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(71) Applicant: **Nippon Steel Corporation**

Tokyo 100-8071 (JP)

(72) Inventors:

- **NISHIDA, Hiroshi**
Kitakyushu-shi, Fukuoka 804-0001 (JP)
- **HIRANO, Shigeru**
Kitakyushu-shi, Fukuoka 804-0001 (JP)

• **TACHIKI, Akira**

Kitakyushu-shi, Fukuoka 804-0001 (JP)

• **HAMAGUCHI, Shinsuke**

Kitakyushu-shi, Fukuoka 804-0001 (JP)

• **TAKAMIYA, Toshiaki**

Kitakyushu-shi, Fukuoka 804-0001 (JP)

• **YOKOYA, Hirokazu**

Kitakyushu-shi, Fukuoka 804-0001 (JP)

(74) Representative: **Vossius & Partner**

Siebertstrasse 4

81675 München (DE)

(54) **STEEL SHEET FOR CONTAINERS**

(57) A steel sheet for a container includes a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², Sn plating layer of 300 mg/m²~3000 mg/m² being plated on the Ni plating layer or the Fe-Ni alloy plating layer, the Ni plating layer, or some or all of the Fe-Ni alloy plating layer and part of the Sn plating being alloyed and a Sn plating layer being

partially left by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~500 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~100 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~100 mg/m² being formed on the alloyed Sn plating layer and the left Sn plating layer.

EP 2 006 416 A1

Description

[Technical Field]

[0001] The present invention relates to a steel sheet for a container which is excellent in, as a material for use in manufacturing a can, drawing-ironing, weldability, corrosion resistance, paints adhesion and film adhesion. This application is based on Japanese Patent Application Nos. 2006-091353 and 2007-069262, the contents of which are incorporated herein by reference.

[Background Art]

[0002] A metal container used for beverages and foods may be classified into a 2-piece can and a 3-piece can. For the 2-piece can, which is represented by a DI can, drawing-ironing is performed, and then a can inner side is painted while a can outer side is painted and printed. In addition, for the 3-piece can, a can inner side is painted, a can outer side is printed, and then a can body is welded.

It is essential for both types of cans to perform the painting process before or after manufacturing the can. Solvent-based paints or water-based paints are used for the painting, and then the printing process is performed. In the painting process, waste (wasted solvent), which is derived from the paints, is discharged as industrial waste, and exhaust gas (mainly carbonic acid gas) is emitted into the air. Recently, an effort to reduce industrial waste and exhaust gas has been made to preserve the global environment. As part of such an effort, a technique to laminate a film comes into the spotlight and has rapidly spread to replace the painting process.

[0003] Hitherto, there have been proposed various methods and related inventions for manufacturing a 2-piece can by laminating a film. For example, Patent Document 1 discloses a method for manufacturing a drawing-ironing can. In addition, Patent Document 2 discloses a drawing-ironing can. In addition, Patent Document 3 discloses a method for manufacturing a thin-walled deep drawing can. In addition, Patent Document 4 discloses a coating steel sheet for a drawing-ironing can.

In addition, for the 3-piece can, Patent Document 5 discloses a film laminated steel strip for a 3-piece can and a method for manufacturing the same. In addition, Patent Document 6 discloses a steel sheet for a 3-piece can having a multi-layered organic film laminated on an outer side of the can. In addition, Patent Document 7 discloses a steel sheet for a 3-piece can having a stripe-shaped multi-layered organic film. In addition, Patent Document 8 discloses a method for manufacturing a 3-piece can stripe laminate steel sheet.

[0004] On the other hand, a chromate film which is subjected to an electrolytic chromate process is used for a steel sheet used as a base of a laminate film in most cases. The chromate film has a two-layered structure including a metal Cr layer and a hydrated oxidation Cr layer formed thereon. Accordingly, the laminate film (an adhesive layer if an adhesive is adhered to the film) secures adhesion with the steel sheet through the hydrated oxidation Cr layer of the chromate film. Although details of a mechanism of this adhesion are not obvious, it is known that this adhesion is obtained by a hydrogen bond of a hydroxyl group of the hydrated oxidation Cr with a functional group, such as a carbonyl group or an ester group, of the laminate film.

[0005] The above-mentioned inventions can obtain an effect of reliably advancing the preservation of the global environment. On the other hand, cost and quality competition between materials such as PET bottles, bottles, paper and so on is intensified in a beverage container market, and there is a need for excellent adhesion and corrosion resistance over the conventional painting technique, and more excellent can manufacturing workability, particularly, film adhesion, worked film adhesion, corrosion resistance and so on for the above-described steel sheet for the laminate container.

