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(71) Applicant: **TOYO SEIKAN KAISHA LIMITED**
**Tokyo (JP)**

(72) Inventors:
- **Tsurumaru, Michiko**
  **Tokyo (JP)**
- **Shibue, Masatsune**
  **Kawasaki, Kanagawa (JP)**
- **Masuda, Kazuhisa**
  **Yokahama-shi, Kanagawa (JP)**
- **Shirane, Zenro**
  **Kawasaki, Kanagawa (JP)**

(74) Representative:
**Baverstock, Michael George Douglas et al**
**BOULT WADE TENNANT**
**27 Furnival Street**
**London, EC4A 1PQ (GB)**

## (54) Drawn and wall-ironed can body having excellent corrosion resistance and flavor retention and production method thereof

(57) A drawn and wall-ironed can body having excellent corrosion resistance and flavor retention and free from peeling of a resin coating at a flange portion is formed of a template coated with a thermoplastic resin on at least one side thereof which turns to the inside of the can body, wherein the thermoplastic resin is essentially composed of a crystalline polyester resin, the average thickness of the resin coating on the inside wall of the can body is 5 to 30 µm, the average tin coating mass is 0.2 to 2.0 g/m$^2$, the effective coverage rate of tin coating is at least 85 %, the surface of the metal of an inner portion at least 2 mm wide from the top end of the flange of the can body is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7. A method for producing such a can body comprises the step of heating a portion of the drawn cup which becomes 2 mm wide from the top end of the flange of the can body to form an iron-tin alloy layer on this portion.

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## Description

This invention relates to a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention properties and improved adhesion of a polyester resin coating of a flange portion thereof and to a production method thereof.

A drawn and wall-ironed can body formed of tinplate has serious defects such as having a large amount of steel exposure on the inner surface of the can body.

Even when the tin coverage of the tinplate is good enough, steel is exposed at the inner surface of the can body which has been contacted with a forming tool at the time of forming.

Particularly when forming is carried out by drawing and wall-ironing, the area of exposed steel becomes large because of the large amount of processing.

Therefore, the inside surface of a can body is coated with an organic coating after drawing and wall-ironing. However, this method cannot provide satisfactory corrosion resistance and flavor retention properties.

Since a drawn and wall-ironed can body made from thermoplastic resin coated tinplate of the prior art is trimmed after drawing and wall-ironing and then subjected to a heat treatment and to the process of necking and flanging, damage of the coating on the inside surface of the can is significant and a polyester resin coating on the inside surface of a flange portion easily peels off the metal, especially when the reduction of necking diameter is large.

Although the drawn and wall-ironed can body may be subjected to chemical finishing, this is not so effective and workability is poor.

JP-A-60-172637 (the term "JP-A" as used herein means an unexamined published Japanese patent application) and JP-A-2-303634 propose a laminated metal can body or production method in which metal plate laminated with a polyester resin is used and the reduction ratio of ironing is specified.

In addition, JP-A-1-55055 proposes a production method for a laminated metal can body in which the drawing and ironing temperature of a polyester resin is close to the glass transition point of a PET film and JPA-3-33506 proposes a laminated metal can body in which a polyester resin coating is formed on a chemical finishing layer and the reduction ratio of ironing is specified. However, in all of these prior art procedures, adhesion between the tin coating and PET is insufficient, the flavor retention is poor, and the strength of the polyester resin is unsatisfactory. Wall-ironing produces pin holes in a laminated film, resulting in exposure of steel at the surface. As a consequence, flavor retention is not improved by specifying a reduction ratio for ironing.

Although both the tin coating and the resin coating are controlled in coating weight in the prior art, a coating having a uniform thickness cannot be obtained and there exist pinholes in the coating since it is impossible to control the thickness of a coating with such simple quantitative control. Therefore, it is considered that satisfactory performance cannot be obtained.

This invention provides a can body having excellent adhesion between the metal surface and the polyester resin coating and a method for producing the same with high workability.

This invention has solved all the problems of the prior art by the following means.

