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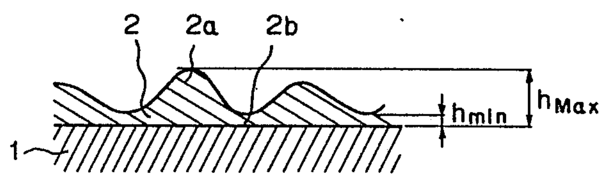
(54) **Process for producing a multilayer-coated strip having excellent corrosion resistance and weldability and useful for containers.**

(57) A multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful for cans and containers is produced by a process in which a steel strip substrate is plated with nickel or a nickel-based alloy to form nickel based coating layers each having an average amount of 2 to 10 mg/m^2, provided with a number of convex and concave portions thereof, portions of which layers having a coating thickness of 0.001 µm or more have a total area corresponding to 10 to 90% of the entire area of the surfaces of the substrate; the nickel based plated substrate is coated with tin to form tin coating layers on the nickel-based coating layers, each of which tin coating layers has an average amount of 200 to 2000 mg/m^2; the resultant precursory coated steel strip is heated at a temperature equal to or higher than the melting point of tin to convert the nickel-based coating layers and the tin coating layers to base coating layers consisting essentially of an Fe-Ni-Sn-based alloy and having a number of convex and concave portions thereof, and intermediate coating layers formed on the base coating layers, consisting essentially of tin and having a number of convex and concave protions thereof; and then an electrolytic chromate treatment is applied onto the intermediate tin coating layers to form surface coating layers consisting of electrolysed chromate.



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PROCESS FOR PRODUCING A MULTILAYER-COATED STEEL STRIP HAVING EXCELLENT CORROSION RESISTANCE AND WELDABILITY AND USEFUL FOR CONTAINERS

BACKGROUND OF THE INVENTION

1. Field of the Invention

The present invention relates to a process for producing a multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful for producing containers. More particularly, the present invention relates to a process for producing a multilayer-coated steel strip having an excellent corrosion resistance and seam weldability, and thus is useful as a steel material for forming cylindrical portions of cans by a seam welding procedure.

2. Description of the Related Art

It is known that an electrolytic tin-plate steel strip (tinplate), an electrolytic chromate-treated steel strip (TFS-CT), and an electrolytic nickel-plated steel strip (TFS-NT) are usable in the production of three piece cans by soldering, bond-bonding, or seam welding.

Formerly, tinplate was most widely used as a steel material for producing cans, but conventional tinplate is not always satisfactory in view of the price thereof. Therefore, in order to reduce the can-producing cost, attempts have been made to reduce the thickness of the tin coating layer on the steel strip, and to utilize a seam-welding method instead of the conventional soldering method for the tinplate. It has been found, however, that when the thickness of the tin coating layer in the tinplate is reduced to a level of 0.20 μm or less, the resultant tinplate exhibits a deteriorated paint corrosion resistance and a reduced seam weldability.

The conventional TFS-NT sometimes used as a steel material for producing seam-welded cans usually exhibits a satisfactory seam weldability, but this weldability is not always satisfactory in practical use. Also, the conventional TFS-NT has a satisfactory paint corrosion resistance in usual use, but the level of the paint corrosion resistance is not always satisfactory when brought into contact with a corrosive material, for example, strongly acidic food.

Accordingly, there is a strong demand for the provision of a surface-coated steel strip which is cheap and has an excellent paint corrosion resistance and seam weldability, and thus is useful for the production of cans and containers.

Japanese Unexamined Patent Publication (Kokai) No. 60-75586 discloses a process for producing a coated steel strip. In this process, a steel strip is coated with a small amount of nickel, and the nickel-coated steel strip is then plated with tin. When the nickel and tin coated-steel strip is heat treated, and the tin coating layer is converted to an Fe-Sn alloy layer, the presence of the small amount of nickel coating layer causes the structure of the Fe-Sn alloy layer to exhibit an enhanced density. Therefore, the resultant coated steel strip exhibits an improved corrosion resistance.

Also, the presence of the nickel coating layer is effective for restricting the Fe-Sn alloy-forming reaction in the heat-treatment, and thus the resultant coated steel exhibits an enhanced seam weldability. Further, the inventors of the present invention have found that the properties, for example, seam weldability and corrosion resistance, of the coated steel strip usable as a steel material for seam welded cans, vary depending on the distribution of metallic tin coating over the surface of a steel strip substrate. That is, it has been found that the properties of the coated steel strip over which the metallic tin layer is unevenly distributed and having an uneven rough surface, are better than those of a coated steel strip over which the metallic tin layer is evenly distributed and having a smooth uniform surface.

Namely, the coated steel strip having an uneven thin tin coating layer exhibits a better seam weldability and corrosion resistance than those of a conventional coated steel strip having an even thin tin coating layer. However, it is very difficult to control the thickness of the unevenness of the thin tin coating layer to a predetermined level, and to produce a coated steel strip having predetermined levels of weldability and corrosion resistance with a stable reproductivity. Fujimoto et al, "Iron and Steel", vol. 72, No. 5, page 39. 1986 discloses that, in order to provide a tin coating layer having an uneven thickness with a stable reproductivity, it is effective to apply an anodic electrolytic treatment to the steel strip in an alkaline treating liquid before the nickel-plating step. Also, it is known that, when a tin-coated steel strip is subjected to a flux treatment, the unevenness in the thickness of the tin coating layer is greatly influenced by the conditions of the flux treatment.