[Patent Document 1] Japanese Patent, Publication No. 1571783

[Patent Document 2] Japanese Patent, Publication No. 1670957

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. H02-263523

[Patent Document 4] Japanese Patent, Publication No. 1601937

[Patent Document 5] Japanese Unexamined Patent Application, First Publication No. H03-236954

[Patent Document 6] Japanese Unexamined Patent Application, First Publication No. H03-113494

[Patent Document 7] Japanese Unexamined Patent Application, First Publication No. H05-111979

[Patent Document 8] Japanese Unexamined Patent Application, First Publication No. H05-147181

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0006] The present invention has been made in consideration of the above problems, and it is an object of the present invention to provide a steel sheet for a container, which is excellent in adhesion, corrosion resistance, weldability, can manufacturing workability and external appearance.

[Means for Solving the Problems]

[0007] The present inventors have reviewed use of a Zr film as a new film to replace a chromate film, discovered that the Zr film or a composite film including the Zr film and a phosphoric acid film or a phenol resin film forms a very strong covalent bond with paints or a laminate film, which may result in excellent can manufacturing workability over a conventional chromate film, and made the present invention based on the discovery as follows.

[0008] (1) A steel sheet for a container, including a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², Sn plating layer of 300 mg/m²~3000 mg/m² being plated on the Ni plating layer or the Fe-Ni alloy plating layer, the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating being alloyed and a Sn plating layer being partially left by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~500 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~100 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~100 mg/m² being formed on the alloyed Sn plating layer and the left Sn plating layer.

[0009] (2) A steel sheet for a container, including a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², Sn plating layer of 300 mg/m²~3000 mg/m² being plated on the Ni plating layer or the Fe-Ni alloy plating layer, the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating being alloyed and a Sn plating layer being partially left by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~15 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~15 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~15 mg/m² being formed on the alloyed Sn plating layer and the left Sn plating layer.

[0010] (3) A steel sheet for a container, including a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², Sn plating layer of 300 mg/m²~3000 mg/m² being plated on the Ni plating layer or the Fe-Ni alloy plating layer, the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating being alloyed and a Sn plating layer being partially left by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~9 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~8 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~8 mg/m² being formed on the alloyed Sn plating layer and the left Sn plating layer.

[0011] (4) A steel sheet for a container, including a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, part of the Sn plating layer being alloyed by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~500 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~100 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~100 mg/m² being formed on the alloyed Sn plating layer.

[0012] (5) A steel sheet for a container, including a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, part of the Sn plating layer being alloyed by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~15 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~15 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~15 mg/m² being formed on the alloyed Sn plating layer.

[0013] (6) A steel sheet for a container, including a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, part of the Sn plating layer being alloyed by a tin melting process, and two or more of a Zr film including the amount of Zr of 1 mg/m²~9 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~8 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~8 mg/m² being formed on the alloyed Sn plating layer.

[0014] (7) In the steel sheet for a container according to one of the above (1) to (6), two or more of the Zr film, the phosphoric acid film and the phenol resin film may be formed by a cathode electrolysis process.

[0015] (8) In the steel sheet for a container according to one of the above aspects (1) to (6), all of the Zr film, the phosphoric acid film and the phenol resin film may be formed by a cathode electrolysis process.

[0016] (9) In the steel sheet for a container according to the above aspect (7) or (8), the cathode electrolysis process

may be performed in an acid solution or a tannin acid-contained acid solution.

[Effects of the Invention]

- 5 **[0017]** The steel sheet for a container of the present invention has excellent drawing-ironing, weldability, corrosion resistance, paints adhesion, film adhesion and external appearance.

[Best Mode for Carrying Out the Invention]

- 10 **[0018]** Hereinafter, a steel sheet of a container with excellent weldability, can manufacturing workability and external appearance according to an embodiment of the present invention will be described in detail.

An original sheet used in the present invention is not particularly limited but may typically use a steel sheet used as a material for a container. A manufacturing method and material quality of the original sheet are not particularly limited, but the original sheet is manufactured from a typical billet manufacturing process through hot rolling, pickling, cold rolling, annealing, skin pass rolling processes and so on. Although a metal surface treatment layer is formed on a surface of the steel sheet, a method of forming the layer is not particularly limited but may use, for example, an electroplating method, a vacuum deposition method, a sputtering method or others methods known in the art, and further may be combined with a heating process to form a diffusion layer.

- 15 **[0019]** In the present embodiment, as one form of the metal surface treatment layer, an Ni plating layer including Ni of 5 mg/m²~150 mg/m², or a Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m² is formed on the surface of the steel sheet, Sn plating layer of 300 mg/m²~3000 mg/m² is plated thereon, and then, a tin melting process is performed to alloy part or all of the underlying Ni layer and part of the Sn plating layer while partially leaving the Sn plating layer. The purpose of performing the Ni or Fe-Ni plating process to form the Ni plating layer is to secure corrosion resistance. Since Ni is high corrosion resistant metal, the corrosion resistance of the alloy layer formed in the tin melting process can be enhanced by plating Ni on the surface of the steel sheet. The amount of Ni used is necessary to be more than 5 mg/m² since the effect of Ni on enhancement of the corrosion resistance of the alloy layer appears when the amount of Ni is more than 5 mg/m². The effect of enhancement of the corrosion resistance of the alloy layer increases with increase of the amount of Ni. However, if the amount of Ni exceeds 150 mg/m², the enhancement effect is saturated. In addition, Since Ni is expensive, it is uneconomical to plate Ni of more than 150 mg/m². Accordingly, it is preferable to plate Ni of 5 mg/m²~150 mg/m².

