorporated each by the predetermined amount in addition to incorporation of silica into the surface modified layer and, further, the ratio for the content of each of Si, P and Al is controlled to an appropriate range, the resultant surface modified layer is made more dense with no pin-hole defects or the like and exhibits an outstanding performance for the resistance to tape peeling under dry condition, as well as the resistance to tape peeling after alkali degreasing.

In the invention, an organic resin may be further incorporated in the surface modified layer. This is because the organic resin has an effect of causing the fine silica particles to deposit firmly in the surface modified layer upon forming the surface modified layer, and further improving the resistance to tape peeling and, further, the resistance to tape peeling after alkali decreasing. The organic resin has no particular restriction and can include, for example, acrylic resin, melamine resin, phenolic resin, epoxy resin, urethane resin, polyester resin, alkyd resin, and polyolefin resin which may be used alone or two or more of them may be used in combination.

Among the organic resins described above, a water

soluble organic resin is used preferably and an organic resin constituted with an organic acid is used particularly preferably. As the organic resin constituted with the organic acid, a poly-(meth)acrylic acid is suitable and those in which acid groups are partially or entirely neutralized with a base can be used. As described above, when the surface modified layer is formed, it is preferred to etch the zinc plated layer by using an aqueous acidic solution. Since the organic resin comprising the organic acid as the constituent ingredient is almost water soluble and the aqueous solution containing such an organic resin is acidic, it is excellent in the stability and the workability when blending to the acidic aqueous solution. The average molecular weight of the poly (meth)acrylic acid when used is preferably 2,000 or more, more preferably, 10,000 or more, further preferably, 100,000 or more. The base in a case of using the salt of the organic resin constituted with the organic acid can include, for example, ammonia or a hydroxide of an alkali metal such as sodium hydroxide or potassium hydroxide.

When the surface modified layer is observed, for example, by FT-IR, since peaks of FT-IR derived from the structure of the organic resin (ester bond, carboxyl group, ketone, amino group, hydroxyl group, and carbon-hydrogen bond, etc.) appear in the spectra, the existence of the organic resin in the surface modified layer can be recognized. Then, in the invention, the organic resin is preferably present

such that the absorbance of FT-IR derived from the structure of the organic resin is from 0.1 to 15. The absorbance of FT-IR indicates the content of the organic resin in the surface modified layer, and the resistance to tape peeling and the resistance to tape peeling after alkali degreasing can be improved by controlling the absorbance of FT-IR to a determined range.

The invention also includes the surface treating agent used for forming the surface modified layer. The surface treating agent is a phosphate type treating agent in the form of a solution containing fine particles of silica such as colloidal silica and it is preferred to control such that the solid concentration is from 0.01 to 14.5 mass% and the amount (mass%, hereinafter simply referred to as %) and the compositional ratio (mass ratio) for the amount of Si, P and Al contained in the treating agent can satisfy the following conditions:

Si: 0.002 - 4.5%

P : 0.0005 - 1.5%

Al: 0.0001 - 0.5%

$1.5 \leq \text{Si/P} \leq 60$, $4.5 \leq \text{Si/Al} \leq 230$

When the solid concentration of the surface treating agent is less than 0.01%, it is difficult to form a surface modified layer of a satisfactory thickness by the treatment for once and treatment for multiple times is necessary making it non-practical. On the contrary, if the concentration is excessively high exceeding 14.5%, solids tend to be formed,

for example, at the gas/liquid boundary in the treating agent, tending to cause product defects such as press flaws or seeds. In view of the above, the solid concentration is preferably 0.05% or more and 10% or less and, more preferably, 0.1% or more and 0.5% or less.

Further, in a case when the Si concentration in the surface treating agent is less than 0.002%, the content of silica as the main component of the barrier layer in the surface modified layer tends become insufficient, thereby making it difficult to obtain a satisfactory resistance to tape peeling. On the other hand, when Si concentration exceeds 4.5%, the content for the ratio of silica in the surface treating agent increases excessively making the content of silica in the surface modified layer excessive, by which the resistance to tape peeling rather tends to lower. In view of the tendency described above, the lower limit for Si concentration in the surface treating agent is more preferably 0.01% and, further preferably, 0.03%. Further, the upper limit is more preferably 4% and, further preferably, 3%. Further, the Si concentration in the surface treating agent can be controlled mainly in accordance with the blending amount of SiO₂ blended as the colloidal silica and further, blending amount of silicate or the like.

The colloidal silica that can be blended as a silica source in the surface treating agent can include preferably, for example, "O", "OS", "OL", "OXS", and "OUP" in "SNOWTEX" series (colloidal silica, manufactured by Nissan Chemical

Industry Co.) and the silicate is preferably Na_4SiO_4 or Na_2SiO_3 .

On the other hand, the concentration of P in the surface treating agent depends on the amount of the phosphate compound blended as phosphate, hydrogen phosphate, phosphite or hydrogen phosphite which is an important factor for dominating mainly the etching effect and the formation of the dense reaction layer. In a case where the concentration of P is excessively low, since the etching effect is insufficient and, formation of the dense aluminum phosphate type reaction layer described above is also insufficient to lower the effect of promoting the deposition of fine silica particles as well, the adhesion or the alkali resistance of the surface modified layer tends to become insufficient. Accordingly, the concentration of P in the treating agent is preferably 0.0005% or more. A more preferred lower limit is 0.001% and a further preferred lower limit is 0.01%.

However, when the concentration of P in the surface treating agent excessively increases, since the appearance of the products tend to become unfavorable and it also causes a problem in view of actual operation that the tank for the surface treating agent tends to be corroded easily, it is preferably 1.5% or less. A more preferred upper limit is 1% and a further preferred upper limit is 0.5%.

Further, the concentration of Al in the surface treating agent mainly depends on the amount of aluminum salt such as of phosphoric acid and, further, on the amount of hydroxides such as of Al which may be added optionally.

Particularly, it constitutes a source for forming the less soluble aluminum phosphate formed as a dense reaction layer in the etching step by phosphoric acid or the like to provide an important function in enhancing the adhesion or the alkali resistance of the surface modifying agent by promoting deposition of silica. For providing the function described above effectively, it is desirable that the concentration of Al in the treating agent is at least 0.0001% or more, preferably, 0.0005% and, further preferably, to 0.001% or more. However, when the concentration of Al is excessively high, since the solids tend to be formed at the gas-liquid boundary, etc. in the processing solution, thereby tending to cause product defects such as press flaws or seeds, it is decreased to 0.5% or less. A more preferred upper limit is 0.4% and, a further preferred upper limit is 0.2%.

Si/P and Si/Al in the surface treating agent gives an effect on the formation amount of the dense reaction layer mainly comprising aluminum phosphate formed at the initial stage of the surface treatment and on the deposition amount of silica as described above. In a case where the content of P and the content of Al are insufficient to the Si content, etching is insufficient relatively making it insufficient for the denseness or the formation amount of the reaction layer mainly comprising aluminum phosphate, as well as the effect of promoting the deposition of silica is also lowered. Therefore, the resistance to tape peeling and resistance to tape peeling after alkali degreasing become insufficient. On

the contrary, when the content of P and the content of Al increase excessively relative to the Si content, the silica concentration in the reaction layer described above tends to be insufficient and it may possibly result in an insufficient resistance to tape peeling.

With the viewpoints described above, Si/P contained in the surface treating agent is preferably 1.5 or more and 60 or less, more preferably, 1.8 or more and 20 or less. Si/Al is preferably 4.5 or more and 230 or less and, more preferably, 6 or more 100 or less.

