

## DESCRIPTION

5      ENVIRONMENTALLY FRIENDLY SURFACE TREATED STEEL SHEET FOR  
      ELECTRONIC COMPONENTS EXCELLENT IN SOLDER WETTABILITY,  
      RESISTANCE TO FORMATION OF WHISKERS, AND STABILITY OF  
      APPEARANCE OVER TIME AND METHOD OF PRODUCTION OF SAME

## TECHNICAL FIELD

10      The present invention relates to a surface treated  
      steel sheet for electronic components used for electronic  
      components of electric products, excellent in  
      solderability, whisker-proof property, and stability of  
      appearance with aging, and not containing lead,  
15      hexavalent chromium, or other substances with  
      environmental impact and a method of production of the  
      same.

## BACKGROUND ART

20      In general, for electronic components of electric  
      products, as surface treated steel sheet having excellent  
      solder wettability, surface treated steel sheet having an  
      Sn plated layer of 8.4 to 11.2 g/m<sup>2</sup> on the surface of the  
      steel sheet (hereunder referred to as "#75 to #100  
      tinplate") and, due to the space between electronic  
      components being narrowed due to the recent reduction of  
25      size of electric products and as a result tinplate  
      causing the problems of direct short circuits, the  
      destruction of an insulating layer, and the like due to  
      acicular single crystals (whiskers) grown from the tin  
      plated layer, aterneplate or a solder plated steel sheet  
30      which does not generate whiskers have become the  
      mainstream. For preventing the generation of whiskers,  
      the methods of alloy plating (Japanese Examined Patent  
      Publication No. 58-2598, Japanese Unexamined Patent  
      Publication No. 49-129, etc.) and post-treatment after  
35      plating (Japanese Examined Patent Publication No. 56-  
      47955, Japanese Examined Patent Publication No. 56-47956,  
      Japanese Unexamined Patent Publication No. 59-143089,

Japanese Unexamined Patent Publication No. 62-77481, etc.) have been proposed in the past. Further, surface treated steel sheet improving the solderability by optimization of the alloy composition and a chromate treated layer (Japanese Unexamined Patent Publication No. 2-270970 and Japanese Unexamined Patent Publication No. 3-183796) has been commercialized.

In recent years, the regulations against hazardous substances with environmental impact have been enforced in view of global environmental problems and, in particular, hexavalent chromium and lead are objects of regulation. Therefore, after lead-tin solder, there is a pressing demand for alternative materials to make plated steel sheet lead free or hexavalent chromium free.

Japanese Unexamined Patent Publication No. 2002-249885 discloses to replace the chromate treated layer with a P+Mg layer, Japanese Unexamined Patent Publication No. 2002-256481, Japanese Unexamined Patent Publication No. 2003-253469, and Japanese Unexamined Patent Publication No. 2003-253470 propose elimination of the chromate treated layer or use of a phosphate layer, Japanese Unexamined Patent Publication No. 2003-105587 proposes replacing a chromate treated layer with a layer containing V, and Japanese Unexamined Patent Publication No. 2003-213454, Japanese Unexamined Patent Publication No. 2004-2204243, and Japanese Unexamined Patent Publication No. 2004-218051 propose replacing the chromate treated layer with an organic resin layer. Some of these are being used commercially.

As described above, there is a strong demand to provide an environmentally friendly surface treated steel sheet for electronic components excellent in both solder wettability and whisker-proof property.

#### DISCLOSURE OF THE INVENTION

The present invention provides a surface treated steel sheet for electronic components which does not include hazardous substances with environmental impact

such as lead and hexavalent chromium, has solder wettability and whisker-proof property, and has a stable surface appearance.