- 20 **[0020]** In addition, if an Ni diffusion layer is to be formed, although a diffusion process is performed to form the Ni diffusion layer in an annealing furnace after plating Ni, even when nitriding treatment is performed before or after the Ni diffusion process or at the same time of the Ni diffusion process, the effect of Ni on the Ni plating layer and the effect of a nitriding treatment layer can be obtained. The electroplating method generally known in the art may be used as the Ni plating and Fe-Ni alloy plating methods.

- 25 **[0021]** The Sn plating process is performed after the Ni plating. The Sn plating used herein is a plating using metal Sn, however impurities may be inevitably mixed into the Sn plating or a very small amount of element may be added to the Sn plating. The Sn plating method is not particularly limited and may be the electroplating method known in the art or a method of digesting and plating melted Sn. The purpose of Sn plating is to secure corrosion resistance and weldability. Since Sn has high corrosion resistance, a Sn alloy formed in the tin melting process, which will be described later, as well as Sn metal shows excellent corrosion resistance. The excellent corrosion resistance of Sn is remarkably enhanced when the amount of Sn is more than 300 mg/m². The corrosion resistance of Sn increases with increase of the amount of Sn plating, but if the amount of Sn plating exceeds 3000 mg/m², the effect of Sn is saturated. Accordingly, it is preferable to set the amount of Sn plating to be less than 3000 mg/m² from an economical point of view.

- 30 **[0022]** In addition, since Sn has low electric resistance and is pressed and spread between electrodes in welding, thereby securing a stable electrical conduction area, Sn shows excellent weldability. The excellent weldability is shown when the amount of Sn exceeds 100 mg/m². In addition, if the amount of Sn plating falls within a range according to the present invention, there is no need to define the upper limit of the amount of Sn. Accordingly, in consideration of the two points, the amount of Sn plating is defined to be 300 mg/m²~ 3000 mg/m².

- 35 **[0023]** The tin melting process is performed after the Sn plating. The purpose of tin melting process is to melt Sn and alloy the melted Sn with an underlying steel sheet or underlying metal to form a Sn-Fe or Sn-Fe-Ni alloy layer, enhance corrosion resistance of the alloy layer, and leave Sn metal partially. The metal tin may be left in various forms of island, pool, stripe and so on. By controlling the tin melting process to leave the Sn metal partially, it is possible to obtain a steel sheet having a plating structure in which the Sn-Fe or Sn-Fe-Ni alloy layer having excellent paints and film adhesion is partially exposed.

In addition, as another form of the metal surface treatment layer of the present invention, Sn of 560 mg/m²~5600 mg/m² is plated on the surface of the steel sheet and some of the Sn plating layer is alloyed by the tin melting process. Although Sn has excellent workability, weldability and corrosion resistance, Sn of more than 560 mg/m² is needed from a viewpoint

of corrosion resistance. The corrosion resistance increases with increase of the amount of Sn plating, but if the amount of Sn plating exceeds 5600 mg/m^2 , the effect of Sn is saturated. Accordingly, it is preferable to set the amount of Sn plating to be less than 5600 mg/m^2 from an economical point of view. In addition, by performing the tin melting process after the Sn plating, the Sn alloy layer is formed to further enhance the corrosion resistance.

[0024] Two or more of a Zr film, a phosphoric acid film and a phenol resin film are formed on the metal surface treatment layer.

The Zr film, the phosphoric acid film and the phenol resin film may show an effect to some degree even when they are separately used, but do not show sufficiently practical performance. However, a composite film including two or more of the Zr film, the phosphoric acid film and the phenol resin film shows excellent practical performance. A composite film including the Zr film and one or more of the phosphoric acid film and the phenol resin film shows further excellent practical performance. In addition, if the amount of film is small, since the Zr film, the phosphoric acid film and the phenol resin film complement their respective characteristics, a composite film including all of the Zr film, the phosphoric acid film and the phenol resin film show more stable practical performance. A single film including two or more of Zr, phosphoric acid compound and phenol shows low practical performance of corrosion resistance and adhesion as compared to the composite film including two or more of the Zr film, the phosphoric acid film and the phenol resin film. The reason for this is not obvious, but it is believed that the mixture of Zr, phosphoric acid compound and phenol hinders performance of individual components.