However, even if the anionic electrolytic treatment or the flux treatment is utilized, the resultant coated steel strip is unsatisfactory from the viewpoint of corrosion resistance and weldability.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a process for producing a multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful for producing cans or containers with an improved reproductivity.

The above-mentioned object can be attained by the process of the present invention which comprises the steps of (A) plating a substrate consisting of a steel strip with metallic nickel or a nickel-based alloy to form, on both the upper and lower surfaces of the

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substrate, nickel-based coating layer, each of which layers is coated in an average amount of 2 to 100 mg/m^2 and is provided with a number of convex and concave portions, and in which layer portions thereof having a coating thickness of 0.001 μm or more have a total area corresponding to 10% to 95% of the entire area of the surfaces of the substrate; (B) coating the nickel-based plated substrate with tin to form tin coating layers on the nickel-based coating layers, each of which tin coating layers is coated in an average amount of 200 to 2000 mg/m^2, to provide a precursory coated steel strip; (C) heating the precursory coated steel strip at a temperature equal to or higher than the melting point of the tin coating layer, to cause the nickel-based coating layers and the tin coating layers to be converted to base coating layers, which are formed on both the upper and lower surfaces of the substrate, consisting essentially of an Fe-Ni-Sn-based alloy and having a number of convex and concave portions, and intermediate coating layers, which are located on the base coating layers, consisting essentially of tin and having a number of convex and concave portions; and (D) applying an electrolytic chromate treatment to the intermediate tin coating layers to form surface coating layers, consisting of electrolysed chromate, on the intermediate tin coating layer.

BRIEF DESCRIPTION OF THE DRAWINGS

Figure 1 is a schematic cross-sectional view of an embodiment of the nickel coating layer formed on a steel strip substrate in the first step of the process of the present invention;

Fig. 2 is a schematic cross-sectional view of another embodiment of the nickel coating layer formed on a steel strip substrate in the first step of the process of the present invention; and,

Fig. 3A to 3C are schematic cross-sectional views of embodiments of the products formed respectively in the second, third, and fourth steps of the process of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

In the first step of the present invention, a substrate consisting of a steel strip to be multilayer-coated is plated with nickel or a nickel-based alloy to form nickel-based coating layers on both the upper and lower surfaces of the substrate to an extent such that the resultant nickel-based coating layers are coated in a small average amount of from 2 to 100 mg/m^2, preferably from 5 to 100 mg/m^2, per surface of the substrate and have an uneven thickness distribution, so as to provide a number of convex and concave portions preferably substantially evenly distributed in the layer.

That is, the uneven nickel based coating layer may be, as shown in Fig. 2, in the form of a land having a number of mountains and hills corresponding to the convex portions and a number of lakes and valleys corresponding to the concave portions, which mountains, hills, lakes, and valleys are substantially evenly distributed in the land. Some of the lakes and valleys (concave portions) may have bottoms thereof formed by nickel or a nickel-based alloy plated on the substrate surfaces. Also, in the bottoms of other lakes and valleys (concave portions), portions of the substrate surfaces may be exposed to the outside. That is, the nickel-based coating layer may incompletely cover the surfaces of the substrate.

Alternatively, the uneven nickel-based coating layer may be, as shown in Fig. 2, in the form of a number of islands corresponding to the convex portions, consisting of nickel or the nickel-based alloy and preferably substantially evenly distributed in one or more seas corresponding to the concave portions connected to each other. Some of the island portions may be in the above-mentioned form of a land having a number of mountains, hills, lakes, and valleys. In the bottoms of the sea portions of the nickel-based coating layer, the corresponding portions of the substrate surfaces are exposed to the outside.

Referring to Fig. 1, a surface of a steel strip substrate 1 is coated with an uneven nickel-based coating layer 2 having convex portions 2a and concave portions 2b.

In Fig. 2, a surface of a steel strip substrate 1 is coated with an islands-in-sea type nickel-based coating layer 2 consisting of a plurality of island-formed nickel-based coating deposits 2c separated from each other. Portions 1a of the surface of the substrate 1 are exposed to the outside but not coated with the nickel-based coating deposit.

The coating thicknesses of the convex portions, that is, the heights from the surface of the substrate to the peaks of the convex portions, may be different. Also, the coating thicknesses of the concave portions, that is, the thickness between the surface of the substrate and the bottoms of the concave portions, may be different.

In the formation of the uneven nickel-based coating layers, the total area of portions of the layers having a coating thickness of 0.001 μm or more must be coated to a level corresponding to 10% to 95%, preferably, 10% to 90%, of the entire area of the surfaces of the substrate to be coated. Also, preferably the convex and concave portions of the resultant nickel-based coating layers satisfy the relationships (1), (2), and (3):

$$h_{max} \geqq 0.002\ \mu m \quad (1)$$

$$h_{min} \geqq 0 \quad (2)$$

and

$$h_{min} > 0,\ h_{max} \geqq 2\ h_{min} \quad (3)$$

wherein hmax represents a largest coating thickness of the convex portions and hmin represents a smallest coating thickness of the concave portions of the nickel-based coating layer.