The present invention relates to:

1. a drawn and wall-iron can body having excellent corrosion resistance and flavor retention, which is formed of tinplate coated with a thermoplastic resin at least on one side thereof which becomes the inside of the can body, wherein the thermoplastic resin is essentially composed of a crystalline polyester resin, the average thickness of the resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass is 0.2 to 2.0 $g/M^2$, the effective coverage rate of the tin coating is at least 85 %, the surface of the metal of the inner portion at least 2 mm wide from the top end of the flange of the can body is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7;
2. a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention as set forth above, wherein said crystalline polyester resin which is a main component of the coating resin has a glass transition temperature (Tg) of at least 55°C and an intrinsic viscosity (IV) of at least 0.65;
3. a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention as set forth above, wherein the effective coverage rate of the tin is a value indicative of the rate of portions having a tin coating mass of at least 0.1 $g/m^2$;
4. a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention as set forth above, wherein the coverage rate of the iron-tin alloy is a value C obtained from the expression $C = A/(A + B)$ wherein A is the amount of tin contained in the alloy present on the 2 mm area from the top end of the flange and B is an amount of free tin present in the same area; 5. a method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention, wherein the average thickness of a resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass is 0.2 to 2.0 $g/m^2$, and the effective coverage rate of the tin coating is at least 85 %, the, surface of the metal of the inner portion at least 2 mm wide from the top

end of the flange of the can body is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7, the method comprising the steps of:

forming a thermoplastic resin coating which is essentially composed of a crystalline polyester resin, has a crystallinity of 5 % or less, a thickness of 15 to 90 μm, a total elongation of at least 100 %, a Tg of at least 55°C and an intrinsic viscosity (IV) of at least 0.65 on the surface of the tinplate having a tin coating mass of 0.4 to 6.0 g/m$^2$, which becomes the inside surface of the can body,
making a cup by at least a single drawing of the thermoplastic resin coated tinplate,
heating the portion of the drawn cup which becomes at least 2 mm wide from the top end of the flange of the can body,
redrawing if necessary
ironing the wall of the cup with a punch and ironing dies having an approach angle of 2 to 8°, and cooling immediately after the final ironing step;

6. a method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention as set forth above, wherein the temperature of the tin coating formed on the inside surface of the cup is maintained lower than 232°C at the time of forming, and the temperature of the tin coating on the inside surface of the neck portion and the flange portion is maintained lower than 232°C by quenching immediately after the final ironing step; and
7. a method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention as set forth above, wherein the thermoplastic resin coating essentially composed of a polyester resin is oriented and crystallized in the step of drawing, wall-ironing and heating.

The first feature of the present invention is that corrosion resistance is improved by enhancing adhesion between the metal and the polyester resin coating.

When the tinplate drawn and wall-ironed cup is subjected to the processes of necking and flanging, the tin coating and the polyester resin coating are separated from each other if the amount of necking is large. This is because adhesion between the tin coating and the polyester resin coating is not good enough. Peeling at a 2 mm inner portion from the top end of the flange of the can body, in particular, easily occurs.

In the present invention, the surface of the metal of a portion at least 2 mm wide from the top end of the flange in which peeling easily occurs is coated with an iron-tin alloy to prevent the peeling of the polyester resin coating. The iron-tin alloy has higher adhesion to the polyester resin coating than the tin coating and has an important function to prevent peeling.

The iron-tin alloy must be formed around the can body at least 2 mm wide from the top end of the flange. If the layer is less than 2 mm wide, peeling cannot be prevented at the time of neck and flange formation.

If the iron-tin alloy coverage rate of a portion at least 2 mm wide from the top end of the flange is less than 0.7, sufficient peeling prevention effect cannot be obtained.

The iron-tin alloy coverage rate C is a value for a 2 mm portion of the tinplate from the top end of the flange obtained from the expression $C = A/(A + B)$ by measuring the amount A of tin contained in the alloy and the amount B of free tin present on the surface in accordance with the method for measuring tin coating mass build-up of a JIS G3303 tin.

To form the iron-tin alloy, the tin coating can be alloyed by heating the edge of the cup obtained by drawing at about 230°C or more.

In this way, the can body of the present invention is produced by alloying the tin coating of the edge of the drawn cup, redrawing and ironing. The can body of the present invention may also be obtained by heating at 230°C or more a portion 2 mm wide or more from the top end of the cup which turns to a flange after drawing and wall-ironing.