Below, the present invention will be described in detail. The present invention is a surface treated steel sheet capable of securing a good whisker-proof property and a good rust-proof property which have been problems in tinplate, while securing more excellent solder wettability, after retort treatment, than aterneplate used for application to electronic components which are currently soldered by dipping in a molten solder bath for a short period of time. These objects are achieved providing surface treated steel sheet for electronic components comprised of steel sheet or Ni plated steel sheet plated with Sn and Zn and then treated it by thermal diffusion or plated by an Sn-Zn alloy to form an Sn-Zn alloy layer wherein the deposited amount of an Sn-Zn alloy layer and the Zn (weight)/Sn (weight) ratio are specified and, further, the conventional chromate layer is replaced by an inorganic coating mainly comprised of phosphoric acid-zinc-magnesium.

That is, the present invention is an environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging, comprising steel sheet or Ni plated steel sheet plated with Sn and Zn and then treated by thermal diffusion or plated with Sn-Zn alloy to form an Sn-Zn alloy layer, said surface treated steel sheet for electronic components characterized in that said Sn-Zn alloy layer is deposited in an amount of 3 g/m<sup>2</sup> or more, the Sn-Zn alloy layer has a Zn (weight)/Sn (weight) ratio of 0.001 to 0.1, more preferably 0.001 to 0.01, and this Sn-Zn alloy layer has an inorganic coating mainly comprised of phosphoric acid-zinc-magnesium in a P+Zn+Mg deposited amount of 0.1 to 100 mg/m<sup>2</sup>, more preferably 0.1 to 10 mg/m<sup>2</sup>.

The method of production of these environmentally

friendly surface treated steel sheet for electronic components is characterized by plating steel sheet or Ni plated steel sheet with Sn and Zn, then treating it by thermal diffusion or plating it with an Sn-Zn alloy to form an Sn-Zn alloy layer, then, without removing a zinc oxide layer on the surface, dipping the sheet in a magnesium diphosphate solution at a temperature of 30°C to 70°C, then immediately rinsing it and drying it at 170°C or less, more preferably setting the dipping treatment temperature in the magnesium diphosphate solution at 50°C to 70°C and setting the drying temperature after the subsequent rinsing at 100°C or less.

The surface treated steel sheet of the present invention has excellent performance in solder wettability, whisker-proof property, and stability of appearance with aging for applications for electronic components. This invention enables the supply of environmentally friendly surface treated steel sheet for electronic components.

#### BRIEF DESCRIPTION OF THE DRAWINGS

FIG. 1 is a view showing the surface layer structure of a cross-section of the layers of a product of the present invention.

FIG. 2 is a view showing the relation among the P+Zn+Mg deposited amount of an inorganic film, the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer, and solder wettability.

FIG. 3 is a view showing the relation between the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer and P+Zn+Mg deposited amount and the change in appearance.

FIG. 4 is a view showing the relation between the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer and the whisker-proof property.

#### BEST MODE FOR WORKING THE INVENTION

Below, the range of limitation of the present invention will be explained.

FIG. 1 shows the surface layer structure of a cross section of the layers of a surface treated steel sheet of a product of the present invention. In the figure, numeral 1 designates an Sn-Zn alloy layer on a steel sheet (not shown) or an Sn-Zn alloy layer of the surface layer of a surface treated layer having an Ni plated layer or Fe-Ni diffused layer (not shown) at the steel sheet interface, while 2 designates an inorganic coating mainly composed of phosphoric acid-zinc-magnesium, the characteristic feature in the present invention, on the Sn-Zn alloy layer. The Sn-Zn alloy layer is the layer which constitutes the basis of the present invention, and the deposited amount is required to be at least  $3.0 \text{ g/m}^2$  or more from the viewpoint of the solder wettability and rust-proof property. The upper limit thereof is not particularly determined in the present invention, but about  $50 \text{ g/m}^2$  is general from the relation with the cost.

As methods for forming an Sn-Zn alloy layer, in addition to electroplating a steel sheet with Sn and Zn, then applying thermal diffusion treatment, there are a method of directly coating a steel sheet with Sn-Zn alloy using electroplating and a method of dipping a steel sheet in a molten Sn-Zn bath, namely the hot dipping method. Further, by using an Ni plated substrate steel sheet as said steel sheet in the above three methods as disclosed in Japanese Unexamined Patent Publication No. 2-270970 and Unexamined Patent Publication No. 3-183796, it is possible to form an Ni plated layer or an Fe-Ni diffusion layer at each interface on a steel sheet and an Sn-Zn alloy on the surface layer. The present invention does not particularly restrict the method for forming an Sn-Zn alloy layer. By forming an Ni plated substrate layer, when an Sn-Zn alloy layer is thin, the Sn-Zn alloy layer is made uniform and the rust-proof property improves.