[0025] The role of the Zr film is to secure the corrosion resistance and the adhesion. The Zr film is formed of Zr compounds such as Zr oxide, Zr hydroxide, Zr fluoride, Zr phosphate or the like, or a composite film including these components. The Zr compounds have excellent corrosion resistance and adhesion. Accordingly, the corrosion resistance and the adhesion increase with increase of the amount of the Zr film, and if the amount of Zr metal exceeds 1 mg/m^2 , the corrosion resistance and the adhesion are secured sufficiently from a practical point of view. In addition, although the increase of the amount of the Zr film enhances the corrosion resistance and the adhesion, if the amount of Zr in the Zr film exceeds 500 mg/m^2 , the Zr film gets too thick, which results in deterioration of the adhesion of the Zr film, and electric resistance increases, which results in deterioration of weldability. Accordingly, it is preferable to set the amount of Zr in the Zr film to be $1 \text{ mg/m}^2 \sim 500 \text{ mg/m}^2$.

[0026] In addition, since spots adhered to the film may appear as external appearance spots if the amount of Zr in the Zr film exceeds 15 mg/m^2 , it is more preferable to set the amount of Zr in the Zr film to be $1 \text{ mg/m}^2 \sim 15 \text{ mg/m}^2$. In addition, to more stabilize the external appearance spots, it is preferable to set the amount of Zr in the Zr film to be $0.1 \text{ mg/m}^2 \sim 9 \text{ mg/m}^2$.

[0027] The role of the phosphoric acid film is to secure the corrosion resistance and the adhesion. The phosphoric acid film is formed of Fe phosphate, Sn phosphate, Ni phosphate, Zr phosphate, or a film such as a phosphate-phenol resin film, or a composite film including these components. These phosphoric acid films have excellent corrosion resistance and adhesion. Accordingly, the corrosion resistance and the adhesion increase with increase of the amount of the phosphoric acid film, and if the amount of P exceeds 0.1 mg/m^2 , the corrosion resistance and the adhesion are secured sufficiently from a practical point of view. In addition, although the increase of the amount of the phosphoric acid film enhances the corrosion resistance and the adhesion, if the amount of P in the phosphoric acid film exceeds 100 mg/m^2 , the phosphoric acid film gets too thick, which results in deterioration of the adhesion of the phosphoric acid film, and electric resistance increases, which results in deterioration of weldability. Accordingly, it is preferable to set the amount of P in the phosphoric acid film to be $0.1 \text{ mg/m}^2 \sim 100 \text{ mg/m}^2$.

[0028] In addition, since spots adhered to the film may appear as external appearance spots if the amount of P in the phosphoric acid film exceeds 15 mg/m^2 , it is more preferable to set the amount of P in the phosphoric acid film to be $0.1 \text{ mg/m}^2 \sim 15 \text{ mg/m}^2$. In addition, to more stabilize the external appearance spots, it is preferable to set the amount of P in the phosphoric acid film to be $0.1 \text{ mg/m}^2 \sim 8 \text{ mg/m}^2$.

[0029] The role of the phenol resin film is to secure the adhesion. The phenol resin film has very excellent adhesion with paints or a laminate film since the phenol resin is an organic substance. Accordingly, the adhesion increases with increase of the amount of the phenol resin film, and if the amount of C exceeds 0.1 mg/m^2 , the adhesion is secured sufficiently from a practical point of view. In addition, although the increase of the amount of the phenol resin film enhances the adhesion, if the amount of C in the phenol resin film exceeds 100 mg/m^2 , electric resistance increases, which results in deterioration of weldability. Accordingly, it is preferable to set the amount of C in the phenol resin film to be $0.1 \text{ mg/m}^2 \sim 100 \text{ mg/m}^2$.

[0030] In addition, since spots adhered to the film may appear as external appearance spots if the amount of C in the phenol resin film exceeds 15 mg/m^2 , it is more preferable to set the amount of C in the phenol resin film to be $0.1 \text{ mg/m}^2 \sim 15 \text{ mg/m}^2$. In addition, to more stabilize the external appearance spots, it is preferable to set the amount of C in the phenol resin film to be $0.1 \text{ mg/m}^2 \sim 8 \text{ mg/m}^2$.

[0031] A method of forming the films as described above includes a method of digesting a steel sheet into an acid solution into which Zr ions, phosphoric ions and low molecular phenol resin are dissolved and a method using a cathode electrolytic process. In the digesting method, adhesion is irregular since various films are formed by etching a base. In

addition, this digesting method is disadvantageous in industrial respects since a long process time is taken. On the other hand, the cathode electrolysis method is very advantageous in industrial respects since it takes a short time, for example, several seconds to several ten seconds, to process a uniform film, in addition to effects of compulsory charge movement, surface cleaning by hydrogen generated at a steel sheet interface and promotion of adhesion by increase of pH. Accordingly, it is preferable to employ the cathode electrolytic method to form the Zr film, the phosphoric acid film and the phenol resin film.

In addition, if a tannin acid is added in the acid solution used in the digesting method and the cathode electrolysis method, the tannin acid is bonded to Fe, a tannin acid Fe film is formed on a surface, which results in enhancement of rust resistance and adhesion. Accordingly, depending on use, the films may be treated in the acid solution in which the tannin acid is added.

