

METHOD FOR POST-TREATMENT OF PLATED STEEL SHEET
FOR SOLDERING

The present invention relates to the post-treatment of plated steel sheet for soldering and especially to the post-treatment solution which exhibits excellent wettability and adhesive strength to solder, hereafter referred to as
5 solderability, as well as excellent corrosion resistance, formability and durability.

Recently, Sn plated steel sheet, Pb-Sn plated steel sheet, Cu plated steel sheet or Zn plated steel sheet have
10 been used as a plated steel sheet suitable for soldering. However, without post-treatment these plated steel sheets easily corrode during packing or after assembling. Therefore, post-treatments such as chromate treatment, phosphate treatment or coating with anti-corrosion primer
15 are applied to said steel sheets.

In the case of chromate treatment, it is not suitable because more than 0.1 mg/dm^2 of Cr^{6+} is necessary in order to provide sufficient corrosion resistance. However, in the case of more than 0.05 mg/dm^2 of Cr^{6+} , a strong flux is
20 necessary for soldering. The use of strong flux causes deterioration of the working environment and decrease of corrosion resistance of the soldered surface. Therefore, the amount of Cr^{6+} is limited to less than 0.05 mg/dm^2 and does not provide sufficient corrosion resistance.

25 On the other hand, the application of an anti-corrosion primer causes a decrease in solderability similar to

chromate treatment and also a decrease in the corrosion resistance of the soldered location.

There is some prior art relating to a process for production of plated steel sheet for soldering, for example, Japanese Patent Application Laid-Open No. Sho. 61-19793 and Japanese Patent Application Laid-Open No. Sho. 54-15432.

However, the present invention is different from these inventions with regard to construction and materials used.

Japanese Patent Application Laid-Open No. Sho. 61-19793

relates to a plated steel sheet having excellent solderability that is summarized as follows: Sn or Sn-Pb alloy is plated on the Zn or Zn type alloy plated steel sheet with the amount of deposit from 0.1 to 100 g/m².

However, the price of Sn is so expensive that the cost of production is high and use of Pb is undesirable from the viewpoint of environmental pollution. The present invention is different from this invention with regard to construction and materials used.

On the other hand, Japanese Patent Application Laid-Open No. Sho. 54-15432 relates to a post-treatment that is summarized as follows: Zn plated steel sheet is covered with acrylic resin from 0.5 to 20 μ m in thickness or paraffin wax from 2 to 20 μ m in thickness. The present invention is different from this invention with regard to materials used and effects on solderability and corrosion resistance.

BRIEF SUMMARY OF THE INVENTION

The electroplated steel sheet is coated with a solution or dispersion to give a dry thickness in the range of 0.02 to 2 μ m.

The solution or dispersion contains from 2 to 100 g/l of at least one water-soluble or water-dispersed material such as:

- 5 a. alkylphenols,
- b. condensates prepared from fatty acids and ethylene
 oxides,
- c. polyethylene glycol-alkylamines,
- d. esters prepared from sorbitan,
- 10 e. surfactants prepared from polypropylene glycols
 (as a hydrophobic group) and polyethylene glycols (as a
 hydrophilic group),
- f. amides prepared from fatty acids and diethanol
 amines, and
- 15 g. esters prepared from sucrose.

Hereinafter, unless otherwise stated, the term "solution" is used, for convenience, to cover both a solution and a dispersion.

Alternatively, there may be employed 2 to 100 g/l water-soluble or water-dispersed halogen-free solder flux such as

- 20 a. abietic acid,
- b. benzoic acid,
- c. saturated fatty acids having 12 to 24 carbon atoms,
- d. unsaturated fatty acids having 12 to 24 carbon atoms,
- e. organic alcohols having 2 to 400 carbon atoms,
- 25 f. esters of fatty acids,
- g. benzotriazole, and metal salts, ammonium
 salts and amine salts thereof.

The post-treatment solution may optionally further contain 1 to 50 g/l phosphoric ester.

The post-treatment solution may further contain 0.01 to 3 g/l of Cr^{6+} and/or 10 to 100 g/l of organic amine soap.