There is no particular restriction on the method of controlling the content of Si, P and Al in the surface treating agent for the base layer has no particular restriction. Since the Si content depends on the content of silica or silicate in the surface treating agent, the content of P depends on the content of phosphoric acid or phosphate in the treating agent, and the content of Al depends on the content of the Al phosphate or hydroxide in the processing agent respectively, the contents for the respective elements can be controlled by properly controlling the contents of the ingredients described above in the surface treating agent.

Further, in a case where the surface treating agent contains the organic resin described above, the addition concentration of the organic resin in the surface treating agent is preferably from 0.01 to 3 g/l as the solid content of the organic resin. When the addition concentration is less than 0.01 g/l, the addition effect of the organic resin

is scarcely obtained and, on the other hand, when the addition concentration exceeds 3 g/l, the resistance to tape peeling after alkali degreasing might be deteriorated.

In the invention, a particularly preferred surface treating agent is an aqueous acidic solution containing colloidal silica, an aluminum salt compound such as aluminum phosphate, hydrogen phosphate, phosphite, or hydrogen phosphite, and an organic resin (preferably poly(meth)acrylic acid or salt thereof). When the surface treating agent is used, the zinc-based plated layer at the surface of a steel sheet is etched under an aqueous acidic solution, during which a dense reaction layer mainly comprising a less soluble aluminum phosphate is formed on the surface of the zinc-based plated layer, silica is deposited to the reaction layer and incorporated reliably being coupled with the effect of the organic resin. Accordingly, These effects form a dense reaction layer relative to zinc leached by etching, to obtain a surface modified layer showing excellent resistance to tape peeling and resistance to tape peeling after alkali degreasing.

More specifically, the surface treating agent is preferably an aqueous acidic solution containing the solid content for each of the ingredients as 0.002 to 5.0% (more preferably, 0.01 to 1.0)% of Al phosphate (or hydrogen phosphate, phosphite, hydrogen phosphite), 0.004 to 10% (preferably, 0.05 to 3)% of colloidal silica; and containing 0.1 to 3 g/l of an organic resin, in a pH range from 1.5 to

4.0. The composition of the surface modified layer can be controlled to the range described above by defining the composition of the surface treating agent to the range described above and, preferably, by applying water rinsing or the like.

As the method of treating the galvanized steel sheet by the surface treating agent can include any of known coating methods, for example, dipping, spray coating or roll coating can be used. In the dipping method, the steel sheet is preferably dipped for about 0.1 to 10 sec. The spray coating method is a more preferred method for promoting the reaction with zinc-based plated layer, and a preferred spray pressure is within a range from 20 to 500 kPa (about 0.2 to 5.0 kgf/cm²) and a preferred spray time is within a range from 0.1 to 10 sec.

After surface treating the galvanized steel sheet with the surface treating agent described above to form a surface treating agent layer (layer to form a surface modified layer after water rinsing - drying), soluble ingredients are preferably removed by appropriate water rinsing. Then, the surface modified layer is obtained by drying under heating, for example, at about 30 to 150°C to remove the water content. The water rinsing in this step is an important processing step, particularly, for improving the alkali resistance and, accordingly, the resistance to tape peeling after alkali degreasing for the surface modified layer obtained finally. That is, according to the various experiments conducted by

the present inventors, it has been confirmed that the content of P or the content of Al in the surface modified layer is sometimes excessive in a case where the layer is dried as it is after treatment with the surface treating agent described above or in a case of a baked surface modified layer, that such content exceeds the preferred content for P of 0.5 to 15 mg/m² or the preferred content for Al of 0.4 to 10 mg/m² described above in the surface modified layer and that it becomes difficult to ensure the resistance to tape peeling after alkali degreasing.

That is, as has been described previously for the prior art, the method of improving the corrosion resistance after alkali degreasing of the galvanized steel sheet by treating the surface of the galvanized steel sheet with a treating agent containing the fine silica particles and the aluminum phosphate has been known and it has also been confirmed that the surface treatment was effective as the primer treatment for improving the adhesion of the organic topcoat layer. However, it has been confirmed by the present inventors that the surface modified layers formed by the surface treating agents containing the fine silica particles and the aluminum phosphate (also including those disclosed in the patent literatures described above) contain a considerably large amount of aluminum phosphate ingredient in the surface modified layer and it sometimes amounts to about 30 mg/m² or more being converted as P and about 15 mg/m² or more being converted as Al. Then, the present inventors have found out

that when the content of P or Al is large, it gives no small undesired effect particularly on the resistance to peeling after alkali degreasing and that it is convenient and desirable to apply water rinsing after the surface treatment for the base layer thereby previously leaching and removing water soluble ingredients among aluminum phosphates (mainly $\text{Al}(\text{H}_2\text{PO}_4)_3$) contained in the surface treating layer in order to decrease the contents for P and Al to the preferred range described above thereby forming a less soluble (excellent in alkali resistance) dense surface modified layer.

As the water rinsing method, dipping or spraying may be considered, and the condition for the water rinsing may be changed properly depending on the content of the water soluble ingredients in the aluminum phosphate ingredients contained in the surface treating agent layer. It is preferred to control the water rinsing time to about 0.5 to 15 sec in the case of dipping, and control the water rinsing time to about 0.5 to 15 sec and the spray pressure to about 20 to 500 kPa (about 0.2 to 5 kgf/cm^2) in the case of spraying, since the water soluble ingredients can be removed more efficiently.

There is no particular restriction for the lower limit of the deposition amount of the surface modified layer on the galvanized steel sheet and it is preferably 4.2 mg/m^2 or more as a dried coating layer after the water rinsing treatment. When the deposition amount is insufficient, since it is difficult to cover the surface of zinc-based plated layer

uniformly, the resistance to tape peeling tends to be insufficient. The lower limit for the deposition amount is more preferably 7 mg/m² and, further preferably, 8 mg/m². On the contrary, when it is excessive, aluminum phosphates formed in the surface treating layer transforms from less soluble AlPO₄ of Al₂(HPO₄)₃ to water soluble Al(H₂PO₄)₃, as well as the denseness of the reaction layer tends to be lowered due to the etching insufficiency for the zinc-based plated surface. They tend to deteriorate the resistance to tape peeling after alkali degreasing. Accordingly, the total deposition amount of the surface modified layer is preferably 130 mg/m² or less. The upper limit for the deposition amount is more preferably 65 mg/m², further preferably, 50 mg/m² and, most preferably, 37 mg/m². The total deposition amount of the surface modified layer is a value obtained by quantitatively determining Si, P and Al in the surface modified layer, for example, by fluorescence X-ray analysis and calculation from the deposition amount assuming that SiO₂, AlPO₄, Zn₃(PO₄)₂ and Al₂O₃ are formed in the modified layer. When a preferred range for the deposition amount of the surface modified layer is expressed approximately by the layer thickness, it is from 0.0021 to 0.0657 μm assuming the specific gravity as 2.

In the surface treated galvanized steel sheet according to the invention, a surface modified layer inherent to the invention as described above is formed. Further, for providing characteristics such as corrosion resistance, finger print resistance, workability and adhesion of coating

layer, or the improvement thereof, a topcoat layer comprising various organic materials such as epoxy resin, acrylic resin, polyamide resin, polyester resin, alkyd resin, urethane resin, polyethylene resin, silicon resin, fluoro resin and aminoplast resin is laminated on the surface modified layer directly or by way of other layer.