In the first step of the process of the present invention, the steel strip substrate, which has been degreased or surface cleaned by an ordinary method, is subjected to a nickel-plating process. In the surface cleaning procedures, the steel strip substrate may be subjected to an anodic electrolytic treatment in a pickling liquid, for example, a sulfuric acid aqueous solution, or a degreasing liquid, for example, a sodium hydroxide aqueous solution.

The surface cleaned steel strip substrate is unevenly plated with nickel or a nickel-based alloy in an amount of 2 to 100 mg/m^2, preferably 5 to 100 mg/m^2, per surface of the substrate. The plating process can be carried out in an ordinary nickel plating liquid, for example, a sulfuric acid watt plating liquid. The composition of the plating liquid, plating current density, plating temperature and time, and other plating conditions are determined so that the resultant nickel-based coating layers are in the above-mentioned specific amount and have the above-mentioned uneven thickness distribution. The plating method is not limited to a specific method and may be an electric plating method or a non-electrolytic plating method, as long as the specific uneven nickel-based coating layers is obtained. Also, after the plating operation is completed, the nickel-based plated substrate may be additionally subjected to an anodic electrolytic treatment. Alternatively, the nickel-based plated substrate may be subjected to a heat treatment at an elevated temperature, to cause the plated nickel or nickel-based alloy to diffuse into the steel strip substrate.

If the amount of the plated nickel or nickel-based alloy is more than 100 mg/m^2, the resultant coating layer will have a substantially even thickness and it will be difficult to provide a coated steel strip having a satisfactory corrosion resistance and weldability.

If the amount of the plated nickel or nickel-based alloy is less than 2 mg/m^2, it will be difficult to provide a dense Fe-Ni-Sn based base layer having a excellent effect for enhancing the corrosion resistance of the resultant coated steel strip.

As stated above, the limitation in the amount of the nickel-based coating layers to the range of from 2 to 100 mg/m^2 per surface of the substrate is very important when causing the resultant nickel-based coating layers to have an uneven coating thickness distribution and to be provided with a number of convex portions and concave portions thereof. This specific form of the nickel based coating layers is essential when providing a multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful as a steel material for producing cans or containers.

Also, if the total area of the portions of the nickel-based coating layers having a thickness of 0.001 µm or more is more than 95% or less than 10% of the entire area of the surfaces of the substrate, the unevenness in the coating thickness of the nickel-based coating layers will be unsatisfactory, and thus the resultant coated steel strip will exhibit an unsatisfactory corrosion resistance and weldability.

The uneven nickel-based coating layer satisfying the above-defined relationships (1), (2), and (3) is very effective for further enhancing the corrosion resistance and weldability of the resultant coated steel strip.

The uneven distribution of the thickness of the nickel-based coating layer can be observed by means of an electron probe micro-analyser or an Auger electron Spectroscopy.

The uneven nickel-based coating layer may consist of nickel or a nickel-based alloy consisting of at least 80% by weight of nickel and 20% by weight or less of an additional metal element consisting of at least one member selected from zinc, phosphorus, cobalt, copper, and chromium. The additional metal element can be alloyed with nickel by the heating treatment and is effective for causing a portion of tin coating layer to remain in the free tin state after the heat treatment. The remaining free tin forms an intermediate tin coating layer on the base coating layer after the heat-treatment step.

In the second step of the process of the present invention, the nickel-based plated substrate is coated with tin in an average amount of 200 to 2000 mg/m^2 per surface of the substrate to provide a precursory coated steel strip. The tin coating procedures are not limited to a specific method, and can be carried out by any conventional tin plating method. However, the tin coating is preferably carried out by an electric plating method.

The average amount of the tin coating layers formed on the nickel based plated substrate is limited to a specific range from 200 to 2000 mg/m^2 per surface of the substrate to provide a resultant coated steel strip having an excellent corrosion resistance and weldability at a low cost.

If the average amount of the tin coating layers is more than 2000 mg/m^2, the excess amount of tin over 2000 mg/m^2 has no effect on the enhancing of the corrosion resistance and weldability of the resultant coated steel strip, and undesirably increased the cost of the resultant coated steel strip. Also, an average amount of less than 200 mg/m^2 of the tin coating layer results in an unsatisfactory seam weldability and corrosion resistance of the resultant coated steel strip.

After the tin coating step is completed, the coated steel strip is usually washed with water and, if necessary, is immersed in a flux comprising, as a principal component, phenol sulfonic acid or ammonium chloride, and finally, is dried. The flux may have a concentration corresponding to from 1/2 to 1/3 of that in an ordinary flux for producing a usual tinplate. The necessity for flux treatment and composition and concentration of the flux can be decided in consideration of the type and constitution of the desired coated steel strip.

In the third step in the process of the present invention, the precursory coated steel strip is heat-treated at a temperature equal to or higher than the melting point of the tin coating layer. This heat treatment may be carried out by, for example, an electric resistance-heating method or high-frequency induction heating method. Further, this heat treatment may be effected in an atmosphere consisting of an inert gas, for example, nitrogen or argon gas.