Next, there are the restrictions related to the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer and an

inorganic coating mainly composed of phosphoric acid-zinc-magnesium. By forming on an Sn-Zn alloy layer having a deposited amount of  $3 \text{ g/m}^2$  or more and a Zn (weight)/Sn (weight) ratio of 0.01 or less an inorganic coating  
5 mainly composed of phosphoric acid-zinc-magnesium to a P+Zn+Mg deposited amount of 0.1 to  $100 \text{ mg/m}^2$ , it becomes possible to suppress the growth of the oxide film after accelerating treatment such as retort treatment and to  
10 secure excellent solder wettability (FIG. 2) and stability of surface appearance (FIG. 3). Further, by setting the lower limit of a Zn (weight)/Sn (weight) ratio to not less than 0.001, it becomes possible to secure a good whisker-proof property as shown in FIG. 4.

FIG. 2 shows the relationships between the deposited  
15 amount of P+Zn+Mg of the inorganic coating mainly composed of phosphoric acid-zinc-magnesium of the surface layer, the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer, and solder wettability, when a deposited amount of an Sn-Zn alloy layer is  $5.0$  to  $20.0 \text{ g/m}^2$ . In  
20 this case, the solder wettability was evaluated by using a device to record the deterioration of a solder meniscus with age, employing Sn-Ag lead-free solder as the solder and two kinds of flux, inactive type and active type, as the flux, and measuring the wettability after test pieces  
25 were subjected to the accelerating treatment in a retort at  $105^\circ\text{C}$  for 8 hours. The results of the evaluation are expressed by "○" when the wet time (zero cross time) is within 3 seconds under the inactive flux, "□" when the same is within 3 seconds under the active flux, and "X"  
30 when the same is not less than 3 seconds under the active flux. As is shown in the figure, the range where the solder wettability is not less than 3 seconds is a Zn (weight)/Sn (weight) ratio of 0.1 or less and a P+Zn+Mg deposited amount of  $0.1 \text{ mg/m}^2$  or more, in particular, with  
35 a Zn (weight)/Sn (weight) ratio of 0.01 or less and a P+Zn+Mg deposited amount of 0.1 to  $10 \text{ mg/m}^2$ , an extremely

good wettability is obtained even under the inactive flux. With regard to the upper limit, it was confirmed there is a tendency to hinder the solder wettability when over 100 mg/m<sup>2</sup>. Therefore, the P+Zn+Mg deposited amount is limited to not more than 100 mg/m<sup>2</sup>. In the case of the inactive flux, not more than 10 mg/m<sup>2</sup> is preferable.

FIG. 3 shows the results regarding the Zn (weight)/Sn (weight) ratio of the Sn-Zn alloy layer and the index of change of appearance before and after a moisture resistance test (values measured by color difference meter: increase of b\* value). An increase of the b\* value before and after a moisture resistance test of less than 1.0 is evaluated as "○", of 1.0 to less than 2.0 as "△", and of 2.0 or more as "X". As shown in FIG. 3, in the range of a P+Zn+Mg deposited amount of the inorganic coating of 0.1 to 100 mg/m<sup>2</sup>, with a Zn (weight)/Sn (weight) ratio of 0.01 or less, almost no change in color difference can be observed, so the test piece is evaluated as "○". If over 0.01 to 0.1, a change in color difference is confirmed, so the test piece is evaluated as "△". Further, if over 0.1, the test piece is evaluated as "X".