Among them, a surface treated galvanized steel sheet having a resin layer formed of a specified emulsion composition as a topcoat layer is preferred. The emulsion composition used for forming the resin layer (topcoat layer) comprises an ethylene-unsaturated carboxylic acid copolymer (also including those in neutralized state) as a main ingredient, contains an amine having a boiling point of 100°C or lower in an amount corresponding to 0.2 to 0.8 mol (20 to 80 mol%) based on one mol of carboxylic groups of the ethylene-unsaturated carboxylic acid copolymer, a monovalent metal compound in an amount corresponding to 0.02 to 0.4 mol (2 to 40 mol%) based on one mol of the carboxylic groups of the ethylene-unsaturated carboxylic acid copolymer, and a crosslinking agent having two or more functional groups capable of reacting with the carboxylic group in an amount of 0.5 to 20 mass% based on 100 mass% of the solid content of the emulsion composition. The emulsion composition does not substantially contain ammonia.

The resin layer obtained from the emulsion composition described above is excellent in various properties such as coatability, lubricity and workability and conductivity

(grounding property) and also excellent in the corrosion resistance and the resistance to tape peeling after degreasing, and such finding has also been filed by the present inventors as Japanese Patent Application No. 2004-30231.

The ethylene-unsaturated carboxylic acid copolymer is a copolymer of ethylene and an unsaturated carboxylic acid such as (meth)acrylic acid. The copolymer can be obtained by polymerization such as a known high temperature high pressure polymerization process. The copolymer is most preferably a random copolymer but it may also be a block copolymer or a copolymer in which an unsaturated carboxylic acid moiety is grafted. An olefinic monomer such as propylene or 1-butene may be used for a portion of ethylene. Further, other known vinylic monomer may be partially copolymerized (by about 10 mass% or less) within a range not hindering the purpose of the invention. The copolymerizing ratio of the unsaturated carboxylic acid to ethylene is preferably 10 to 40 mass% of the unsaturated carboxylic acid based on 100 mass% of the entire monomer amount.

Since the ethylene-unsaturated carboxylic acid copolymer has carboxylic groups, it can be emulsified (into aqueous dispersion) by neutralization with an organic base or metal ion. In this case, an amine having a boiling point of 100°C or lower is used as the organic base. Amines having a boiling point higher than 100°C tend to remain on a steel sheet when the resin coating layer is dried to increase the

water absorption of the topcoat layer and, therefore, lower the corrosion resistance or the resistance to tape peeling. Accordingly, the emulsion composition used for forming the topcoat layer does not contain amines having a boiling point above 100°C. Further, since the effect of adding ammonia was not recognized, the composition neither contains ammonia. The boiling point means a boiling point under an atmospheric pressure.

Specific examples of the amines having a boiling point of 100°C or lower (hereinafter referred to as amines) can include, for example, tertiary amines such as triethyl amine, N,N-dimethylbutyl amine, N,N-dimethylallyl amine, N-methylpyrrolidine, tetramethyldiamino methane, and trimethyl amine; secondary amines such as N-methylethyl amine, diisopropyl amine and diethyl amine; and primary amines such as propyl amine, t-butyl amine, sec-butyl amine, isobutyl amine, 1,2-dibutylpropyl amine, and 3-pentyl amine. One or more amines can be used in admixture. Among them, the tertiary amines are preferred and triethyl amine is most preferred.

The amount of the amines is within a range from 0.2 to 0.8 mol (20 to 80 mol%) based on one mol of the carboxylic groups in the ethylene-unsaturated carboxylic acid copolymer. This is because the corrosion resistance or the resistance to tape peeling is preferred within the range described above. When the content of the amines is less than 0.2 mol, the grain size of the resin particles in the emulsion increases

and the above mentioned effect can not be provided. On the other hand, when it exceeds 0.8 mol, the viscosity of the emulsion composition increases to sometimes cause gelation, which is not preferred. The upper limit for amount of the amines is more preferably 0.6 mol and, further preferably, 0.5 mol. A more preferred lower limit for the amount of the amines is 0.3 mol.

For the preparation of the emulsion composition, a monovalent metal ion is also used. This is effective for the improvement of the solvent resistance or film hardness. The monovalent metal compound preferably includes one or more metals selected from sodium, potassium and lithium, and hydroxides, carbonates or oxides of the metals are preferred. Among them, NaOH, KOH, LiOH are preferred and NaOH is most preferred having good performance. Further, the compounds of bivalent or higher valent metals are not used since the effect by the addition is not recognized.

The amount of the monovalent metal compound is within a range from 0.02 to 0.4 mol (2 to 40 mol%) based on one mol of the carboxylic groups in the ethylene-unsaturated carboxylic acid copolymer. When the amount of the metal compound is less than 0.02 mol, emulsion stability is insufficient. On the other hand, when it exceeds 0.4 mol, the hygroscopicity of the resultant resin layer (particularly to alkaline solution) increases to deteriorate the corrosion resistance and the resistance to tape peeling after degreasing, which is not preferred. The lower limit for the amount of the metal

compound, is more preferably 0.03 mol, and, further preferably, 0.1 mol, while the upper limit for the amount of the metal compound is, more preferably, 0.5 mol and, further preferably, 0.2 mol.

The amines and the monovalent metal compound described above are used within the preferred range for the amount as described above and they are used for neutralizing the carboxylic groups of the ethylene-unsaturated carboxylic acid copolymer for emulsification. Accordingly, it is not preferred that the total amount (amount for neutralization) is excessive, since the viscosity of the emulsion composition increases abruptly to sometimes cause solidification, as well as the excess alkali content deteriorates the corrosion resistance and requires enormous energy for evaporation. However, it is neither preferred that the amount for neutralization is insufficient, since this deteriorates the emulsifying property. Accordingly, the total amount of the amines and the monovalent metal compound to be used is preferably within a range from 0.3 to 1.0 mol based on one mol of the carboxylic groups in the ethylene-unsaturated carboxylic acid copolymer.

In the neutralizing step (emulsifying step) of the ethylene-unsaturated carboxylic acid copolymer by the amines and the monovalent metal ions, it is preferred that the amine having a boiling point of lower than 100°C and the monovalent metal compound are added about at the same time to the copolymer or the amine having the boiling point of lower than

100°C is added previously. Although the reason is not apparent, when the amine having the boiling point of lower than 100°C is added subsequently, the effect of improving the corrosion resistance and the resistance to tape peeling is sometimes insufficient.

In the emulsion composition, a crosslinking agent having two or more functional groups capable of reacting with the carboxyl groups are blended. This is blended for chemically crosslinking the ethylene-unsaturated carboxylic acid copolymer to improve the strength of the layer. The amount of the crosslinking agent is 1 to 20 mass% (more preferably, 5 to 10 mass%) in 100 mass% of the solid content of the emulsion composition. When it is less than 1 mass%, crosslinking effect by the chemical bonding is insufficient, making it difficult to provide the effect of improving the corrosion resistance and the resistance to tape peeling. On the other hand, when it is blended in excess of 20 mass%, the crosslinking density of the resin layer increases excessively to increase the hardness and the layer can not follow the deformation upon pressing to cause cracking and, as a result, lower the corrosion resistance and the coatability, which is not preferred. The ratio for the amount of the crosslinking agent to the ethylene-unsaturated carboxylic acid copolymer is preferably changed appropriately change the amount of the crosslinking agent according to the amount of the carboxylic groups in the copolymer. Usually, the crosslinking agent is preferably from 0.5 to 50 mass parts (more preferably, 5 to

20 mass parts) based on 100 mass parts of the copolymer.