The heat treatment applied to the precursory coated steel strip is effective for converting the nickel-based coating layers and tin coating layers to base coating layers formed on the two surfaces of the substrate, and consisting essentially of an Fe-Ni-Sn-based alloy and having a number of convex and concave portions, and intermediate coating layers formed on the base coating layers, consisting essentially of tin and having a number of convex and concave portions.

Preferably, the heat treatment is controlled to an extent such that the content of tin in the resultant base Fe-Ni-Sn-based alloy coating layers corresponds to about 1/3, that is, from 30% to 35% of the entire weight of the original tin-coating layers.

The heat treatment at a temperature equal to or higher than the melting point of the original tin coating layer results in the conversion of the nickel-based coating layers and the tin coating layers to base Fe-Ni-Sn-based alloy coating layers and intermediate tin coating layers, which are effective for imparting an excellent corrosion resistance and weldability to the resultant coated steel strip.

The above-mentioned conversion will be further explained by referring to Figs. 3A to 3C.

Referring to Fig. 3A, a precursory coated steel strip 10 which has been produced by the first and second steps of the process of the present invention, has a steel strip substrate 11, an islands-in-sea type nickel-based coating layer 12 having a number of islands 12a, wherein the islands 12a are separated from each other, and sea-shaped portions 12b between the islands 12a, and a tin coating layer 13. When the precursory coated steel strip is heated at a temperature equal to or higher than the melting point of the tin coating layer, the tin coating layer 13 is melted and the nickel-based coating layer 12 is alloyed with a portion of iron in the steel strip substrate 11 and a portion of tin in the tin coating layer 13.

The alloying rate of nickel or nickel based alloy with the iron and tin is proportional to the concentration of nickel or nickel-based alloy in the alloying system. Therefore, each of the nickel-based islands 12a are rapidly converted to a corresponding alloy coating while growing three-dimensionally. Namely, each alloy coating becomes thicker than the corresponding nickel-based islands and spreads on the substrate surface. The spread alloy coatings are connected to each other and form a continuous alloy coating layer which substantially completely covers the surface of the substrate, as shown in Fig. 3B.

Referring to Figs. 3A and 3B, the resultant alloy coating layer 14 has a number of convex portions 14a corresponding to the nickel-based islands 12a and a number of concave portions 14b corresponding to the sea-shaped portion 12b in the nickel-based coating layer 12 in Fig. 3A.

The tin melt exhibits a larger wetting affinity and a smaller free interface energy to the Fe-Ni-Sn-based alloy layer surface than to the nickel based alloy layer surface and to the steel strip surface. Note, the larger the thickness of the Fe-Ni-Sn-based alloy layer, the greater the wetting affinity of the tin melt thereto. Accordingly, the thickness of the tin melt layer 15 on the Fe-Ni-Sn-based alloy layer 14 corresponds to the thickness of the Fe-Ni-Sn-based alloy layer 14 as shown in Fig. 3B, when the heat-treatment is stopped and the alloy coating layer and tin melt layer are cooled to room temperature, the resultant tin coating layer 15 has a number of convex portions 15a and concave portions 15b thereof respectively corresponding to the convex portions 14a and the concave portions 14b of the alloy coating layer 14.

If the nickel-based coating layer has an even thickness, the conversion of the nickel-based coating layer progresses at an even converting rate throughout the layer, and the resultant alloy coating layer has a substantially even thickness. Accordingly, the even base alloy coating layer causes the intermediate tin coating layer to have a substantially even thickness.

The even tin coating layer sometimes can be converted to an uneven tin coating layer as shown in Fig. 3B by a flux treatment under a certain condition. However, the conversion by the flux treatment is not always successful. Sometimes, the flux treatment fails to convert the even tin coating layer to an uneven tin coating layer. Sometimes, the flux treated tin coating layer contains uneven portions and even portions thereof. In other words, the flux treatment cannot stably convert the even tin coating layer to an uneven tin coating layer and, therefore, is not valuable for stably producing the coated steel strip having an enhanced corrosion resistance and weldability.

However, in the process of the present invention, the uneven tin coating layers can be stably produced by utilizing the uneven nickel-based coating layers formed on the steel strip substrate surfaces. The uneven tin coating layers are very effective for producing the coated steel strip having an enhanced weldability and corrosion resistance, and therefore, useful for cans and containers.

Preferably, in the intermediate tin coating layers, the convex portions are spaced 1 to 30 μm apart, and have a coating thickness of 0.20 μm or more, the concave portions have a coating thickness of 0 to 0.07 μm, and the average coating thickness of the entire intermediate tin coating layers is 0.17 μm or less.

In the fourth step of the process of the present invention, an electrolytic chromate treatment is applied, as a final passive state-forming step, to the heat-treated steel strip to form electrolysed chromate surface coating layers on the intermediate tin coating layers. The resultant surface coating layers have substantially plain surfaces. That is, the thicknesses of portions of the surface coating layers formed on the convex portions of the intermediate tin coating layers is larger than that of portions of the surface coating layer formed on the concave portions of the intermediate tin coating layer. In other words, referring to Fig. 3C, the surface coating layer 16 has a number of downward convex portions 16a formed on the concave portions 15b of the intermediate tin coating layer 15 and a number of upward concave portions 16b formed on the convex portions 15a of the intermediate tin coating layer 15.