[0032] Hereinafter, embodiments of the present invention and comparative examples will be described and results are shown in the following tables 1 to 3. To begin with, a surface treatment layer is formed on a steel sheet having thickness of 0.17 mm~0.23 mm using following processes (1) to (3).

[0033] (1) After removing fat from an original sheet, which was already cold rolled, annealed and skin pass rolled, and pickling the original sheet, Sn is plated on the original sheet using a ferrosan bath. Thereafter, a tin melting process is performed to manufacture a Sn-plated steel sheet having a Sn alloy layer.

[0034] (2) After removing fat from an original sheet, which was already cold rolled, annealed and skin pass rolled, and pickling the original sheet, a Fe-Ni alloy is plated on the original sheet using a sulfuric acid-hydrochloric acid bath. Subsequently, Sn is plated on the Fe-Ni alloy using a ferrosan bath. Thereafter, a tin melting process is performed to manufacture a Ni, Sn-plated steel sheet having a Sn alloy layer.

[0035] (3) Ni is plated on a cold-rolled original sheet using a Watt bath, a Ni diffusion layer is formed in annealing, and after removing fat from the Ni diffusion layer and pickling the Ni diffusion layer, Sn is plated on the Ni diffusion layer using a ferrosan bath. Thereafter, a tin melting process is performed to manufacture a Ni, Sn-plated steel sheet having a Sn alloy layer.

[0036] After forming the surface treatment layer through the above processes, a Zr film, a phosphoric acid film and a phenol resin film are formed using following processes (4) to (11).

[0037] (4) The steel sheet is digested into a treatment solution in which Zr fluoride, phosphoric acid and phenol resin are dissolved, cathode-electrolyzed, and then dried to form the Zr film, the phosphoric acid film and the phenol resin film.

[0038] (5) The steel sheet is digested into a treatment solution in which phosphoric acid and phenol resin are dissolved, cathode-electrolyzed, and then dried to form the phosphoric acid film and the phenol resin film.

[0039] (6) The steel sheet is digested into a treatment solution in which Zr fluoride and phosphoric acid are dissolved, cathode-electrolyzed, and then dried to form the Zr film and the phosphoric acid film.

[0040] (7) The steel sheet is digested into a treatment solution in which Zr fluoride and phenol resin are dissolved, cathode-electrolyzed, and then dried to form the Zr film and the phenol resin film.

[0041] (8) The steel sheet is digested into a treatment solution in which Zr fluoride, phosphoric acid and tannin acid are dissolved, cathode-electrolyzed, and then dried to form the Zr film and the phosphoric acid film.

[0042] (9) The steel sheet is digested into a treatment solution in which Zr fluoride, phosphoric acid and phenol resin are dissolved, and then dried to form the Zr film, the phosphoric acid film and the phenol resin film.

[0043] (10) The steel sheet is digested into a treatment solution in which phosphoric acid and phenol resin are dissolved, and then dried to form the phosphoric acid film and the phenol resin film.

[0044] (11) The steel sheet is digested into a treatment solution in which Zr fluoride and phosphoric acid are dissolved, and then dried to form the Zr film and the phosphoric acid film.

[0045] For the above-processed samples, a performance evaluation is made in terms of following evaluation items (A)~(H). A sample is manufactured by laminating a 20 μ m thick PET film at temperature of 200°C, and a performance evaluation is made for the sample in terms of the following items (A)~(D).

(A) Workability

[0046] The 20 μ m thick PET film is laminated on both sides of the sample at temperature of 200°C, and can manufacturing work such as drawing and ironing are performed step by step. The performance evaluation for the sample is made in four steps (◎ : very good, ○ : good, Δ : a little scratched, and x : cut and work impossible).

(B) Weldability

[0047] The sample is welded while varying current under a condition of welding wire speed of 80 m/min using a wire seam welder, synthetic judgment is made from a proper current range from the minimum current from which sufficient welding strength can be obtained to the maximum current at which welding defects such as dusts and welding spatters are seen. The performance evaluation for the sample is made in four steps (◎ : very good, ○ : good, Δ : inferior, and

x : welding impossible).

(C) Film adhesion

5 [0048] The 20 μm thick PET film is laminated on both sides of the sample at temperature of 200°C, drawing-ironing is performed to manufacture a can, and a retort treatment is performed at 125°C for 30 min. The peeling of the film is evaluated in four steps (⊙ : no peeling, ○ : almost no peeling which is no problem in practical use, Δ : a little peeling, and x : mostly peeling).

10 (D) Paints adhesion

[0049] An epoxy-phenol resin is coated on the sample, printing is performed at 200°C for 30 min, and lattice eyes having depth reaching a binding band are inscribed at 1 mm intervals, and the sample is peeled using a tape. The peeling for the sample is evaluated in four steps (⊙ : no peeling, ○ : almost no peeling which is no problem in practical use, Δ : a little peeling, and x : mostly peeling).