The term "effective tin coverage rate" denotes the rate of portions having a tin coating mass as much as 0.1 g/m$^2$ or more. If the effective tin coverage rate is less than 85 %, under film corrosion occurs and corrosion resistance deteriorates.

The above feature of the present invention is that the corrosion resistance of a drawn and wall-ironed can body coated with a thermoplastic resin on tinplate is remarkably improved by controlling the thickness of the resin coating on the inside wall of the can body to 5 to 30 μm, the average tin coating mass to 0.2 to 2.0 g/m$^2$ and the tin effective coverage rate to at least 85 %.

The inventor of the present invention considers that the reasons why no steel is exposed from the tin coating when the cup is drawn and wall-ironed after the tinplate is coated with the thermoplastic resin are: (1) the processing tool does not contact the tin coating directly and (2) the forming force is not applied to the tin coating abruptly because the thermoplastic resin serves as a buffer and the resin itself transmits processing force to the tin coating. Therefore, since the thermoplastic resin to be coated has good formability, a crystalline polyester resin is suitable.

The second function of the present invention is excellent flavor retention.

When the flavor component of the contents of the can body is absorbed by the material of the inside coating of the can body, the flavor of the contents changes. Even when the material of the inside coating of the can body dissolves into the contents the flavor of the contents changes.

In this way, flavor changes are caused not only by the exposure of the steel on the inside tin coating of the can body but also by the coated resin.

Studies conducted by the inventor have revealed that the amount of absorption of the flavor component of the contents decreases greatly when a crystalline polyester resin having a Tg of at least 55°C and an intrinsic viscosity (IV) of at least 0.65 is used as the thermoplastic resin and an isophthalic acid based copolyester resin is particularly preferred.

In addition, polyethylene terephthalate, polybutylene terephthalate, polyethylene naphthalate, and copolymers and blends thereof may be used as the crystalline polyester.

The copolymer component of copolyethylene terephthalate may be an acid component or an alcohol component. Illustrative examples of the acid component include aromatic dibasic acids such as isophthalic acid, phthalic acid and naphthalenedicarboxylic acid; aliphatic dicarboxylic acids such as adipic acid, azelaic acid, sebacic acid and decanbodyodicarboxylic acid; and alicyclic dicarboxylic acids such as cyclohexanedicarboxylic acid. Illustrative examples of the alcohol component include aliphatic diols such as butane diol and hexane diol; and alicyclic diols such as cyclohexane dimethanol. They may be used alone or in combination of two or more.

These crystalline polyesters may be used as a single layer or a composite layer consisting of two or more layers.

Flavor retention is greatly affected by the exposure of the steel on the tinplate.

The inventor has conducted various studies to reduce the dissolution of iron and has found that a drawn and wall-ironed can body almost free from iron dissolution can be obtained by:

forming a thermoplastic resin coating which is essentially composed of a crystalline polyester resin, has a crystallinity of 5 % or less, a thickness of 15 to 90 µm, a total elongation of at least 100 %, a Tg of at least 55°C and an intrinsic viscosity (IV) of at least 0.65 on the surface of the tinplate having a tin coating mass of 0.4 to 6.0 g/$M^2$, which becomes the inside surface of the can body,
making a cup by at least a single drawing of the thermoplastic resin coated tinplate,
heating the portion of the drawn cup which becomes at least 2 mm wide from the top end of the flange of the can body,
redrawing if necessary
ironing with a punch and ironing dies having an approach angle of 2 to 80, and
cooling immediately after the final ironing step.

The resin coating maybe formed on both sides of the tinplate. However, since the outside surface of the can body has no direct connection with corrosion resistance and flavor retention and may be printed, a thermoplastic resin coating is not necessary for the outside surface of the tinplate.

Since the tin coating on the inside surface of the can body of the present invention is coated with a resin, chemical finishing after drawing and ironing is not necessary. Therefore, since chemical finishing is not required, the amount of water used in the can making line can be reduced to ½ to 1/3 that of the prior art, and the amount of industrial waste water can be reduced considerably. Although the tin coating is as thin as 0.01 to 0.25 µm, it exhibits sufficient corrosion resistance and excellent flavor retention by preventing the dissolution of iron. To form such a thin tin coating having an effective coverage rate of at least 85 % has been impossible in the prior art.