There is no particular restriction for the crosslinking agent having two or more functional groups in one molecule capable of reacting with the carboxylic groups and preferred examples including, for example, glycidyl group-containing crosslinking agents, for example, polyglycidyl ethers such as sorbitol polyglycidyl ether, (poly)glycerol polyglycidyl ether, pentaerythritol polyglycidyl ether, trimethylolpropane polyglycidyl ether, neopentylglycol diglycidyl ether, and (poly)ethylene glycol diglycidyl ether, and polyglycidyl amines; and aziridinyl group-containing crosslinking agents, for example, bifunctional aziridine compounds such as 4,4'-bis(ethyleneimine carbonylamino)diphenyl methane, N,N'-hexamethylene-1,6-bis(1-aziridine carboxyamide), N,N'-diphenylmethane-4,4'-bis(1-aziridine carboxyamide), and toluene bisaziridine carboxyamide; and tri- or higher functional aziridine compounds such as tri-1-aziridinyl phosphine oxide, tris[1-(2-methyl)aziridinyl] phosphine oxide, trimethylolpropane-tris(β -aziridine propionate), tris-2,4,6-(1-aziridinyl)-1,3,5-triazine, and tetramethylpropane tetraaziridinyl propionate, or derivatives thereof. Among them, one or more of the crosslinking agents may be used. Particularly, the aziridinyl group-containing crosslinking agent is preferred. The polyfunctional aziridine and the mono-functional aziridine (ethyleneimine or the like) may be used together.

Silica particles may be incorporated in an amount of 5

to 40 mass% (more preferably, 20 to 30 mass%) being converted as the solid content in the emulsion composition. This is effective for the improvement of the corrosion resistance, coatability and flaw resistance, and also effective for the improvement of the corrosion resistance and the resistance to tape peeling after degreasing. In a case where the amount of the silica particles is insufficient, the effects are less developed. On the other hand, when it is excessive, the ratio of the silica particles becomes excessively high to deteriorate the film forming property and the resin layer sometimes suffer from cracking during drying step, which may undesirably leads to the lowering of the corrosion resistance. Further, the silica particles act as an abrasive to increase the lubricity of the layer, lower the friction coefficient and cause abrasion to a die during fabrication to shorten the life of the die.

For obtaining the maximum effect of the silica particles, it is preferred that the average grain size of the silica particles is within a range from 1 to 200 nm. In a case where the grain size of the silica particles exceeds 200 nm, it roughens the surface of the resin layer, failing to obtain dense resin layer and, further, silica particles act also as an abrasive to deteriorate the workability. The corrosion resistance of the layer is improved as the grain size of the silica particles is smaller. However, since the effect described above is saturated when the particle is extremely fine, the lower limit for the grain size is

preferably 1 nm. In a case where a particular importance is attached to the corrosion resistance after degreasing, the average grain size of the silica particles is preferably within a range from 4 to 20 nm. Such silica particles are usually known as colloidal silica and, for example, "XS", "SS", "40", "N", and "UP" in the "SNOWTEX" series (colloidal silica manufactured by Nissan Chemical Industry Co.) can be used preferably.

The emulsion composition of the invention preferably contains a wax. In a case where the wax is contained by 0.5 to 20 mass% (more preferably, 0.5 to 10 mass% and, further preferably, 0.5 to 5 mass%) being converted as the solid content, the lubricity, flaw resistance, deep drawability, punching property and resistance to mold abrasion necessary for pressing or punching, and blackening resistance at the sliding surface during fabrication of the obtained resin layer are favorable. However, it is not preferred that the amount of waxes is excessive, since the wax is softening - liquefied or bloomed and is thickened at the boundary between the resin layer and the coating layer after coating or at the boundary between the surface treatment layer and the resin layer, which deteriorate the corrosion resistance and the resistance to tape peeling after degreasing.

There is no particular restriction on the wax and any of known waxes such as natural waxes, for example, micro-crystalline wax and paraffin wax; synthesis wax, for example, polyethylene wax; and mixtures thereof can be used. It is

preferred to select those having a softening point of from 80 to 140°C. A most preferred wax is a spherical polyethylene wax, with an average grain size of 0.1 to 3 μm (more preferably, 0.3 to 1.0 μm). This is because the lubricity, the punching property, the resistance to die abrasion and the deep drawability can be improved remarkably. As the spherical polyethylene wax commercial products can be used preferably including, for example, "DIJET E-17" (manufactured by Goou Chemical Co.), "KUE-1", "KUE-5", and "KUE-8" (manufactured by Sanyo Kasei Industry Co.), "W-100", "W-200", "W-300", "W-400", "W-500", "W-640", "W-700" in "CHEMIPEARL" series (manufactured by Mitsui Chemical Co.), and "ELEPON-20" (manufactured by Nikka Chemical Co.).

The emulsion composition used in the invention preferably contains the ethylene-unsaturated carboxylic acid copolymer, the amines, the monovalent metal compound and the crosslinking such as aziridine compound as the essential ingredients and, further, silica particles and the wax used optionally. It is preferred in the ethylene-unsaturated carboxylic acid copolymer to adjust the amount for the aziridine compound, the silica particles and the wax such that the resin ingredients is 50 mass% or more for the solid content of the emulsion composition.

The emulsion composition is prepared by a method of at first charging the ethylene-unsaturated carboxylic acid copolymer as the essential ingredient together with the aqueous medium, for example, into a homogenizer equipment,

optionally heating them at 70 to 250°C, adding the amines and the monovalent metal compound each appropriately in the form of an aqueous solution or the like (either the amine is added previously or the amines and the monovalent metal compound are added substantially at the same time) and then stirring them under a high shearing force. The silica particles, the wax and the crosslinking agent may be added at any stage, but it is preferred that heating is not applied after the addition of the crosslinking agent, so as not to proceed the crosslinking reaction and cause gelation.

In the emulsion composition, diluting solvent, skin-preventive agent, leveling agent, defoamer, penetration agent, emulsifier, film forming aid, coloration pigment, viscosity improver, silane coupler and other resins may be properly added within a range not hindering the purpose of the invention. Various kinds of additives that can be blended with the emulsion composition can also be used when other resin composition is used for forming the topcoat resin layer.

The resin layer may be formed on a metal sheet by coating the emulsion composition described above on one or both surfaces of the metal sheet by using a known drying method, that is, roll coating, spraying or curtain flow coating and dried under heating. The temperature for drying under heating is preferably at a temperature at which the crosslinking reaction between the crosslinking agent used and the carboxylic groups proceeds. Further, in a case of using the spherical polyethylene wax as the lubricant, the drying

is preferably conducted within a range from 70 to 130°C since the workability in the subsequent fabrication step is favorable when the spherical shape is kept.

The deposition amount (thickness) of the resin layer is preferably from 0.2 to 2.5 g/m² after drying. When it is excessively thin, uniform coating on the metal sheet is difficult and it is difficult to obtain an intended well-balanced layer properties such for workability, corrosion resistance and coatability. However, it is not preferred that the deposition amount exceeds 2.5 g/m², since the grounding conductivity, that is, electroconductivity is deteriorated, for example, in a case of use for computer housings. Further, the peeling amount of the resin layer increases upon pressing to cause deposition and accumulation of the peeled layer to the die thereby causing troubles in the press molding, and it is wasteful in view of the production cost as well. A more preferred lower limit for the deposition amount of the resin layer is 0.5 g/m² and a more preferred upper limit is 2.0 g/m².

A surface treated galvanized steel sheet as a most preferred embodiment of the invention can be obtained by forming the resin layer described above on the surface modified layer. The surface treated galvanized steel sheet may be used as it is after the working steps, or used after applying electrodeposition coating, powder coating or silk printing (at about 130 to 160°C for about 20 to 30 min) depending on the application use.

The surface treated galvanized steel sheet according to the invention do not contain deleterious hexa-valent chromium at all, and is excellent in the resistance to tape peeling and the resistance to tape peeling after alkali degreasing recognized at first by the present inventors as the subject. Further, in a case where the layer obtained from the specified emulsion composition is selected as the topcoat layer, it is possible to provide a surface treated galvanized steel sheet formed with a layer excellent in various fundamental properties such as coatability, lubricity, workability and corrosion resistance, as well as outstandingly excellent in the resistance to tape peeling and the resistance to tape peeling after alkali degreasing. Accordingly, this can be effectively utilized generally as surface treated galvanized steel sheet which is applicable, for example, to automobiles, home electric appliances and building materials.