DETAILED DESCRIPTION OF THE INVENTION

The detailed method according to the present invention will be described below:

The main components of the present invention are selected from:

- a. alkylphenols,
- b. condensates prepared from fatty acids and ethylene oxides such as polyethylene glycol alkylphenyl ether, polyethylene glycol alkyl ether and polyethylene glycol-fatty acid esters,
- c. polyethylene glycol-alkylamines such as N-polyethylene glycol-alkyl amine and polyethylene glycol-alkyl ether,
- d. esters prepared from sorbitan and fatty acids including sorbitan-fatty acid ester and polyethylene glycol-sorbitan fatty acid ester,
- e. surfactants prepared from polypropylene glycol (as hydrophobic group) and polyethylene glycol (as hydrophilic group) such as polypropylene glycol-polyethylene glycol ether,
- f. amides prepared from fatty acid and diethanol amines such as fatty acid-diethanol amides, and

g. esters prepared from fatty acids and sucrose such as sucrose-fatty acid esters.

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As the solder flux without halogen there may be mentioned:

- a. abietic acid,
- b. benzoic acid,
- 10 c. saturated fatty acids which have 12 to 24 carbon atoms, such as stearic acid, lauric acid, palmitic acid,
- d. unsaturated fatty acids which have 12 to 24 carbon atoms such as oleic acid,
- e. organic alcohols having 2 to 400 carbon atoms such as
- 15 fatty alcohols, glycerol, ethylene glycol and polyethylene glycol,
- f. esters of fatty acids such as fatty acid-glycerol esters,
- g. benzotriazole

- 20 Phosphoric esters including soaps with organic amines or mono-basic or di-basic acids with one or two alkyl groups may be used.

If the alkyl group is large and is not soluble in water, it is possible to add ethylene oxide or neutralize
25 with alkali in order to improve the hydrophilic properties.

The effects of the present invention are controlled by the amount of coating on the plated sheet,

and are not influenced by concentration of post-treatment solution. However, a specified concentration is preferred in order to facilitate operation. Halogen ion is not preferred because it decreases corrosion resistance.

5 In order to stabilize the post-treatment solution and to improve the corrosion resistance and abrasion resistance, Cr^{6+} and/or a soap of an organic amine are used. A concentration of Cr^{6+} over 3 g/l remarkably decreases solderability and is not suitable.

10 Soaps of organic amines include dodecylamine, oleoyl imidazoline, aminopropyl beef tallow amine, rosin amine. The amine may be used as a salt with carbonic acid. The concentration of amine over 100 g/l has some effects on corrosion resistance but less effect on solderability and is
15 not preferred.

Moreover, well-known water-soluble or water-dispersible anti-corrosion agents are available, but in this case, it is important to restrict the amount of addition in order not to decrease the solderability. For example addition of acrylic
20 emulsion increases the abrasion resistance but inversely decreases the solderability.

The pH value of the solution is suitably in the range of from 3 to 10. If the pH of the solution is under 3, the stability of the solution decreases. If the pH of the
25 solution is over 10, drying properties of the post-treatment decrease.

The temperature of the post-treatment is not limited, however, at over 80°C, the stability of the post-treatment

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solution decreases, resulting in gelation. An ordinary temperature in the range from 20 to 40°C is suitable and economical.

The coating method is not restricted and roll-coating, 5 knife-coating, dipping followed by wringer roll or air-knife treatment are used. The post-treatment product must be sufficiently dry to be handled.

The dry film thickness in the range of 0.02 to 2 μm is suitable. A dry film thickness below 0.02 μm , has no 10 effects on the corrosion resistance. At a dry film thickness above 2 μm , corrosion resistance increases but solderability does not increase.

In the present invention, the post-treatment solution which may further contain Cr^{6+} or organic amine soap, can be 15 applied on an Sn plate, Pb-Sn plate, Cu plate or Zn plate. Solderability and corrosion resistance of said steel sheets increase, even after aging. Steel sheets are not restricted to said steel sheet.

U The reason why the properties of the coated steel sheet 20 of the present invention improve, has not been clarified. However, formation of oxides, hydroxides and carbonates is inhibited by coating the present post-treatment solution on said plated steel sheet.

Moreover, it is considered that since the present 25 post-treatment dissolves or reduces the metal oxides which have formed on the plated steel sheet over time, the wetting and diffusion of solder are promoted and solderability is improved. According to said phenomenon, the present

post-treatment film covers the plated steel sheet uniformly and increases the corrosion resistance.