Both the tin coating and the resin coating on the can body wall are thinned by a large amount of forming. The thermoplastic resin coating is formed, the crystallinity of the resin is oriented, and the coating has higher strength and improved barrier resistance.

Preferably, forming is carried out by maintaining the temperature lower than 232°C during forming. This is because forming at a temperature at which tin does not melt is effective to maintain the uniformity of the tin coating and prevent decrease in the coverage rate as the melting point of tin is 232°C.

The third feature of the present invention is that forming is carried out by maintaining the temperature of the coated resin on the punch side below the tack point of the resin during drawing and ironing.

Since the temperature Of the outside surface of the can body is elevated to 250°C during ironing and this heat diffuses into the inside of the can body, the temperature of the resin coating also rises. When the temperature rises too high, oriented crystals of the resin coating cannot be obtained and, due to insufficient strength of the resin coating, forming defects easily occur. When the temperature exceeds the tack point, the resin coating sticks to the punch, causing a strip-out failure after forming.

Effective means for preventing this is to cool the forming dies and the cup from the outside surface of the cup with coolant immediately after forming so as to maintain the resin of the cup at a temperature below the tack point.

Strippability from the punch sleeve after the final ironing step is greatly affected by the surface roughness of the coated resin. When the resin surface has significant roughness, the resin is pressed to the surface of the punch during ironing and vacuum adhesion is caused between the resin surface and the punch surface. Therefore, a large force is required to separate the resin from the punch after forming. As a result, the edge of the cup may be bent at the time of stripping out the cup, causing a forming failure. Therefore, to improve strippability from the punch sleeve, it is effective to make the resin surface smooth.

Setting the forming temperature of the resin coating to a temperature near Tg is preferred in order to improve formability. For instance, when the temperature of the coolant is set to 50°C in the case of PET, a good result can be obtained.

To obtain good formability of the resin coating, it is preferred that annealing is carried out by heating the drawn cup at 80 to 200°C to remove strain.

As the resin coating easily slides with the punch during ironing, it is effective from the viewpoint of formability to reduce the approach angle of the ironing die and increase the friction between the coating and the punch. When the resin coating slides with the punch, a wavy defect in the resin coating occurs. Preferably, the approach angle of the ironing die is set to 2 to 8°, particularly to 6° or less. Since the surface roughness of the metal underlying the resin coating is slightly increased by drawing, resin coating defects are easily caused by significant roughness of the punch surface or foreign matter present on the surface of the punch during ironing.

Therefore, it is necessary to smooth the surface of the punch and eliminate foreign matter.

Further, according to the present invention, since the thermoplastic resin coating which is essentially composed of a polyester and formed on the tinplate can be oriented and crystallized in the steps of drawing, ironing and heating, corrosion resistance and flavor retention are improved.

## Examples

The following examples and comparative examples are given to further illustrate the present invention.

In these examples and comparative examples, drawing and ironing conditions, and can making conditions are as follows, and the measurements of the coverage rate of the tin coating and the coverage rate of the iron-tin alloy, and the evaluations of the peeling of the flange portion, flavor retention and filled can storage tests were carried out as follows.

1. Drawing and ironing conditions and can body making conditions

Examples and Comparative Examples except Example 10-1, Examples 11-1 to 11-4, comparative Examples 11-1 and 11-2 were performed under the following drawing and ironing conditions and can-making conditions.

A O.245 mm thick metal plate coated with a resin on one side thereof was blanked to a blank diameter of 142 mm and drawn to a first draw ratio of 1.6 to form a cup so that the resin coated surface thereof turned into the inside of the can body. Thereafter, the cup was redrawn to a second draw ratio of 1.3 and subjected to three steps of ironing to form a drawn and wall-ironed cup having a can body diameter of 65.8 mm, a metal thickness of the can body wall of 80 μm and a metal thickness of the neck portion of 135 μm. This drawn and wall-ironed cup was trimmed to a height of 123 mm, washed, dried, printed on the outside surface thereof, and heated at 200°C for 30 seconds. The inner diameter of the top portion of the can body was reduced to 57.25 mm (diameter 206) and a flange was formed to obtain a drawn and wall-ironed can body. The forming speed in the redrawing step and the three steps of ironing was 200 cpm.