The invention is to be described more specifically with reference to examples, but the invention is no way restricted to the following examples and the invention can be modified appropriately within a range conforming with the gists described above and to be described later, and all of the modifications are included within the technical range of the invention. In the following examples, "%" and "parts" means "mass%" and "mass parts" unless otherwise specified.

Experimental Example 1 (Nos. 1 to 29)

Galvanized steel sheets each applied with zinc plating by a deposition amount of 20 g/m² by an electric plating method on the surface of a steel sheet of 0.8 mm thickness (part number: SECC), alkali degreased and then water washed and dried were used as raw material sheets. Surface treating agents each comprising a mixture of an aqueous solution of aluminum hydrogen phosphate (manufactured by Nippon Chemical Industry Co., 50% solid content), colloidal silica ("SNOWTEX-O"; manufactured by Nissan Chemical Industry Co.) and water were used. The concentration for each of Si, P, and Al in the treating agent was changed and the content for each of Si, P, and Al in the surface modified layer was changed as shown in Tables 1 and 2, by changing the amounts of aqueous solution of aluminum hydrogen phosphate, colloidal silica and water, and optionally adding phosphoric acid and metal aluminum.

Each of the galvanized steel sheets after the degreasing was dipped in the surface treating agent for 2 sec and then pulled up and, after removing an excess solution by a wringer roll, water washed under a spray pressure of 50 kPa for five sec and dried at 40°C to form a surface modified layer on the zinc-plated layer. Water rinsing was not conducted for No. 29 in Table 2.

Separately, a composition for forming a topcoat resin layer was prepared by blending and stirring an epoxy type crosslinking agent ("RICABOND AP355B"; manufactured by Chuo Rika Industry Co.) by 5% as solid content (value based on

100% of the solid content of the composition for forming the topcoat resin layer, here and hereinafter), silica particles of 10 to 20 nm grain size ("SNOWTEX 40"; manufactured by Nissan Chemical Industry Co.) by 30% as solid content and spherical polyethylene wax ("CHEMIPEARL W700"; manufactured by Mitsui Chemical Co.) by 5% as solid content to a polyolefin dispersion ("CHEMIPEARL (registered trade mark) S100", manufactured by Mitsui Chemical Co.). The composition was coated on the surface modified layer of each galvanized steel sheet by bar coating, and dried under heating at a sheet temperature of 90° for one min, to obtain surface treated galvanized steel sheets formed with the topcoat resin layer with the deposition amount of 1 g/m².

For each of the test specimens thus obtained, evaluation test was conducted for the concentration (%) of Si, P, and Al in the surface treating solution, the amount (mg/m²) for Si, P and Al in the surface modified layer, the total deposition amount (mg/m²) of the surface modified layer, and the resistance to tape peeling and the resistance to tape peeling after alkali degreasing, and the results are shown in Table 1.

[Evaluation Method]

(1) Amounts of Si, P and Al

The concentration for each of Si, P and Al in the surface treating solution were measured by ICP emission spectrometric apparatus (manufactured by Seiko Advance Co.), the amount (mg/m²) for each of Si, P and Al in the surface

modified layer was measured by fluorescence X-ray apparatus (trade name: "MIF-2100"; manufactured by Shimazu Seisakusho), respectively. The total deposition amount (mg/m^2) of the surface modified layer is a value obtained on the basis of the result of quantization for Si, P and Al by fluorescence X-ray spectrochemical analysis, by calculation based on the assumption that they are formed as SiO_2 , AlPO_4 , $\text{Zn}_3(\text{PO}_4)_2$ and Al_2O_3 in the modified layer.

(2) Resistance to tape peeling

After appending a filament tape (#9510, manufactured by Surion Tech) on the surface of a test specimen and storing the specimen in an atmosphere of $40^\circ\text{C} \times 90\%\text{RH}$ for 24 hours and 48 hours, the filament tape was peeled, the ratio of area for the residual topcoat layer was observed, and the resistance was evaluated according to the following standards.

◎: residual ratio, 100%

○ - ◎: residual ratio, 95% or more and less than 100%

○: residual ratio, 90% or more and less than 95%

△: residual ratio, 70% or more and less than 90%

×: residual ratio, less than 70%

(3) Resistance to tape peeling after degreasing

After dipping a test specimens into a degreasing solution in which an alkali degreasing agent ("CL-N364S"; manufactured by Nippon Parkerizing Co.) was adjusted to 20 g/l at 60°C , pulling up the specimen, and water rinsing and drying the same, a cellophane tape (manufactured by Nichiban Co.) was appended to the surface of the specimen and peeled

after 24 hours and 48 hours, the residual ratio for the remaining topcoat layer was observed and evaluated according to the standards identical with those for the resistance to tape peeling in the normal state.

Table 1

No.	Concentration in surface treating agent (%)				Ratio		Treating method	Water rinsing	Amount in surface treatment layer (mg/m ²)				Ratio		Total deposition amount of surface treatment layer (mg/m ²)	Resistance to tape peeling		Resistance to tape peeling after degreasing		Section
	Si	P	Al		Si/P	Si/Al			Si	P	Al		Si/P	P/Al		24h	48h	24h	48h	
1	0.65	0.1	0.03		6.5	21.7	dipping	applied	6.5	1.2	1.0		5.4	1.2	18.8	◎	○	◎	○	Example of the invention
2	0.3	0.05	0.02		6.0	15.0	dipping	applied	4.1	1.0	0.8		4.1	1.3	12.9	◎	○	◎	○	Example of the invention
3	0.08	0.02	0.007		4.0	11.4	dipping	applied	3.3	0.8	0.7		4.1	1.1	10.2	◎	○	◎	○	Example of the invention
4	0.02	0.005	0.002		4.0	10.0	dipping	applied	1.9	0.9	0.6		2.1	1.5	8.1	◎	△	◎	○	Example of the invention
5	0.005	0.0007	0.0003		7.1	16.7	dipping	applied	1.1	0.5	0.5		2.2	1.0	4.5	◎	△	◎	○	Example of the invention
6	1.0	0.16	0.06		6.3	16.7	dipping	applied	8.2	1.5	1.2		5.5	1.3	23.8	◎	○	◎	○	Example of the invention
7	2.0	0.3	0.1		6.7	20.0	dipping	applied	11.8	2.0	1.9		5.9	1.1	33.5	◎	△	◎	△	Example of the invention
8	4.2	0.7	0.25		6.0	16.8	dipping	applied	14.4	2.8	1.4		5.1	2.0	44.6	◎	△	◎	△	Example of the invention
9	3.8	1.3	0.4		2.9	9.5	dipping	applied	15.0	2.9	1.4		5.2	2.1	46.5	◎	△	◎	△	Example of the invention
10	0.08	0.04	0.012		2.0	6.7	dipping	applied	4.0	0.7	0.6		5.7	1.2	11.4	◎	○	◎	○	Example of the invention
11	0.08	0.05	0.015		1.6	5.3	dipping	applied	4.1	0.9	0.7		4.6	1.3	12.6	◎	○	◎	○	Example of the invention
12	0.08	0.03	0.009		2.7	8.9	dipping	applied	3.7	0.7	0.8		5.3	0.9	11.0	◎	○	◎	○	Example of the invention
13	1.0	0.1	0.03		10	33	dipping	applied	10.1	1.8	1.6		5.6	1.1	28.8	◎	○	◎	△	Example of the invention
14	2.0	0.1	0.03		20	67	dipping	applied	11.3	1.7	1.6		6.6	1.1	31.1	◎	△	◎	△	Example of the invention
15	4.0	0.13	0.038		31	105	dipping	applied	12.0	1.9	1.8		6.3	1.1	33.5	◎	△	◎	△	Example of the invention
16	4.4	0.1	0.03		44	147	dipping	applied	13.0	1.8	1.8		7.2	1.0	35.4	◎	△	◎	△	Example of the invention
17	4.2	0.07	0.02		60	210	dipping	applied	12.6	1.1	1.3		11.5	0.8	32.0	◎	△	◎	○	Example of the invention
18	4.5	1.3	0.5		3.5	9.0	dipping	applied	25.1	13.6	9.2		1.8	1.5	114.3	◎-○	△	○	△	Example of the invention