The present invention is based on the above-mentioned concept. By coating the present post-treatment solution on the plated steel sheet uniformly, a plated steel sheet having excellent solderability and corrosion resistance can be continuously produced.

Specific embodiments of the present invention are as follows:

EXAMPLE 1

A cold-rolled steel sheet having thickness of 0.5 mm was used as the substrate and was treated by ordinary alkali cleaning and pickling. After water spraying, the substrates were electroplated in a sulfuric acid bath at the weight of 5 g/m² of Zn deposit and were treated in accordance with the present invention. In this regard, a post-treatment solution containing 10 g/l of ammonium stearate, 20 g/l of glycerol and 5 g/l of paraffin wax was coated on the Zn plated steel sheet by a dipping method and the thus-coated steel sheet was dried at the temperature of 60°C to form a coating of 0.5 μm thickness thereon.

Examples 2-13 of the present invention were treated according to the same procedure as Example 1, except for the type and amount of deposit and post-treatment.

COMPARATIVE EXAMPLE I

The same substrates as in Example 1 were treated by ordinary alkali cleaning and pickling. After water spraying, the substrate was electroplated in a sulfuric acid

bath at the weight of 10 g/m^2 of Zn deposit and was electroplated in a phenolsulfonic acid bath (40°C , 30A/d m^2) according to Japanese Laid-Open Patent Application No. Sho 61-19793.

5 Comparative Example 2 was performed according to Japanese Laid-Open Patent Application No. Sho 54-15432. Comparative Examples 3-12 were performed according to the same procedure as Comparative Example 2, except for the type and amount of the deposit and post-treatment. The
10 conditions for the post-treatments were summarized in Table 1 and the evaluation of properties was summarized in Tables 2 and 3.

As shown in Tables 2 and 3, post-treatment solution of this invention showed excellent effects on corrosion
15 resistance, solderability and aging tests. Ordinary chemical treatments such as chromate treatment or phosphate treatment (Comparative Examples 3-5) showed effects on corrosion resistance but decreased the wettability of the
20 solder particularly after aging. Furthermore, the color of the surface after aging had changed and decreased the corrosion resistance.

Comparative Examples 6-8, which lacked the phosphate esters or Cr^{6+} from Examples 6-8, showed excellent solderability, but inferior effects on corrosion resistance and solderability was decreased after aging.

25 Comparative Examples 9-11, which contained halogen in the fluxes for soldering, showed poor corrosion resistance and inferior effects on solderability after aging compared to the present post-treatment.

As mentioned in Examples 1-13, in Table 1 and 2, excellent corrosion resistance, solderability and formability were obtained and these properties are retained after aging of plated steel sheet, by using the present invention.

Evaluation: The metal substrates which were prepared in Examples 1-13 and Comparative Examples 1-12 were evaluated by the following test methods. The results were shown in Tables 1 and 2.

(1) Spreadability of solder: a sample steel sheet, 50 x 50 mm in size, was floated on the solder-bath at a temperature of 250°C. The amount of 0.4 g of bended wire solder, that is, resin flux cored solder (JIS Z 3283) was placed on the sample steel sheet for 30 seconds. The area of solder spread was measured after cooling.

○: Area of spread solder $> 200\text{mm}^2$

△: $200\text{mm}^2 > \text{area of spread solder} > 50\text{mm}^2$

×: Area of spread solder $< 50\text{mm}^2$

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(2) Combination strength of solder: a bundle of twenty wires ($\phi=0.18\text{mm}$) was placed on the test steel sheet and joined with the resin flux solder (RH 50) and was subjected to a pull off test (Bundle of twenty copper wires and solder steel sheet were pulled in opposite directions and evaluated as to the appearance of separated place).

○: No separation among wire, solder and soldered steel sheet

×: Separation between, wire and solder, or solder and soldered steel sheet

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(3) Corrosion resistance: a sample steel sheet was subjected to 2 cycles of a salt spray test (JIS Z 2371: salt spray 8 hours and dry 16 hours) and evaluated from generation of red rust.

5 ○: No red rust

 X: entirely red rust

(4) Formability: sample steel sheets were subjected to the Erichsen test (Er=7 mm) and Du Pont impact test (1/2" x 1kg x 30 cm) and were evaluated as to formability by the
10 adhesive tape test.