(E) Corrosion resistance

20 [0050] An epoxy-phenol resin is coated on the sample, printing is performed at 200°C for 30 min, and cross cuts having depth reaching a binding band are inscribed, the sample is digested into a test solution as a mixture solution of 1.5% citric acid-1.5% salt at 45°C for 72 hours, cleaned, dried and peeled using a tape. Corrosion under film and corrosion of flat portion of the cross cuts are evaluated in four steps (⊙ : no corrosion under film, ○ : a little corrosion which is no problem in practical use, Δ : very little corrosion under film and a little corrosion of flat portion, and x : severe corrosion under film and somewhat corrosion of flat portion).

25 (F) Rust resistance

[0051] The sample is left alone for two months under an atmosphere of repeated drying and wetting (humidity of 90%, 2hr $\leftrightarrow$ humidity of 40%, 2hr). The rust for the sample is evaluated in four steps (⊙ : no rust, ○ : almost no rust which is no problem in practical use, Δ : a little rust, and x : mostly rust).

(G) External appearance

35 [0052] The sample is observed with the naked eye. Spots on the Zr film, the phosphoric acid film and the phenol resin film are evaluated in five steps (⊙⊙ : no spot, ⊙ : almost no spot which is no problem in practical use, ○ : a little spot, Δ : some spot, and x : remarkable spot).

(H) Condition of Sn metal

40 [0053] Sn is plated after Ni is plated, the tin melting treatment is additionally controlled, and then the Sn metal is observed using an optical microscope. The Sn metal is evaluated in three steps (○ : remaining throughout surface, Δ : partially remaining on surface, and x : no remaining).

[0054] For the amount of adhesion of the film, a quantitative analysis is made for the amount of Zr and P using fluorescent X-rays, and the amount of C is obtained by a total carbon measuring method.

45 [0055]

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[Table 1]

No.	Surface treatment layer				Zr, phosphoric acid, resin film				Evaluation						
	Treatment method	Amount of Ni (mg/m ²)	Amount of Sn (mg/m ²)	Remaining Sn	Treatment method	Amount of adhesion of Zr (mg/m ²)	Amount of adhesion of P (mg/m ²)	Amount of adhesion of C (mg/m ²)	Workability	Weldability	Film adhesion	Paints adhesion	Corrosion resistance	Rust resistance	External appearance
	1/3	5/150	300/3000		4/11	1/500	0.1/100	0.1/100							
		-	560/5600			1/15	0.1/15	0.1/15							
						1/9	0.1/8	0.1/8							
Embodiment 1	1	-	650	-	4	440	87	97	⊙	⊙-⊙	○	⊙	⊙	⊙	○
Embodiment 2	1	-	1400	-	6	240	95	-	⊙	⊙-⊙	○	⊙	⊙	⊙	○
Embodiment 3	1	-	2800	-	4	11	4	3	⊙	⊙	○	⊙	⊙	⊙	○
Embodiment 4	1	-	5200	-	5	-	0.4	9	⊙	⊙	○	⊙	⊙	⊙-⊙	⊙
Embodiment 5	2	15	2700	○	4	480	65	30	⊙	⊙-⊙	⊙	⊙	⊙	⊙	○
Embodiment 6	2	85	750	○	4	14	1.5	10	⊙	⊙	⊙	⊙	⊙	⊙	○
Embodiment 7	2	125	400	○	6	12	10	-	⊙	⊙	⊙	⊙	⊙	⊙	○
Embodiment 8	2	50	950	○	4	32	95	24	⊙	⊙	⊙	⊙	⊙	⊙	○
Embodiment 9	3	40	1000	○	4	240	15	88	⊙	⊙-⊙	⊙	⊙	⊙	⊙	○
Embodiment 10	3	20	2000	○	5	-	0.6	14	⊙	⊙	⊙	⊙	⊙	⊙-⊙	○
Embodiment 11	1	-	2800	-	5	-	87	94	⊙	○	○	⊙	⊙	⊙	○
Embodiment 12	1	-	2800	-	7	13	-	0.3	⊙	⊙	○	⊙	⊙	⊙-⊙	○
Embodiment 13	1	-	2800	-	6	3	13	-	⊙	⊙	○	⊙	⊙	⊙-⊙	○
Embodiment 14	2	85	750	○	5	-	10	7	⊙	⊙	⊙	⊙	⊙	⊙	○
Embodiment 15	3	125	1000	○	7	8	-	10	⊙	⊙	⊙	⊙	⊙	⊙	○
Embodiment 16	1	-	2800	-	8	11	1.5	0.5	⊙	⊙	○	⊙	⊙	⊙	○

[0056]

[Table 2]