Table 2

No.	Concentration in surface treating agent (%)				Ratio			Treating method	Water rinsing	Amount in surface treatment layer (mg/m ²)				Ratio			Total deposition amount of surface treatment layer (mg/m ²)	Resistance to tape peeling		Resistance to tape peeling after degreasing		Section
	Si	P	Al		Si/P	Si/Al				Si	P	Al		Si/P	P/Al			24h	48h	24h	48h	
19	4.3	1.0	0.8		4.3	5.4		dipping	applied	22.3	3.2	6.4		7.0	0.5		67.2	◎-○	△	△	△	Reference example
20	0.001	0.0006	0.0002		1.7	5.0		dipping	applied	0.8	0.5	0.5		1.6	1.0		3.8	×	×	△	△	Comparative example
21	0.004	0.0002	0.00006		6.7	20.0		dipping	applied	0.5	0.4	0.3		1.3	1.3		2.8	×	×	△	×	Comparative example
22	0.001	0.1	0.03		0.01	0.03		dipping	applied	0.8	1.8	1.6		0.4	1.1		8.9	△	×	○	△	Comparative example
23	0.1	0.0002	0.00006		1667	500		dipping	applied	0.8	0.4	0.2		2.0	2.0		3.7	×	×	△	×	Comparative example
24	8.2	2.0	0.7		4.1	11.7		dipping	applied	38.2	15.3	10.2		2.5	1.5		150.3	○	△	×	×	Comparative example
25	8.4	3.0	0.4		2.8	21.0		dipping	applied	40.1	17.7	10.0		2.3	1.8		169.9	○	△	×	×	Comparative example
26	4.4	5.1	0.5		0.9	8.8		dipping	applied	27.3	16.2	9.5		1.7	1.7		134.4	◎-○	△	△	×	Comparative example
27	3.7	1.3	0.7		2.8	5.3		dipping	applied	14.6	13.1	11.5		1.1	1.1		83.0	◎-○	△	△	△	Comparative example
28	8.0	1.5	0.5		5.3	16.0		dipping	applied	33.5	9.1	8.6		3.7	1.1		108.9	△	×	△	△	Comparative example
29	0.6	0.3	0.15		2.0	4.0		dipping	Not applied	45.1	20.1	15.5		2.2	1.3		181.0	○	○	×	×	Comparative example

Table 1 shows examples of the invention. In each of the examples, the content for each of Si, P and Al, and Si/P and P/Al in the surface modified layer was within an appropriate range, and each of the examples showed an excellent resistance to tape peeling both in the dried state and after degreasing. Since P/Al is less than the appropriate range in No. 19 in Table 2, it was somewhat inferior in the resistance to tape peeling and resistance to tape peeling after degreasing, compared with the examples of the invention.

Nos. 20 to 23 are examples in which the addition amounts for Si, P and Al do not partially or entirely reach the predetermined amount in the surface modified layer since the concentrations for Si, P, and Al in the surface modifying agent is partially or entirely insufficient, and both of the resistance to tape peeling and the resistance to tape peeling after alkali degreasing were inferior to those in the examples of the invention.

Nos. 24 to 28: since the concentrations for Si, P, Al in the surface modifying agent are partially or entirely excessive, the deposition amounts for Si, P and Al in the surface modified layer partially or entirely exceed the predetermined amount, and both the resistance to tape peeling and the resistance to tape peeling after alkali degreasing are inferior to those of the examples of the invention.

No. 29: Since water rinsing was not applied, deposition amounts for P and Al in the surface modified layer

exceed the predetermined amounts. While the resistance to tape peeling was favorable, the alkali resistance of the surface modified layer became poor due to excessive amounts of P and Al and the resistance to tape peeling after alkali degreasing was poor.

Experimental Example 2 (Nos. 30 - 48)

Surface modified layers were prepared by using not dipping but spraying. That is, after spraying each of surface treating agents of the compositions shown in Table 3 (preparation method identical with Experimental Example 1) at a spray pressure of 50 kPa for 2 sec, an excess solution was removed by a wringer roll. Then, they were further washed with water at a spray pressure of 50 kPa for 5 sec and dried at 40°C to form surface modified layers on zinc plated layer. In the same manner as in Experimental Example 1, excepting the procedures described above, surface treated galvanized steel sheets formed with topcoat layers were obtained. Each of the test specimens thus obtained was evaluated in the same manner as in Experimental Example 1 and the results are shown in Table 3.

Table 3

No.	Concentration in surface treating agent (%)				Ratio		Treating method	Water rinsing	Amount in surface treatment layer (mg/m ²)				Ratio		Total deposition amount of surface treatment layer (mg/m ²)	Resistance to tape peeling		Resistance to tape peeling after degreasing		Section
	Si	P	Al		Si/P	Si/Al			Si	P	Al		Si/P	P/Al		24h	48h	24h	48h	
30	4.4	1.5	0.5		2.9	8.8	spraying	applied	29.0	14.7	9.9		2.0	1.5	127.6	◎-○	○	◎-○	△	Example of the invention
31	4.1	1.4	0.4		2.9	10	spraying	applied	22.3	13.2	9.0		1.7	1.5	106.3	◎-○	○	◎-○	△	Example of the invention
32	3.5	1.3	0.4		2.7	8.8	spraying	applied	17.3	12.0	8.0		1.4	1.5	90.8	◎-○	○	◎-○	△	Example of the invention
33	2.3	0.9	0.3		2.8	8.3	spraying	applied	12.0	9.2	7.5		1.3	1.2	63.3	◎	○	◎-○	○	Example of the invention
34	1.5	0.9	0.2		1.7	7.5	spraying	applied	9.0	8.5	6.7		1.1	1.3	54.6	◎	◎-○	◎	○	Example of the invention
35	1.5	0.6	0.2		2.5	7.5	spraying	applied	8.8	6.8	5.2		1.3	1.3	47.5	◎	◎-○	◎	○	Example of the invention
36	1.4	0.2	0.07		7.0	20	spraying	applied	8.7	4.3	3.8		2.0	1.1	35.7	◎	◎-○	◎	○	Example of the invention
37	1.0	0.1	0.03		10	33	spraying	applied	6.7	3.8	3.1		1.8	1.2	29.9	◎	◎-○	◎	○	Example of the invention
38	0.5	0.06	0.02		8.3	25	spraying	applied	5.3	2.7	2.4		2.0	1.1	22.1	◎	◎-○	◎	○	Example of the invention
39	0.4	0.04	0.01		10	40	spraying	applied	5.2	4.0	1.0		1.3	4.0	33.4	◎	◎-○	◎	○	Example of the invention
40	0.5	0.08	0.02		6.3	25	spraying	applied	5.5	3.0	1.4		1.8	2.1	26.8	◎	◎-○	◎	○	Example of the invention
41	0.5	0.02	0.008		25	63	spraying	applied	4.1	2.0	1.2		2.1	1.7	18.1	◎	◎-○	◎	○	Example of the invention
42	0.07	0.005	0.003		14	23	spraying	applied	3.8	1.1	0.7		3.5	1.6	13.2	◎	◎-○	◎	◎-○	Example of the invention
43	0.008	0.0008	0.0003		10	27	spraying	applied	2.0	0.9	0.6		2.2	1.5	8.3	◎	△	◎	◎-○	Example of the invention
44	0.001	0.0004	0.00007		2.5	14	spraying	applied	0.8	0.4	0.3		2.0	1.3	3.4	×	×	×	×	Comparative example
45	0.007	0.0004	0.0002		18	35	spraying	applied	1.1	0.4	0.6		2.8	0.7	4.4	△	△	△	△	Comparative example
46	4.5	1.7	0.6		2.6	7.5	spraying	applied	19.2	16.1	2.5		1.2	6.4	134.9	△	△	△	×	Comparative example
47	2.2	1.8	0.7		1.2	3.1	spraying	applied	14.3	18.2	12.1		0.8	1.5	112.2	◎	◎-○	△	×	Comparative example
48	7.0	1.0	0.4		7.0	18	spraying	applied	37.2	10.0	8.1		3.7	1.2	120.7	△	×	△	×	Comparative example