 ○: No separation between plated steel sheet and post-treatment

 X: Separation between plated steel sheet and post-treatment

15 (5) Aging: sample steel sheets were subjected to a thermo-hygrostat(60°C, RH 95%) for 1,000 hours and evaluated as to the appearance (or color change), corrosion resistance and solderability in the same way as in evaluations (1)-(4).

Table 1 : Preparation and Condition of Specimens

Example	Type of Plating	Amount of Deposit (g/m ²)	Post-treatment Solution of This Invention (g/l)	Thickness (μm)
1	Zn plated	5	ammonium stearate 10 glycerol 20 paraffin wax 5	0.5
2	Zn plated	10	derivative of benzotriazole 2 salt of phosphoric ester and amine 1 CrO ₃ 0.2	0.05
3	Sn plated	5	oleic acid 50 phosphoric ester 10	3
4	Cu plated	3	ester prepared from fatty acid and glycerol 20 paraffin wax 10	0.2
5	Sn-Pb plated	10	ethylene glycol 30 CrO ₃ 1	1
6	Zn plated	5	polyethylene glycol alkylphenyl ether (Emaruzitto-16: Daiichikogyo Seiyaku Co.LTD) 10 CrO ₃ 1	0.5
7	Zn plated	10	polypropylene-glycol polyethylene-glycol ether (Epan-720:Daiichikogyo Seiyaku Co.LTD) 100 phosphoric ester 5	0.5
8	Sn plated	2	polyethylene glycol oleate ester (Noigen-ES90:Daiichikogyo Seiyaku Co.LTD) 2 CrO ₃ 0.02	2
9	Sn plated	5	polyethylene glycol stearate (Noniolite-T40:Kyoeisya Yushi Co.LTD) 5 phosphoric ester 1	0.02
10	Cu plated	3	sorbitan oleate (Noniolite-SPS: Kyoeisya Yushi Co.LTD) 50 CrO ₃ 1	0.2
11	Sn-Pb plated	10	polyoxyethylene alkylpropylene diamine (Noniolite-DNT-10:Kyoeisya Yushi Co.LTD) 10 CrO ₃ 1	0.5
12	Zn plated	5	phosphoric ester (monobasic) 100 CrO ₃ 0.02	2

Table 1 : Preparation and Condition of Specimens

Example	Type of Plating	Amount of Deposit (g/m ²)	Post-treatment Solution of This Invention (g/l)	Thickness (μm)
1 2	Sn plated	2	phosphoric ester 5 CrO ₃ 3 Rosin (amine salt) 10	0.01
1 3	Cu plated	3	phosphoric ester 50 dodecylamine 100	0.5
Compara- tive Example 1	Zn plated	10	Sn plated (according to Japanese Pat. Application No Sho 61-19793) 0.5	---
2	Zn plated	10	paraffin wax (according to Japanese Pat. Application No Sho 54-15432) 100	3
3	Sn plated	5	phosphate treatment	2 g/m ² as P
4	Sn plated	5	chromate treatment	0.05mg/dm ² as Cr
5	Cu plated	3	chromate treatment	0.05mg/dm ² as Cr
6	Zn plated	5	same as example 6 except CrO ₃	0.5
7	Zn plated	10	same as example 7 except phosphoric ester	2
8	Sn plated	2	same as example 8 except CrO ₃	0.02
9	Zn plated	5	aniline hydrochloride 20	dipping (1 sec.)
1 0	Zn plated	10	substituted by hydrazinium hydrochlo- ride for benzotriazole in example 2	0.02
1 1	Zn plated	2	substituted by Sn(IV)chloride for paraffin wax	0.05mg/dm ² as Cr
1 2	Zn plated	10	-----	----

Table 2 : Evaluation of Characteristics

Sample Number	Corrosion Resistance	Solderability		Formability	Change of Color
		Spreadability	Strength		
Example 1	○	○	○	○	○
2	○	○	○	○	○
3	○	○	○	○	○
4	○	○	○	○	○
5	○	○	○	○	○
6	○	○	○	○	○
7	○	○	○	○	○
8	○	○	○	○	○
9	○	○	○	○	○
10	○	○	○	○	○
11	○	○	○	○	○
12	○	○	○	○	○
13	○	○	○	○	○
Comparative Example 1	Δ-○	○	○	○	Δ-○
2	○	Δ	Δ	○	○
3	Δ	X	X	○	Δ-○
4	X	○	○	○	Δ
5	Δ	○	○	○	X
6	X	○	○	○	X
7	X	○	○	○	X
8	X	○	○	○	X