The upward concave portions 16b of the surface coating layers having a small coating thickness exhibit an excellent weldability. Also, the downward convex portions 16a of the surface coating layers having a large coating thickness exhibit a superior corrosion resistance. Therefore, as a whole, the coated steel strip of the present invention exhibits an enhanced weldability and corrosion resistance and is useful for cans and containers. When the coated steel strip having the above-mentioned uneven surface coating layer is subjected to a seam welding procedure, the concave portions of the uneven surface coating layers having a small coating thickness serve to stabilize the flow of the electric current, and thus to improve the seam weldability of the coated steel strip. Also, the thick convex portions of the surface coating layers are effective for enhancing the corrosion resistance of the coated steel strip.

The uneven surface coating layers consisting essentially of electrolysed chromate can be produced by a conventional electrolytic chromate-treating method usable for TFS-CT. Usually, the electrolytic chromate treatment is carried out in accordance with a cathodic reduction method in an aqueous solution of chromic anhydride in the presence or absence of anions, for example, sulfuric anions or fluoride anions. Also, any known means for reducing co-depositing anions in the electrolysed chromate layer can be applied to the electrolytic chromate treatment.

The electrolysed chromate surface coating layer may consist essentially of chromium oxide hydrate alone. The surface coating layer is preferably in an average amount, in terms of metallic chromium, of 3 to 30 mg/m^2 per surface of the substrate. If the average amount is less than 3 mg/m^2, the resultant coating steel strip sometimes exhibits an unsatisfactory corrosion resistance and a poor bonding property to paint. Also, if the average amount of the surface coating layers is more than 30 mg/m^2, the resultant coating steel strip sometimes exhibits an unsatisfactory weldability.

The electrolysed chromate surface coating layer may comprise hot alkali-soluble chromium fractions and hot alkali-insoluble chromium fractions.

In the surface coating layers, the proportion in weight of the hot alkali-soluble fractions to the hot alkali-insoluble fractions is not limited to a specific level. However, in the concave portions of the surface coating layers, preferably the proportion of the hot alkali-insoluble fractions is larger than that of the hot alkali-insoluble fractions.

The present invention will be further explained by way of specific examples, which, however, are merely representative and do not restrict the scope of the present invention in any way.

In the example, the following tests were carried out.

(A) Seam Welding Test

A specimen, that is, a piece of a multilayer coated steel strip, was formed into a peripheral portion of a can in which edge portions of the specimen were overlapped to a width of 0.4 mm. The overlapped portion of the specimen was seam welded under a pressure of 45 hgf at a can-forming rate of 45 mpm. The value of the second order welding current was varied to determine a range of values of the second order welding current, in which range an optimum seam welding was obtained.

The lower limit of the optimum range of the second order welding current corresponded to a second order welding current value at which the resultant welded portion exhibited a lowest value of satisfactory welding strength. Also, the upper limit of the optimum second order welding current value range corresponded to an upper limit of the second order welding current value range in which the seam welding procedure can be carried out without the generation of an undesirable splash phenomenon.

The welding strength of the welded portion was determined by an impact test and a peeling test in which a V-shaped notch was formed in the welded portion of the specimen and the welded two ends of the specimen were peeled from each other by a pair of pincers.

The appearance of the seam welded portion of the specimen was evaluated by naked eye observation in which the generation and intensity of expulsion and surface flash on the welded portion were observed.

The specimen to be subjected to the seam welding test was preliminarily heated at a temperature of 210°C for 20 minutes in an electric air oven.

(B) Underpaint Rust Resistance Test

Two surfaces of a specimen were coated with an ordinary epoxy-phenol coating material for cans, in an amount of 55 mg/dm^2 per surface of the specimen, by a roll coating method and the resultant coating layers were heated at a temperature of 205°C for 10 minutes and then further heated at a temperature of 190°C for 10 minutes. The resultant paint layers were scratched with a cutting knife and then subjected to an Ericksen process at a height of 5 mm by using an Ericksen testing machine.

The resultant testing specimen was subjected to a salt water spraying test for one hour, by spraying an aqueous solution of 5% by weight of NaCl. Then the specimen was left in a thermo-hydrostat at a temperature of 25°C at a relative humidity of 85% for 14 days. The generation of rust in the scratched portions in the specimen was observed by the naked eye.

In each example, all of the procedures were repeated twice. The seam welding test and the rust resistance test were applied to both the first product and the second product of each example.