FIG. 4 shows the result on the relation between the Zn (weight)/Sn (weight) ratio of an Sn-Zn alloy layer and the whisker-proof property. The test for evaluating the whisker-proof property was carried out by subjecting the test pieces to 90 degree bending and bulging processing, and then aging for 3 months in the atmosphere of 60°C in temperature and 90% in relative humidity which was similar to a moisture resistance test. The evaluation itself was carried out by visual inspection and a scan electron microscope, and the results of the evaluation are expressed by "○" when the occurrence of whiskers is less than 100 μm and "X" when the same is not less than 100 μm. As is shown in FIG. 4, with regard to the

whisker-proof property, the occurrence of whiskers is less than 100  $\mu\text{m}$  when the Zn (weight)/Sn (weight) ratio is not less than 0.001 without regard as to the P+Zn+Mg deposited amount of the inorganic coating.

5        From the above results, the range of the Zn (weight)/Sn (weight) ratio is limited to not less than 0.001 from the viewpoint of the whisker-proof property, not more than 0.1 from the viewpoint of the solder wettability under the active flux, and not more than 0.01  
10       from the viewpoint of the solder wettability under the inactive flux. The range of the P+Zn+Mg deposited amount of the inorganic coating is limited to 0.1 to 100  $\text{mg}/\text{m}^2$  (with inactive flux, up to 10  $\text{mg}/\text{m}^2$  is preferred).

15       Next, the limitations in the method of production of the inorganic coating mainly comprised of phosphoric acid-zinc-magnesium in the present invention will be explained.

20       Japanese Unexamined Patent Publication No. 2002-249885 proposes a surface treated steel sheet formed with an inorganic coating mainly comprised of magnesium phosphate over the Sn-Zn alloy layer. In this case, however, as shown in the examples, the method is disclosed of forming the Sn-Zn alloy layer, then post-treating the sheet by sulfuric acid and then dipping in a  
25       magnesium diphosphate solution. By removing the zinc oxide film on the Sn-Zn alloy layer by sulfuric acid in this way, the magnesium diphosphate solution will not react with the zinc and therefore an inorganic coating mainly comprised of magnesium phosphate is formed.  
30       However, in the present invention, by not removing the zinc oxide film on the Sn-Zn alloy layer and directly reacting the zinc oxide of the zinc oxide film and the magnesium diphosphate solution, an inorganic coating mainly comprised of phosphoric acid-zinc-magnesium is  
35       formed. As a result, a dense, stable (insoluble in water) coating is obtained. Even at the lower limit of 0.1  $\text{mg}/\text{m}^2$ , the antioxidation action can be maintained. Further, in

the production process, after the sheet is dipped in the magnesium diphosphate solution, it may be rinsed. The current rinsing and drying processes in continuous treatment line configurations can be used as they are.

5           The concentration of the treatment solution, that is, the magnesium diphosphate solution, should be within the range of 1 to 100 g/L to avoid problems, more preferably 10 to 50 g/L. Further, the unavoidable entering phosphoric acid, sulfuric acid, and other  
10       diphosphoric acid salts (Na, Ca, Al, NH<sub>4</sub>, etc.) are not particularly limited.

          Regarding the temperature of the treatment solution, this has a major effect on the direct reaction between the zinc oxide of the zinc oxide film on the Sn-Zn alloy  
15       layer and the magnesium diphosphate solution, so it is preferably a higher temperature. To end the reaction in a short time (10 seconds or less) on a continuous treatment line, 30°C or more is necessary. More preferably, the  
20       temperature is 50°C or more enabling a short, homogeneous reaction to be secured. The upper limit is 70°C or less where the amount of evaporation from the solution becomes great.

          Regarding the treatment method, dipping is preferable. Electrolysis is also possible, but the cost  
25       increases and the control of the current density is difficult since the amount deposited is extremely small. There are many practical problems to this.

          Regarding the rinsing and drying process after treatment, this is the same as the continuous treatment  
30       of general steel sheet. The drying temperature has to be 170°C or less in terms of the stability of the coating. If over 170°C, the hydrates in the coating will decrease and the bonding of the coating will fall. Therefore, the upper limit of the drying temperature is 170°C, more  
35       preferably generally 100°C or less.