No.	Surface treatment layer				Zr, phosphoric acid, resin film				Evaluation						
	Treatment method	Amount of Ni (mg/m ²)	Amount of Sn (mg/m ²)	Remaining Sn	Treatment method	Amount of adhesion of Zr (mg/m ²)	Amount of adhesion of P (mg/m ²)	Amount of adhesion of C (mg/m ²)	Workability	Weldability	Film adhesion	Paints adhesion	Corrosion resistance	Rust resistance	External appearance
Embodiment 17	2	85	750	○	8	8	2	0.7	⊙	⊙	○	⊙	⊙	⊙	⊙
Embodiment 18	1	-	650	-	9	423	86	85	⊙	⊙-⊙	○	○	⊙	⊙	○
Embodiment 19	1	-	1400	-	11	225	90	-	⊙	⊙-⊙	○	○	⊙	⊙	○
Embodiment 20	1	-	2800	-	9	14	4	4	⊙	⊙	○	○-⊙	⊙	⊙-⊙	⊙
Embodiment 21	1	-	5200	-	10	-	0.4	13	⊙	⊙	○	○-⊙	⊙-⊙	○-⊙	⊙
Embodiment 22	2	15	2700	○	9	425	85	85	⊙	⊙-⊙	○	○	⊙	⊙	○
Embodiment 23	2	85	750	○	9	14	4	4	⊙	⊙	○-⊙	○-⊙	⊙	⊙	○
Embodiment 24	2	125	400	○	11	10	10	-	⊙	⊙	○-⊙	○-⊙	⊙	⊙	○
Embodiment 25	2	50	950	○	9	3	12	12	⊙	⊙	○-⊙	○-⊙	⊙	⊙	○
Embodiment 26	3	40	1000	○	9	240	15	88	⊙	⊙-⊙	○	○	⊙	⊙	○
Embodiment 27	3	20	2000	○	10	-	0.5	13	⊙	⊙	○-⊙	○-⊙	○-⊙	○-⊙	○
Embodiment 28	1	-	2800	-	10	-	90	91	⊙	○	○	○-⊙	⊙	⊙	○
Embodiment 29	1	-	2800	-	11	2	12	-	⊙	⊙	○	○-⊙	○-⊙	○-⊙	○
Embodiment 30	2	85	750	○	10	-	10	10	⊙	⊙	○-⊙	○-⊙	○-⊙	○-⊙	○
Embodiment 31	1	-	650	-	5	-	7	5	⊙	⊙	○	○	○-⊙	○-⊙	⊙
Embodiment 32	1	-	1400	-	6	8	6	-	⊙	⊙	○	○-⊙	○-⊙	○-⊙	⊙
Embodiment 33	1	-	2800	-	7	5	-	4	⊙	⊙	○	○	○-⊙	○-⊙	⊙
Embodiment 34	1	-	5200	-	4	8	5	0.3	⊙	⊙	○	○	⊙	⊙	⊙
Embodiment 35	1	-	2000	-	4	6	0.4	6	⊙	⊙	○	○	⊙	⊙	⊙
Embodiment 36	1	-	1100	-	4	3	5	4	⊙	⊙	○	○	⊙	⊙	⊙
Embodiment 37	2	8	2700	○	5	-	6	6	⊙	⊙	○	○	○-⊙	○-⊙	⊙
Embodiment 38	2	85	750	○	6	7	7	-	⊙	⊙	○-⊙	○	○-⊙	○-⊙	⊙
Embodiment 39	2	125	400	○	7	6	-	6	⊙	⊙	○	○	○-⊙	○-⊙	⊙
Embodiment 40	2	50	950	○	4	7	6	0.4	⊙	⊙	○	○	⊙	⊙	⊙
Embodiment 41	3	40	1000	○	4	5	0.3	5	⊙	⊙	○	○	⊙	⊙	⊙
Embodiment 42	3	20	2000	○	4	2	4	6	⊙	⊙	○	○	⊙	⊙	⊙

[0057]

[Table 3]

No.	Surface treatment layer				Zr, phosphoric acid, resin film				Evaluation						
	Treatment method	Amount of Ni (mg/m ²)	Amount of Sn (mg/m ²)	Remaining Sn	Treatment method	Amount of adhesion of Zr (mg/m ²)	Amount of adhesion of P (mg/m ²)	Amount of adhesion of C (mg/m ²)	Workability	Weldability	Film adhesion	Paints adhesion	Corrosion resistance	Rust resistance	External appearance
Comparative example 1	1	-	400	-	6	3	-	-	⊙	⊙	○	○	Δ	Δ	⊙
Comparative example 2	2	2	350	○	7	0.8	-	3	⊙	⊙	x	x	x	x	⊙
Comparative example 3	3	7	200	○	5	-	0.07	3	⊙	Δ	⊙	⊙	Δ	Δ	⊙
Comparative example 4	2	85	450	○	7	5	-	0.05	X	X	Δ	Δ	Δ	X	⊙
Comparative example 5	2	85	750	○	4	40	115	120	x	x	x	x	x	Δ	Δ

[0058] As shown in the above tables 1 to 3, the embodiments 1 to 42 satisfy the conditions prescribed in the present invention. On the other hand, the above comparative examples 1 to 5 do not satisfy the conditions prescribed in the present invention. All the embodiments 1 to 42 obtain good evaluation results for all the evaluation items (A) to (H). Particularly, in the embodiments 31 to 42, two or more of the Zr film in which the amount of Zr is 0.1~9 mg/m², the phosphoric acid film in which the amount of P is 0.1~8 mg/m², and the phenol resin film in which the amount of C is 0.1~8 mg/m² are formed. On this account, it is possible to obtain excellent external appearance. On the other hand, the comparative examples 1 to 5 do not obtain good evaluation result for all the evaluation items (A) to (H).