Experimental Example 3 (Nos. 49 to 72)

Surface treating agents of the compositions shown in Table 4 (also in Table 5) were prepared by using mixed solutions of the aqueous solution of aluminum hydrogen phosphate, colloidal silica ("SNOWTEX-O" described above), three kinds of polyacrylic acids and water. At first, the surface treated galvanized steel sheets before forming the topcoat layers were obtained at first by spraying (under the same conditions as those in Experimental Example 2). Topcoat layers were formed to them in the same manner as in Example 1 to form Nos. 49 to 60.

Then, separately, an emulsion of an ethylene - acrylic acid copolymer was obtained by adding 626 parts of water, and 160 parts of an ethylene - acrylic acid copolymer (acrylic acid 20 mass%, melt index (MI) 300) to an autoclave, 40 mol% of triethylamine, adding 15 mol% of NaOH based on one mol of carboxylic groups in the ethylene - acrylic acid copolymer and stirring at a high speed in an atmosphere of 150°C and 5 Pa. Successively, an emulsion composition was prepared by blending and stirring a glycidyl group-containing crosslinking agent ("EPICLON CR5L"; (CR5L for short) ; "EPICLON" is a registered trade mark; manufactured by Dainippon Ink Chemical Industry Co.) by 5% as solid content (value based on 100% of solid content in the emulsion composition, here and hereinafter) and an aziridinyll group-containing crosslinking agent (4,4'-bis (ethyleneiminocarbonylamino) diphenyl methane; "CHEMITITE DZ-22E"; (DZ-22E for short) ; "CHEMITITE" is

a registered trade mark; manufactured by Nippon Catalyst Co.) by 5% as solid content, as a crosslinking agent, silica particles with a grain size of 10 to 20 nm ("SNOWTEX 40"; manufactured by Nissan Chemical Industry Co.) by 30% as solid content and spherical polyethylene wax with an average grain size of 1 μm having a softening point 120°C by 5% as solid content. The emulsion composition was coated on the surface modified layer of the surface treated galvanized steel sheets before forming the topcoat layer by bar coating, dried under heating at a sheet temperature of 90°C for one min, to form a topcoat resin layer with a deposition amount of 1 g/m² (Nos. 61 to 72).

Each of the test specimens thus obtained was evaluated in the same manner as in Experimental Example 1 and the results are shown in Tables 4 and 5. In the Tables, PA1 is polyacrylic acid with a weight average molecular weight (Mw) of 100,000 to 200,000, PA2 is a polyacrylic acid with Mw of 20,000 to 30,000, and PA3 is a polyacrylic acid with Mw of 8,000. The absorbance of the resin in the surface modified layer is a value measured by FT-IR and the analysis conditions are as shown below.

[FT-IR analysis method]

Measuring method: high sensitivity reflection method

(incident angle 75°, IR light was irradiated as parallel polarized light)

Comparative material: gold vapor deposited mirror

Resolution power: 4 cm⁻¹

Number of accumulation: 500 times

Apparatus: JIR-5500 type Fourier transformation IR

spectrophotometer manufactured by Nippon Denshi Co.

IR-RSC110 reflection measuring unit (variable angle type)

IR-SEM100 specimen switching stage

A peak area at 1496 cm^{-1} to 1776 cm^{-1} for a steel sheet with no addition of polyacrylic acid was subtracted from a peak area at 1496 cm^{-1} to 1776 cm^{-1} for a steel sheet with addition of polyacrylic acid and the balance was determined as an absorbance derived from the polyacrylic acid in the surface modified layer. Fig. 1 to Fig. 3 show FT-IR spectra measured under the foregoing conditions for No. 38 described in Table 3, No. 52 described in Table 4 and sodium polyacrylate (standard specimen). No. 52 in Fig. 2 is a system containing PA1 by 0.50 g/l in the surface treating agent, in which absorption at 1346 cm^{-1} , 1421 cm^{-1} , 1457 cm^{-1} , and 1592 cm^{-1} was observed, which was not observed in the spectrum for No. 38 not containing polyacrylic acid in the surface treating agent. The peaks are identical with the absorption of sodium polyacrylate shown in Fig. 3.

Table 4

No.	Concentration in surface treating agent (%)				Ratio			Organic acid salt				Treating method	Water rinsing	Amount in surface treatment layer (mg/m ²)				Ratio		Absorbance of resin	Total deposition amount of surface treatment layer (mg/m ²)	Resistance to tape peeling		Resistance to tape peeling after degreasing		Section
	Si	P	Al		Si/P	Si/Al		Kind	Addition conc.	(g/l)				Si	P	Al		Si/P	P/Al			24h	48h	24h	48h	
49	0.5	0.06	0.02		8.3	25		PA1	0.05			spraying	applied	5.1	2.5	2.0		2.0	1.3	0.4	21.2	⊙	⊙	⊙	⊙	Example of the invention
50	0.5	0.06	0.02		8.3	25		PA1	0.10			spraying	applied	4.8	2.9	1.7		1.7	1.7	0.9	23.9	⊙	⊙	⊙	⊙ - ⊙	Example of the invention
51	0.5	0.06	0.02		8.3	25		PA1	0.25			spraying	applied	6.2	2.6	1.8		2.4	1.4	2.3	24.7	⊙	⊙	⊙	⊙ - ⊙	Example of the invention
52	0.5	0.06	0.02		8.3	25		PA1	0.50			spraying	applied	6.6	3.1	2.1		2.1	1.5	4.7	27.9	⊙	⊙	⊙	⊙	Example of the invention
53	0.5	0.06	0.02		8.3	25		PA1	0.75			spraying	applied	7.5	2.8	2.0		2.7	1.4	9.5	28.3	⊙	⊙	⊙	⊙	Example of the invention
54	0.5	0.06	0.02		8.3	25		PA1	3.0			spraying	applied	5.5	2.7	2.3		3.0	1.2	14.8	28.3	⊙	⊙	⊙	⊙	Example of the invention
55	0.5	0.06	0.02		8.3	25		PA2	0.10			spraying	applied	5.5	2.7	1.8		2.0	1.5	1.1	23.9	⊙	⊙	⊙ - ⊙	⊙	Example of the invention
56	0.5	0.06	0.02		8.3	25		PA2	0.25			spraying	applied	5.1	2.1	2.0		2.4	1.1	2.5	19.5	⊙	⊙	⊙ - ⊙	⊙	Example of the invention
57	0.5	0.06	0.02		8.3	25		PA3	0.10			spraying	applied	4.5	2.6	1.9		1.7	1.4	1.4	20.8	⊙	⊙	⊙	⊙	Example of the invention
58	0.5	0.06	0.02		8.3	25		PA3	0.25			spraying	applied	3.3	2.6	2.2		1.3	1.2	3.0	17.5	⊙	⊙	⊙	⊙	Example of the invention
59	0.5	0.06	0.02		8.3	25		PA1	0.005			spraying	applied	5.8	2.7	1.9		2.1	1.4	0.003	24.2	⊙	⊙	⊙	⊙	Reference example
60	0.5	0.06	0.02		8.3	25		PA1	5.0			spraying	applied	9.0	7.2	3.9		1.3	1.8	17.2	53.8	⊙	⊙	⊙	△	Reference example