#### EXAMPLES

The present invention will further be explained based on the examples hereunder. The evaluation results of the performances in the examples wherein detailed conditions are varied and the comparative examples are summarized in Table 1.

(Example 1)

Low carbon cold rolled steel sheets produced by cold rolling and annealing in a usual manner were subjected to degreasing and pickling, by a usual method, and then coated, in order, with Ni plating under the treatment conditions shown in the item (1), Sn plating under the treatment conditions shown in the item (2) and Zn plating under the treatment conditions shown in the item (3). In succession, the steel sheets were subjected to a heat treatment at a steel sheet surface temperature of 250 to 350°C for not less than 0.5 second in the atmosphere using an electric resistance heating method, and the Sn-Zn alloy coatings were formed thereon. Further, the steel sheets were formed with inorganic coatings mainly comprised of phosphoric acid-zinc-magnesium under the conditions shown in the item (4) and, after that, to various kinds of evaluation tests.

(1) Ni plating

(i) Bath conditions

$\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ : 200 to 300 g/L

$\text{H}_2\text{SO}_4$ : 0 to 50 g/L

$\text{H}_3\text{BO}_3$ : 40 g/L

(ii) Plating conditions

Bath temperature: 40 to 50°C

Current density: 5 to 30 A/dm<sup>2</sup>

(2) Sn plating

(i) Bath conditions

Tin sulfate: 20 to 30 g/L

Phenolsulfonic acid: 20 to 30 g/L

Ethoxylated  $\alpha$ -naphtholsulfonic acid: 2 to 3 g/L

(ii) Plating conditions

Bath temperature: 35 to 45°C

Current density: 2 to 30 A/dm<sup>2</sup>

(3) Zn plating

(i) Bath conditions

5 Bivalent Zn ions: 60 to 120 g/L

Phenolsulfonic acid: 50 to 150 g/L

Ethoxylated  $\alpha$ -naphthol: 2 to 7 g/L

(ii) Plating conditions

Bath temperature: 40 to 50°C

10 Current density: 5 to 30 A/dm<sup>2</sup>

(4) Treatment for forming phosphoric acid-zinc-magnesium layer

(i) Bath conditions

15 Magnesium diphosphate aqueous solution: 1 to 20 g/L

(ii) Treatment conditions

Bath temperature: 60 to 70°C (dip for 1 to 5 seconds)

(iii) Rinsing

20 Ordinary temperature (dip for 1 to 5 seconds)

(iv) Drying

100°C (5 seconds)

(Example 2)

25 Low carbon cold rolled steel sheets produced by cold rolling and annealing, in a usual manner, were subjected to degreasing and pickling by a usual method, and then, in order, coated with Ni plating under the treatment conditions shown in the item (1) of Example 1 and Sn-Zn alloy plating under the treatment conditions shown in the item (5) below and subjected to the treatment for forming an inorganic coating mainly comprised of phosphoric acid-zinc-magnesium under the conditions shown in the item (4) of Example 1 and, after that, to various kinds of evaluation tests.

35 (5) Sn-Zn alloy hot dip plating

(i) Bath conditions

Sn-Zn alloy (Zn (weight)/Sn (weight) ratio = 0.001 to 0.1)

(ii) Plating conditions

Bath temperature: 250 to 300°C

5 Dipping time: 1 second

Plating amount: 30 to 40 g/m<sup>2</sup> (wiping control)

(Example 3)

Low carbon cold rolled steel sheets produced by cold rolling and annealing in a usual manner were subjected to  
10 degreasing and pickling by a usual method, and then, in order, coated with Ni plating under the treatment conditions shown in the item (1) of Example 1, and Sn-Zn alloy plating under the treatment conditions shown in the item (6) and subjected to the treatment for forming an  
15 inorganic coating mainly comprised of phosphoric acid-zinc-magnesium under the conditions shown in the item (4) of Example 1 and, after that, to various kinds of evaluation tests.