[Industrial Applicability]

[0059] According to the present invention, it is possible to obtain a steel sheet for a container having excellent drawing-ironing, weldability, corrosion resistance, paints adhesion, film adhesion and external appearance.

Claims

1. A steel sheet for a container, comprising a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², wherein Sn plating layer of 300 mg/m²~3000 mg/m² is plated on the Ni plating layer or the Fe-Ni alloy plating layer, wherein the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating are alloyed and a Sn plating layer is partially left by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~500 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~100 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~100 mg/m² are formed on the alloyed Sn plating layer and the left Sn plating layer.
2. A steel sheet for a container, comprising a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², wherein Sn plating layer of 300 mg/m²~3000 mg/m² is plated on the Ni plating layer or the Fe-Ni alloy plating layer, wherein the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating are alloyed and a Sn plating layer is partially left by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~15 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~15 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~15 mg/m² are formed on the alloyed Sn plating layer and the left Sn plating layer.
3. A steel sheet for a container, comprising a Ni plating layer or a Fe-Ni alloy plating layer formed on a surface of the steel sheet, the Ni plating layer including Ni of 5 mg/m²~150 mg/m², and the Fe-Ni alloy plating layer including Ni of 5 mg/m²~150 mg/m², wherein Sn plating layer of 300 mg/m²~3000 mg/m² is plated on the Ni plating layer or the Fe-Ni alloy plating layer, wherein the Ni plating layer, or part or all of the Fe-Ni alloy plating layer and part of the Sn plating are alloyed and a Sn plating layer is partially left by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~9 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~8 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~8 mg/m² are formed on the alloyed Sn plating layer and the left Sn plating layer.
4. A steel sheet for a container, comprising a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, wherein part of the Sn plating layer is alloyed by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~500 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~100 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~100 mg/m² are formed on the alloyed Sn plating layer.
5. A steel sheet for a container, comprising a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, wherein part of the Sn plating layer is alloyed by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~15 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~15 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~15 mg/m² are formed on the alloyed Sn plating layer.
6. A steel sheet for a container, comprising a Sn plating layer of 560 mg/m²~5600 mg/m², which is formed on a surface of the steel sheet, wherein part of the Sn plating layer is alloyed by a tin melting process, and wherein two or more of a Zr film including the amount of Zr of 1 mg/m²~9 mg/m², a phosphoric acid film including the amount of P of 0.1 mg/m²~8 mg/m², and a phenol resin film including the amount of C of 0.1 mg/m²~8 mg/m² are formed on the alloyed Sn plating layer.

EP 2 006 416 A1

7. The steel sheet according to any one of Claims 1 to 6, wherein two or more of the Zr film, the phosphoric acid film and the phenol resin film are formed by a cathode electrolysis process.
8. The steel sheet according to any one of Claims 1 to 6, wherein all of the Zr film, the phosphoric acid film and the phenol resin film are formed by a cathode electrolysis process.
9. The steel sheet according to Claim 7 or 8, wherein the cathode electrolysis process is performed in an acid solution or a tannin acid-contained acid solution.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/056717

A. CLASSIFICATION OF SUBJECT MATTER

C23C28/00(2006.01)i, B32B15/08(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C23C28/00, B32B15/08

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y <u>A</u>	JP 62-103390 A (Nippon Steel Corp.), 13 May, 1987 (13.05.87), Page 2, upper right column, line 3 to page 6, lower right column, line 9 (Family: none)	1-7, 9 <u>8</u>
Y <u>A</u>	JP 2006-009047 A (Toyo Seikan Kaisha, Ltd.), 12 January, 2006 (12.01.06), Par. Nos. [0016] to [0042] & WO 2005/123991 A1	1-7, 9 <u>8</u>
Y <u>A</u>	JP 2003-175564 A (Kawasaki Steel Corp.), 24 June, 2003 (24.06.03), Par. Nos. [0007] to [0030] (Family: none)	1-7, 9 <u>8</u>



Further documents are listed in the continuation of Box C.



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Date of the actual completion of the international search

07 May, 2007 (07.05.07)

Date of mailing of the international search report

15 May, 2007 (15.05.07)

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2007/056717

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y <u>A</u>	JP 2006-001630 A (Toyo Seikan Kaisha, Ltd.), 05 January, 2006 (05.01.06), Par. Nos. [0009] to [0030] (Family: none)	1-7, 9 <u>8</u>

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- JP H05147181 B [0005]