Table 5

No.	Concentration in surface treating agent (%)				Ratio		Organic acid salt		Treating method	Water rinsing	Amount in surface treatment layer (mg/m ²)				Ratio		Absorbance of resin	Total deposition amount of surface treatment layer (mg/m ²)	Resistance to tape peeling		Resistance to tape peeling after degreasing		Section
	Si	P	Al	Si/Al	Kind	Addition conc.	Si	P			Al	Si/P	P/Al	24h	48h	24h			48h				
61	0.5	0.06	0.02	8.3	25	PA1	0.05	spraying	applied	5.1	2.5	2.0	1.3	0.4	21.2	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
62	0.5	0.06	0.02	8.3	25	PA1	0.10	spraying	applied	4.8	2.9	1.7	1.7	0.9	23.9	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Example of the invention
63	0.5	0.06	0.02	8.3	25	PA1	0.25	spraying	applied	6.2	2.6	1.8	2.4	2.3	24.7	⊙	⊙	⊙	⊙	⊙	⊙	⊙	Example of the invention
64	0.5	0.06	0.02	8.3	25	PA1	0.50	spraying	applied	6.6	3.1	2.1	2.1	4.7	27.9	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
65	0.5	0.06	0.02	8.3	25	PA1	0.75	spraying	applied	7.5	2.8	2.0	2.7	9.5	28.3	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
66	0.5	0.06	0.02	8.3	25	PA1	3.0	spraying	applied	8.2	2.7	2.3	3.0	14.8	28.3	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
67	0.5	0.06	0.02	8.3	25	PA2	0.10	spraying	applied	5.5	2.7	1.8	2.0	1.1	23.9	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
68	0.5	0.06	0.02	8.3	25	PA2	0.25	spraying	applied	5.1	2.1	2.0	2.4	2.5	19.5	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
69	0.5	0.06	0.02	8.3	25	PA3	0.10	spraying	applied	4.5	2.6	1.9	1.7	1.4	20.8	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
70	0.5	0.06	0.02	8.3	25	PA3	0.25	spraying	applied	3.3	2.6	2.2	1.3	3.0	17.5	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Example of the invention
71	0.5	0.06	0.02	8.3	25	PA1	0.005	spraying	applied	5.8	2.7	1.9	2.1	0.003	24.2	⊙	⊙	⊙	⊙	⊙	⊙	⊙ - ○	Reference example
72	0.5	0.06	0.02	8.3	25	PA1	5.0	spraying	applied	9.0	7.2	3.9	1.3	17.2	53.8	⊙	⊙	⊙	⊙	⊙	⊙	○	Reference example

It can be seen that the organic resin-added system is more excellent in the resistance to tape peeling and the resistance to tape peeling after alkali degreasing over the conventional non-addition type. Further, it can be seen that the examples formed with the topcoat layer comprising the emulsion composition neutralized by the specified neutralization method (shown in Table 5) show outstandingly excellent resistance tape peeling and resistance to tape peeling after alkali degreasing.

Industrial applicability

Since the surface modified layer is formed on the zinc-based plated layer in a galvanized steel sheet by the surface treating agent containing a specified amount of Si, P and Al and, optionally, an organic resin, the resistance to tape peeling and, further the resistance to tape peeling after alkali degreasing are excellent. Further, by the selection of the layer obtained from the specified emulsion composition as the topcoat layer, surface treated galvanized steel sheet formed with a layer excellent in various properties such as coatability, lubricity, workability, and corrosion resistance and also having outstanding performance in the resistance to tape peeling after degreasing step can be provided. The manufacturing method according to the invention is suitable to production of a surface treated galvanized steel sheet excellent in the resistance to tape peeling and, particularly, the resistance to tape peeling after alkali degreasing.

WHAT IS CLAIMED IS:

1. A surface treated galvanized steel sheet having at least a surface modified layer and a topcoat layer formed on a zinc-based plated layer in a galvanized steel sheet, wherein the surface modified layer contains from 1 to 30 mg/m² of SiO₂ being converted as Si, from 0.5 to 15 mg/m² of P and from 0.4 to 10 mg/m² of Al.

2. The surface treated galvanized steel sheet according to claim 1, wherein the content (mass ratio) for each of Si, P and Al contained in the surface modified layer satisfies the following relations (1), and (2):

$$0.5 \leq \text{Si/P} \leq 20 \quad (1)$$

$$0.7 \leq \text{P/Al} \leq 5 \quad (2).$$

3. The surface treated galvanized steel sheet according to claim 1, wherein surface modifying agent further contains an organic resin.

4. The surface treated galvanized steel sheet according to claim 3, wherein the organic resin is contained such that the absorbance derived from the structure of the organic resin becomes 0.1 to 15 when the surface modified layer is observed under FT-I.

5. The surface treated galvanized steel sheet according to

claim 1, wherein the deposition amount of the surface modifying agent is within a range from 4.2 to 130 mg/m².

6. The surface treated galvanized steel sheet according to claim 1, wherein the topcoat layer is a resin layer obtained from an emulsion composition comprising an ethylene-unsaturated carboxylic acid copolymer as a main ingredient, the emulsion composition contains, in addition to the ethylene-unsaturated carboxylic acid copolymer, an amine having a boiling point of 100°C or lower in an amount of 0.2 to 0.8 mol based on one mol of carboxylic groups of the ethylene-unsaturated carboxylic acid copolymer, and a monovalent metal compound in an amount of from 0.02 to 0.4 mol based on one mol of the carboxylic acids of the ethylene-unsaturated carboxylic acid copolymer; and the emulsion composition further contains a crosslinking agent having two or more functional groups capable of reacting with the carboxylic groups in an amount from 1 to 20 mass% based on 100 mass% of the solid content of the emulsion condition.

7. An SiO₂-containing phosphate surface treating agent for forming a surface modified layer on a galvanized steel sheet wherein the solid concentration is from 0.01 to 14.5% (mass% here and hereinafter) and the amount and the compositional ratio (mass ratio) for Si, P, and Al contained in the treating agent can satisfy the following conditions:

Si: 0.002 - 4.5%

P : 0.0005 - 1.5%

Al: 0.0001 - 0.5%

$1.5 \leq \text{Si/P} \leq 60$, $4.5 \leq \text{Si/Al} \leq 230$

8. The surface treating agent according to claim 7, wherein the surface treating agent further contains an organic resin.

9. The surface treating agent according to claim 8, wherein the organic resin is water soluble.

10. The surface treating agent according to claim 8, wherein the organic resin is contained by 0.01 to 3 g/l as solid content in the surface treating agent.

11. A method of manufacturing a surface treated galvanized steel sheet according to claim 1 which comprises forming a surface treating agent layer on the surface of a galvanized steel sheet by the surface treating agent described in claim 7, applying water rinsing to remove excess P and/or Al from the surface treating agent layer, drying the same, and thereby forming a surface modified layer.

12. The manufacturing method according to claim 11, wherein the surface treating agent layer is formed by spray coating.