Examples 1 to 5 and Comparative Examples 1 to 3

In each of Examples 1 to 5 and Comparative Examples 1 to 3, two surfaces of a substrate consisting of a steel strip, which had been surface cleaned by an ordinary cleaning method, were plated with nickel in a plating aqueous solution containing 200 g/l of $NiSO_4 \cdot 7H_2O$, 60 g/l of $NiCl_2 \cdot 6H_2O$, and 50 g/l of H_3PO_3 at the temperature of 50°C at the pH selected from the range of from 1.8 to 4.0 and at the cathodic current density selected from the range of from 5 to 50 A/dm^2 as shown in Table 1. The resultant nickel coating layers consisted of the plated nickel in an amount in the range of from 2 to 120 mg/m^2 per surface of the substrate, as shown in Table 1. The resultant nickel coating layers were in the form as indicated in Table 1 and had the largest coating thickness (hmax) and the percentage RA of the total area portions of the nickel coating layers having a coating thickness f 0.001 µm or more based on the entire area of the surfaces of the substrate, as shown in Table 1.

The form and thickness of the nickel coating layers were determined by AES and EPMA analyses.

In Examples 1 to 5 in accordance with the process of the present invention, the largest thickness (hmax) of the nickel coating layers was 0.002 µm or more and the percentage RA of the portions of the nickel coating layers having a coating thickness of 0.001 µm or more was in the range of from 10% to 95%.

The nickel-coated steel strip was plated with tin in a tin plating aqueous liquid containing 25 g/l of tin sulfate, 30 g/l of phenol sulfonic acid, and 2 g/l of ethoxylated α-naphthol sulfonic acid at a temperature in the range of from 40 to 50°C at a cathodic current density of 20 A/dm^2. The average amount of the resultant tin coating layers was in the range of from 800 to 1000 mg/m^2 per surface of the substrate, as shown in Table 1.

The resultant precursory coated steel strip was immersed in an aqueous flux solution containing 1 to 2 g/l of phenol sulfonic acid at a temperature of 45°C, and then dried.

The flux-treated precursory coated steel strip was heat-treated by an electric resistance heating method at a temperature of from 240°C to 280°C for 2 seconds to 6 seconds in the air atmosphere. The heating temperature and time were decided so that the resultant Fe-Ni-Sn alloy base layer contained tin in an amount corresponding to about 1/3 of the entire amount of tin plated on the substrate.

The heat-treated steel strip was subjected to an electrolytic chromate treatment in an aqueous treating solution containing 2 to 100 g/l of CrO_3 , 0.1 to 1.0 g/l of H_2SO_4 and 0 to 3 g/l of Na_2SiF_6 at a temperature of from 40°C to 60°C at a cathodic current density in the range of from 5 to 90 A/dm^2 so as to form electrolysed chromate surface coating layers in an average amount of 12 to 17 mg/m^2, in terms of metallic chromium, per surface of the substrate.

The distribution of the electrolysed chromate in the surface coating layers was determined from the characteristic X-ray intensity of chromium measured by EPMA analysis.

In Table 1, the term "even distribution" refers to a distribution of thickness of the intermediate tin coating layers in such a manner that the ratio of the average thickness T_V of the downward convex portions to the average thickness T_C of the upward concave portions of the surface coating layers is 1 or more and less than 1.2. Also the term "uneven distribution" refers to a distribution of thickness of the intermediate tin coating layers in such a manner that the ratio of the average thickness T_V of the downward convex portions to the average thickness T_C of the upward concave portions of the surface coating layers is 1.2 or more.

Preferably, the surface coating layers have an uneven thickness distribution.

The results of the seam welding test and the rust resistance test in the examples and comparative examples are shown in Table 1.

<u>Examples 6 and 7</u>

In each of Examples 6 and 7, the same procedures as those described in Example 1 were carried out with the following exception.

The nickel-plating step was carried out so that the resultant nickel coating layers were as indicated in Table 1.

The tin-coating step was carried out in an aqueous plating solution containing 75 g/l of stannous chloride, 25 g/l of sodium fluoride, 50 g/l of potassium hydrogen fluoride, and 45 g/l of sodium chloride at a temperature in the range of from 40 to 50°C and at a cathodic current density in the range of from 20 to 40 A/dm^2, so that the resultant tin coating layers had the average amount as indicated in Table 1.

No flux treatment was applied to the tin-coated steel strip. The tin-coated steel strip was washed with water and then subjected to the heat treatment.

The results of the tests are shown in Table 1.

Comparative Examples 4 and 5

In each of Comparative Examples 4 and 5, the same procedures as those mentioned in Example 1 were carried out except that the nickel plating step was omitted, and in Comparative Example 5, the average amount of the tin coating layer was 1100 mg/m^2 per surface of the substrate.

The results of the tests are indicated in Table 1.

Referential Example

An ordinary tinplate #25 having tin coating layers in an amount of 2800 mg/m^2 per surface of the tinplate was subjected to the same electrolytic chromate treatment and tests as those mentioned above.

The results are shown in Table 1.