Table 2: Evaluation of Characteristics

Sample Number	Corrosion Resistance	Solderability		Formability	Change of Color
		Spreadability	Strength		
Comparative Example 9	X	○	○	○	X
10	X	○	○	○	X
11	X	○	○	○	X
12	X	○	○	○	X

Table 3 : Evaluation of Characteristics After
1,000 Hours Aging

Sample Number	Corrosion Resistance	Solderability		Formability
		Spreadability	Strength	
Example 1	○	○	○	○
2	○	○	○	○
3	○	○	○	○
4	○	○	○	○
5	○	○	○	○
6	○	○	○	○
7	○	○	○	○
8	○	○	○	○
9	○	○	○	○
10	○	○	○	○
11	○	○	○	○
12	○	○	○	○
13	○	○	○	○
Comparative Example				
1	△	X	X	○
2	△	X	X	○
3	△	X	X	○
4	X	X-△	X-△	○
5	△	X	X	○
6	X	△	△	○
7	X	△	△	○
8	X	△	△	○

Table 3 : Evaluation of Characteristics After
1000 Hours Aging

Sample Number	Corrosion Resistance	Solderability		Formability
		Spreadability	Strength	
Comparative Example				
9	X	Δ	Δ	○
10	X	Δ	Δ	○
11	X	Δ	Δ	○
12	X	Δ	Δ	○



CLAIMS:

1. A method of treating plated steel sheet in preparation for soldering by providing a coating thereon having a dry thickness of 0.02 to 2 μm ,

said coating being formed by applying a solution or dispersion containing 2 to 100 g/l of at least one of the following water-soluble or water-dispersed materials:

- a. alkylphenols,
- b. condensates prepared from fatty acids and ethylene oxides,
- c. polyethylene glycol-alkylamines,
- d. esters prepared from sorbitan,
- e. surfactants prepared from polypropylene glycol as a hydrophobic group and polyethylene glycol as a hydrophilic group,
- f. amides prepared from fatty acid and diethanol amine, and
- g. esters prepared from sucrose, and

the pH value of said solution being from 3 to 10.

2. A method of treating plated steel sheet in preparation for soldering by providing a coating thereon having a dry thickness in the range of 0.02 to 2 μm , said coating being formed by applying a solution or dispersion containing 2 to 100 g/l of at least one of the following water-soluble or water-dispersed materials:

- a. abietic acid,
- b. benzoic acid,
- c. saturated fatty acids having 12 to 24 carbon atoms,



d. unsaturated fatty acids having 12 to 24 carbon atoms,

e. organic alcohols having 2 to 400 carbon atoms,

f. esters of fatty acids,

g. benzotriazoles, and metal salts, ammonium salts or amine salts thereof, and

the pH of said solution being from 3 to 10.

3. The method according to claim 1, wherein said solution or dispersion contains from 1 to 50 g/l phosphoric ester or from 0.01 to 3 g/l of Cr^{6+} or both phosphoric ester and Cr^{6+} within the ranges given.

4. The method according to claim 2, wherein said post-treatment solution or dispersion contains from 1 to 50 g/l of phosphoric ester or from 0.01 to 3 g/l of Cr^{6+} or both phosphoric ester and Cr^{6+} within the ranges given.

5. The method according to claim 1, wherein the said solution or dispersion further contains from 10 to 100 g/l of organic amine soap.

6. The method according to claim 2, wherein the said solution or dispersion further contains from 10 to 100 g/l of organic amine soap.

7. Plated steel sheets coated with a layer 0.02 to 2 μm in thickness comprised of at least one water-soluble or water-dispersed material as defined in either of claims 1 and 2.

8. A method as claimed in any one of claims 1 to 6 in which the plated steel sheet so treated is subjected to a soldering step.



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9. The method of treating plated steel sheet as claimed in either of claims 1 and 2 substantially as herein described with reference to any one of the examples.

10. Coated plated steel sheets as claimed in claim 7 substantially as herein described with reference to any one of the examples.