(6) Sn-Zn alloy electroplating

20 (i) Bath conditions

Alkanolsulfonic acid: 10 to 200 g/L

Bivalent zinc ions: 1 to 50 g/L

Bivalent tin ions: 100 to 500 g/L

(ii) Plating conditions

25 Bath temperature: 50 to 60°C

Current density: 10 to 200 A/dm<sup>2</sup>

(Comparative Example 1-1)

A comparative example was prepared by applying a chromate treatment under the conditions shown in the item  
30 (7) below instead of the treatment shown in the item (4) of Example 1, with the other conditions being the same as Example 1.

(7) Chromate treatment

(i) Bath conditions

35 CrO<sub>3</sub>: 50 to 100 g/L

(ii) Bath temperature: 40 to 50°C (dip for 5 seconds)

(Comparative Example 1-2)

5 A comparative example prepared by eliminating the chromate treatment shown in the item (7) from Comparative Example 1-1, with the other conditions being the same as Example 1.

(Comparative Example 1-3)

10 A comparative example prepared by dipping in a sulfuric acid bath before the treatment shown in item (4) of Example 1, removing the zinc oxide film on the Sn-Zn layer. The other conditions are the same as Example 1.

(Comparative Example 1-4)

15 A comparative example prepared by dipping in a sulfuric acid bath before the treatment shown in item (4) of Example 1, removing the zinc oxide film on the Sn-Zn layer, and increasing the dipping time at the bath temperature of 60 to 70°C under the treatment conditions of item (4) to 10 to 15 seconds, with the other conditions being the same as Example 1.

(Comparative Example 1-5)

20 A comparative example prepared by making the rinsing and drying temperature after treatment under the treatment conditions of item (4) of Example 1 a temperature of 180°C, with the other conditions being the same as Example 1.

25 (Comparative Example 1-6)

A comparative example prepared by making the Zn (weight)/Sn (weight) ratio of the Sn-Zn alloy layer of Example 1 a ratio of 0.0005, with the other conditions being the same as Example 1.

30 (Comparative Example 2)

Electroplated tinplate having the Sn plating amount of 11.2 g/m<sup>2</sup> per each surface (referred to as "#100 tinplate").

(Comparative Example 3)

35 Lead plated steel sheet having the Pb plating amount of 30 g/m<sup>2</sup> per each surface (referred to as "terneplate").

The above-mentioned examples according to the present invention and comparative examples were subjected to the evaluation tests shown in the items (a) to (c) below and their properties were evaluated. It should be noted that, with regard to the examples, the Sn-Zn alloy plating amount ( $\text{g/m}^2$ ), Zn (weight)/Sn (weight) ratio, and the P+Zn+Mg deposited amount of the inorganic coating were measured by the methods shown in the items (1) to (3) below before they were subjected to the evaluation.

(a) Solder Wettability Test

The solder wettability test was carried out by using a device to record the deterioration of a solder meniscus with age (SWET-2100, manufactured by Tarutin Kester, Co., Ltd.), employing Sn-Ag-Bi lead-free solder (SA2515, manufactured by Tarutin Kester, Co., Ltd.) as the solder and two kinds of flux, non-chloride flux (NA200, manufactured by Tamura Giken Co., Ltd.) and active flux containing chlorine (NS828, manufactured by Nihon Superior Co., Ltd.) as the flux, and wettability was measured after the test pieces were subjected to the accelerating treatment in a retort at  $105^\circ\text{C}$  for 8 hours. The results of the evaluation are expressed by "○" when the wet time (zero cross time) is within 3 seconds under the inactive flux, "□" when the same is within 3 seconds under the active flux, and "X" when the same is not less than 5 seconds under the active flux.

(b) Whisker-Proof Test

The whisker-proof test was carried out by subjecting the test pieces to 90 degree bending and bulging processing, and then aging for 3 months in the atmosphere of  $60^\circ\text{C}$  in temperature and 90% in relative humidity of a moisture resistance test. The evaluation itself was carried out by visual inspection and by a scan electron microscope, and the results of the evaluation are expressed by "○" when the occurrence of whiskers is less than  $100\text{ }\mu\text{m}$  and "X" when the same is not less than  $1000$

μm.