Table 1

Example No.	Nickel coating layer: Amount (mg/m^2/surface)	Nickel coating layer: Type of coating layer	Nickel coating layer: Largest thickness hmax (μm)	Nickel coating layer: Area percent RA (*)1 (%)	Tin coating layer amount (mg/m^2/surface)	Type of electrolysed chromate surface coating layer	Seam welding test: Optimum second order welding current (hA): First run	Seam welding test: Optimum second order welding current (hA): Second run	Seam welding test: General evaluation	Under paint rust resistance test: Rust resistance: First run	Under paint rust resistance test: Rust resistance: Second run	Under paint rust resistance test: General evaluation
Example 1	15	Uneven, islands-in-sea type	0.054	70	800	Uneven (*)2	3.8 - 4.2	3.8 - 4.2	Excellent	Excellent	Excellent	Excellent
2	10	"	0.066	54	800	"	3.8 - 4.2	3.8 - 4.2	"	"	"	"
3	35	"	0.092	42	1000	"	4.1 - 4.5	4.1 - 4.5	"	"	"	"
Comparative Example 1	1	"	0.010	30	800	Even (*)3	3.7 - 3.8	3.6 - 3.65	Bad	Bad	Bad	Bad
Example 4	20	"	0.023	95	800	"	3.8 - 4.0	3.8 - 4.0	Good	Good	Excellent	Good
Comparative Example 2	26	Even, continuous	-	-	800	"	None	None	Very bad	Bad	Good	Bad
3	120	"	-	-	1000	"	None	None	"	Good	Excellent	Good
Example 5	12	Uneven, islands-in-sea type	0.018	92	800	Uneven	3.8 - 4.0	3.9 - 4.0	Good	Excellent	Good	Good
6	18	"	0.048	62	800	Even	3.8 - 4.2	3.8 - 4.2	Excellent	Excellent	Excellent	Excellent
7	18	"	0.048	62	620	Uneven	3.6 - 3.8	3.6 - 3.8	Good	Good	Good	Good

Table 1 (Continued)

Example No.	Nickel coating layer				Tin coating layer amount (mg/m²/ surface)	Type of electro-lysed chromate surface coating layer	Seam welding test			Under paint rust resistance test		
	Amount (mg/m²/ surface)	Type of coating layer	Largest thick-ness hmax (μm)	Area percent RA (*)1 (%)			Optimum second order welding current (hA) First run	Optimum second order welding current (hA) Second run	General evalua-tion	Rust resistance First run	Rust resistance Second run	General evalua-tion
Compar-ative Example 4	-	-	-	-	800	Even	None	3.6 - 3.7	Very bad	Bad	Very bad	Very bad
Compar-ative Example 5	-	-	-	-	1100	"	4.0 - 4.3	4.1 - 4.5	Good	Bad	Good	Bad
Referen-cial Example	-	-	-	-	2800	"	4.6 - 5.2	4.6 - 5.2	Excellent	Excellent	Excellent	Excellent

Note: $(*)_1$ - Percentage of the total area of portions of the nickel coating layers having a thickness of 0.001 μm or more based on the entire area of the substrate surfaces.

$(*)_2$, $(*)_3$ - Uneven: $CrT_V/CrT_C \geqq 1.2$ wherein T_V - An average thickness of convex portions of surface coating layers.

Even: $1 \leqq CrT_V/CrT_C < 1.2$ T_C - An average thickness of concave portions of surface coating layers.

In Examples 1, 2, 3 and 6, the resultant multilayer-coated steel strips exhibited excellent seam weldability and corrosion resistance compatible with those of the ordinary tinplate, although the amounts of the tin coating layers in Examples 1, 2, 3 and 6 are in a low level of from 800 or 1000 mg/m^2, whereas the ordinary tinplate had a large amount of tin coating layers of 2800 mg/m^2.

Also, from Examples 1 to 7 in comparison with Comparative Examples 1 to 5, it is clear that the presence of the uneven nickel coating layers on the substrate surfaces is very effective for enhancing the seam weldability and corrosion resistance of the resultant coated steel strip.

CLAIMS

1. A process for producing a multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful for containers, comprising the steps of:

(A) plating a substrate consisting of a steel strip with metallic nickel or a nickel-based alloy to form, on both the upper and lower surfaces of the substrate, nickel-based coating layers, each of which layers is in an average amount of 2 to 100 mg/m^2 and is provided with a number of convex portions and concave portions thereof, and in which layers said portions thereof have a coating thickness of 0.001 μm or more and have a total area corresponding to 10% to 95% of the entire area of the surfaces of the substrate;

(B) coating the nickel-based plated substrate with tin to form tin coating layers on the nickel based coating layers, each of which tin coating layers is in an average amount of 200 to 2000 mg/m^2, to provide a precursory coated steel strip;

(C) heating the precursory coated steel strip at a temperature equal to or higher than the melting point of the tin coating layer, to cause the nickel based coating layers and the tin coating layers to be converted to base coating layers which are formed on both the upper and lower surfaces of the substrate, consist essentially of an Fe-Ni-Sn-based alloy and have a number of convex portions and concave portions thereof, and intermediate coating layers which are formed on the base coating layers, consist essentially of tin and have a number of convex portions and concave portions thereof; and

(D) applying an electrolytic chromate treatment onto the intermediate tin coating layers to form surface coating layers consisting of electrolysed chromate, on the intermediate tin coating layers.

2. The process as claimed in claim 1, wherein the

convex and concave portions in the nickel-based coating layers satisfy the relationships (1), (2) and (3):

$$hmax \geqq 0.002\ \mu m \quad (1)$$

$$hmin \geqq 0 \quad (2)$$

and

$$\text{where } hmin > 0,\ hmax \geqq 2\ hmin \quad (3)$$

wherein hmax represents a largest coating thickness of the convex portions and hmin represents a smallest coating thickness of the concave portions in the nickel-based coating layers.