(c) Appearance Change Test

The appearance change test was performed by aging a test piece in an atmosphere of 60°C and 90% relative humidity of a moisture resistance test for one month. The evaluation was performed by measurement of the  $b^*$  value by a color difference meter (made by Minolta Camera, CR-300) and judging a difference before and after the test of less than 2.0 as "○" and of 2.0 or more as "X".

10        <1> Deposited Amount of Sn-Zn Alloy Layer ( $\text{g}/\text{m}^2$ )

The masses of Sn and Zn were found using a fluorescent X-ray spectrometer from mass calibration curves prepared in advance. The sum was deemed the deposited amount of the Sn-Zn alloy layer.

15        <2> Zn (weight)/Sn (weight) Ratio

The Zn (weight)/Sn (weight) ratio was calculated from the masses of Sn and Zn obtained by the same method as shown in the item <1>.

20        <3> P+Zn+Mg Deposited Amount of Inorganic Coating

For P, the mass was found using a fluorescent X-ray spectrometer from the mass calibration curve prepared beforehand. For Mg, the mass was found using an atomic adsorption spectrometer from a mass calibration curve for a solution of the surface layer dissolved in acid.

25 Further, for the amount of Zn in the layer, the ratio of intensities of P and Zn in the surface layer was measured by Auger electron spectroscopy, and the amount of Zn was found by calculation from the amount of P. The sum of these was deemed the P+Zn+Mg deposited amount.

30        Table 1 shows the details and the evaluation results of the performances of the examples and comparative examples. Examples 1-1 to 1-4 are examples in which an Sn-Zn alloy layer is formed by electroplating followed by thermal diffusion alloying treatment, Examples 2-1 and 2-2 are examples of formation by hot dip plating, and  
35 Example 3 is an example of formation by alloy

electroplating.

Comparative Example 1-1 is an example of electroplating, then the thermal diffusion treatment, then formation of a chromate film, while Comparative Example 1-2 is an  
5 example of no chromate treatment. Comparative Examples 1-3 and 1-4 are examples of treating in a sulfuric acid before dipping in the magnesium diphosphate aqueous solution in Example 1-1. Comparative Example 1-5 is an  
10 example of making the drying temperature 180°C in the rinsing and drying step after the dipping in the magnesium diphosphate aqueous solution in Example 1-1. Comparative Example 1-6 is an example of making the Zn (weight)/Sn (weight) ratio of the Sn-Zn alloy layer in  
Example 1-1 a ratio of 0.0005. Comparative Examples 2 and  
15 3 show the cases of #100 tinplate and terneplate, respectively, which are the current comparative materials.

As seen in the examples, the layer mainly comprised of phosphoric acid-zinc-magnesium is better than chromate  
20 treatment in solder wettability, has no problems in change of appearance with aging, and exhibits excellent properties equal or better than those of the #100 tinplate and the terneplate which are included in the comparative examples.