3. The process as claimed in claim 1, wherein in the intermediate tin coating layer, a number of the convex portions are spaced apart in the range of from 1 to 30 µm, the coating thickness of the concave portions is 0.07 µm or less, the coating thickness of the convex portions is 0.20 µm or more and the average coating thickness of the entire tin coating layers is 0.17 µm or less.

4. The process as claimed in claim 1, wherein the electrolysed chromate surface coating layers have substantially plain surfaces thereof.

5. The process as claimed in claim 1, wherein the electrolysed chromate surface coating layers has an average amount of 3 to 30 mg/m^2 in terms of metallic chromium, per surface of the steel strip substrate.

6. A multilayer-coated steel strip having an excellent corrosion resistance and weldability and useful for containers, comprising:

(a) a substrate consisting of a steel strip; and

(b) multi-coating layers formed on both the upper and lower surfaces of the substrate and comprising:

(i) base coating layers formed on the substrate surfaces, consisting essentially of an Fe-Ni-Sn-based alloy and having a number of convex portions and concave portions thereof, (ii) intermediate coating layers formed on the base coating layers, consisting essentially of tin and having a number of convex portions and concave portions thereof, and (iii) surface coating layers formed on the intermediate coating layers by an electrolytic chromate treatment,

the base and intermediate coating layers having been provided by plating the substrate with metallic nickel or a nickel-based alloy to form nickel based coating layer on both the upper and lower surfaces of the substrate, each of which layers is in an average amount of 2 to 100 mg/m^2 and is provided with a number of convex and concave portions thereof and in which layers portions thereof having a coating thickness of 0.001 µm or more have a total area corresponding to 10% to 90% of the entire area of the surfaces of the substrate, by coating the nickel-based plated substrate with tin to form, on the nickel based coating layers, tin coating layers each of which layers is in an average amount of 200 to 2000 mg/m^2, to provide a precursory coated steel strip, and then by heating the precursory coated steel strip at a temperature equal to or higher than the melting point of the tin coating layers.

Fig. 1

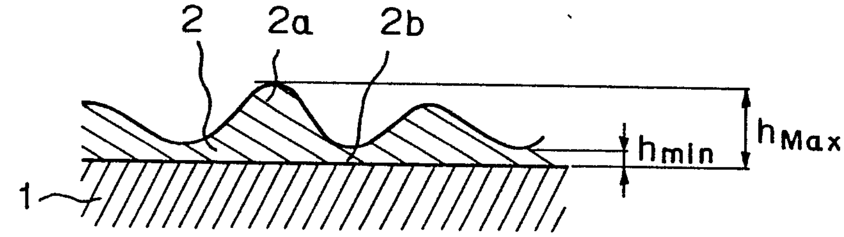

Fig. 2

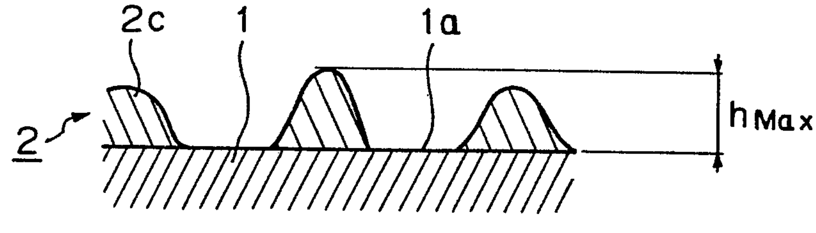

Fig. 3A

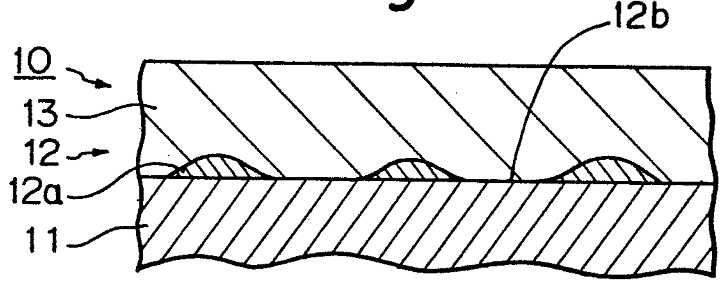

Fig. 3B

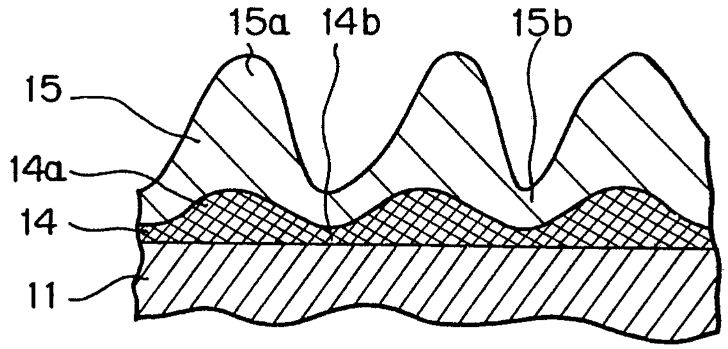

Fig. 3C