Table 1

|                             | Method of production of Sn-Zn alloy layer | Sn-Zn alloy layer              |                               | Inorganic coating           |                                            | (a)<br>Solder wettability | (b)<br>Change in appearance | (c)<br>Whisker-proof property |
|-----------------------------|-------------------------------------------|--------------------------------|-------------------------------|-----------------------------|--------------------------------------------|---------------------------|-----------------------------|-------------------------------|
|                             |                                           | Deposition (g/m <sup>2</sup> ) | Zn (weight)/Sn (weight) ratio | Treatment conditions        | P+Zn+Mg deposition (mg/m <sup>2</sup> )    |                           |                             |                               |
| Ex. 1-1                     | Electroplating+ thermal diffusion         | 10                             | 0.001                         | (4)                         | 0.2                                        | ○                         | ○                           | ○                             |
| Ex. 1-2                     | "                                         | 10                             | 0.1                           | "                           | 2                                          | □                         | ○                           | ○                             |
| Ex. 1-3                     | "                                         | 15                             | 0.01                          | "                           | 1                                          | ○                         | ○                           | ○                             |
| Ex. 1-4                     | "                                         | 5                              | 0.1                           | "                           | 2                                          | □                         | ○                           | ○                             |
| Ex. 2-1                     | Electroplating+ hot dip plating           | 35                             | 0.01                          | "                           | 2                                          | ○                         | ○                           | ○                             |
| Ex. 2-2                     | "                                         | "                              | 0.001                         | "                           | 0.1                                        | ○                         | ○                           | ○                             |
| Ex. 3                       | Electro alloy plating                     | 10                             | 0.001                         | "                           | 1                                          | ○                         | ○                           | ○                             |
| Comp. Ex. 1-1               | Electroplating+ thermal diffusion         | 10                             | 0.1                           | (7)                         | Converted by metal Cr, 2 mg/m <sup>2</sup> | ×                         | ×                           | ○                             |
| Comp. Ex. 1-2               | "                                         | "                              | 0.1                           | None                        | 0                                          | ×                         | ×                           | ○                             |
| Comp. Ex. 1-3               | "                                         | "                              | 0.1                           | Sulfuric acid pretreatment  | P+Mg deposition 0.01                       | ×                         | ×                           | ○                             |
| Comp. Ex. 1-4               | "                                         | "                              | "                             | "                           | P+Mg deposition 0.1                        | ×                         | ×                           | ○                             |
| Comp. Ex. 1-5               | "                                         | "                              | 0.01                          | (4)<br>Drying 180°C         | 0.5                                        | ×                         | ×                           | ○                             |
| Comp. Ex. 1-6               | "                                         | "                              | 0.0005                        | (4)                         | 1                                          | ○                         | ○                           | ×                             |
| Comp. Ex. 2 (#100 tinplate) | "                                         | Sn=12                          | -                             | Dichromic acid electrolysis | Converted by metal Cr, 5 mg/m <sup>2</sup> | □                         | ○                           | ×                             |
| Comp. Ex. 3                 | Hot dip plating (terneplate)              | Pb+Sn=35                       | -                             | None                        | 0                                          | □                         | ○                           | ○                             |

CLAIMS

1. An environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging, comprising steel sheet or Ni plated steel sheet plated with Sn and Zn and then treated by thermal diffusion or plated with Sn-Zn alloy to form an Sn-Zn alloy layer, said surface treated steel sheet for electronic components characterized in that said Sn-Zn alloy layer is deposited in an amount of 3 g/m<sup>2</sup> or more, the Sn-Zn alloy layer has a Zn (weight)/Sn (weight) ratio of 0.001 to 0.1, and this Sn-Zn alloy layer has an inorganic coating mainly comprised of phosphoric acid-zinc-magnesium in a P+Zn+Mg deposited amount of 0.1 to 100 mg/m<sup>2</sup>.

2. An environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging as set forth in claim 1, characterized in that said Sn-Zn alloy layer as a Zn (weight)/Sn (weight) ratio of 0.001 to 0.01.

3. An environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging as set forth in claim 2, characterized in that the inorganic coating mainly comprised of phosphoric acid-zinc-magnesium on said Sn-Zn alloy layer has a P+Zn+Mg deposited amount of 0.1 to 10 mg/m<sup>2</sup>.

4. A method of production of an environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging as set forth in any one of claims 1 to 3, characterized by plating steel sheet or Ni plated steel sheet with Sn and Zn, then treating it by thermal diffusion or plating it with an Sn-Zn alloy to form an Sn-Zn alloy layer, then, without

removing a zinc oxide layer on the surface, dipping the sheet in a magnesium diphosphate solution at a temperature of 30°C to 70°C, then immediately rinsing it and drying it at 170°C or less.

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5. A method of production of an environmentally friendly surface treated steel sheet for electronic components excellent in solder wettability, whisker-proof property, stability of appearance with aging as set forth in claim 4, characterized by setting the dipping

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treatment temperature in the magnesium diphosphate solution at 50°C to 70°C and setting the drying temperature after the subsequent rinsing at 100°C or less.