Example 10-1 was different from the above Examples and Comparative Examples in the drawing and ironing conditions, but the same in the conditions of forming the neck and flange portions. Examples 11-1 to 11-4, and Comparative Examples 11-1 and 11-2 are the same in drawing and ironing conditions, but different in conditions of forming the neck and flange portions. The differences are described in each of the Examples and Comparative Examples.

2. Cup heating conditions

The first drawn cup was placed upright and a high-frequency induction heating coil was placed above the cup so that a high-frequency magnetic flux was applied to the edge of the cup. The high-frequency induction heating coil was placed 3 mm away from the edge of the cup. High-frequency output was adjusted and the temperature of the cup edge was controlled. The temperature of the cup edge was evaluated by color change by applying several types of heat sensitive paints to the surface of the resin on the inside of the cup. The conditions of each Example and Comparative Example include a processing time of 1.0 second and a cup edge ultimate temperature of about 300°C, when not specified.

3. Measurement of effective coverage rate of the tin coating

After a resin coating on the inside wall of the can body including neck and flange portions was removed, the inside wall of the can body was divided into 2.0 mm long sections in a circumferential direction so that EPMA for tin was made on 10 out of the sections under the following conditions to obtain a coverage rate of the tin coating for each of the sections from the following expression. The minimal value among the thus obtained coverage rates of the tin coating for these sections is taken as the effective coverage rate of the tin coating of the can body. Measurement method: WDS, detection crystal: PET, acceleration voltage: 10 kV, sample current: 1 x 10E-8A, beam diameter: 1.0 μm, detection X ray: SnLα ray, time constant: 1.0 (s), scanning speed: 50 μm/minute. coverage rate of tin coating (%) = (length of a portion having a tin mass of 0.1 g/M$^2$ or more (mm)) x 100/2.0 (mm)

4. Measurement of coverage rate of iron-tin alloy

The crystalline polyester resin from the flange of the can body to the neck portion of the can body was dissolved in a solvent such as 1,1,1,3,3,3-hexafluoro-2-propanol, a 2 mm wide portion from the top end of the flange was cut out, the edge of the flange and a cut surface were sealed with a resin, and the surface of the metal which was in contact with the thermoplastic resin was measured for the amount of tin contained in the alloy (A) and the amount of free tin on the surface (B) in accordance with "Method of Testing Tin Coating Build-up, Electrolytic Peeling Method" of JIS G3303. At this point, the current density was 10 ma/cm$^2$.

The coverage rate of the iron-tin alloy © was defined by the following expression.

$$C = A/(A + B)$$

When the metal surface after the thermoplastic resin was dissolved was enlarged to a magnification of 5,000 or more by an electron scanning microscope, a columnar or granular iron-tin alloy was observed and could be identified because it was distinctly different from the smooth surface of metal tin.

5. Evaluation method for Peeling of flange portion

A neck portion was necked in up to diameter 206 or diameter 202, and further a flange was formed. Thereafter, 1,000 can bodies were examined for the peeling of their flanges. Cans having peeled off resin were evaluated as X and the number of such can bodies was counted. As for the standard for the peeling of the flange, the peeling of a 0.5 mm or more portion from the flange edge was evaluated as X at any spot of the flange of the can body. Or the peeling of one or more lines in the direction of the height in the flange portion of the can body was evaluated as X. No peeling was evaluated as O.

6. Evaluation of flavor retention

When the flavor component of the contents in the can body is absorbed by the material of the inside coating of the can body, the flavor of the contents changes. Also, when the material of the inside coating of the can body dissolves into the contents, the flavor of the contents changes. Flavor retention was evaluated according to a sensor test on the flavor of contents in a filled can storage test and flavor component absorption rate.

In the sensor test on the flavor of contents, Coca Cola light (a carbonated drink manufactured by Coca Cola Bottling) was filled into a can and kept at room temperature for 3 months, and the sensory difference between it and the liquid of the drink which was not kept was checked. No difference at a significance level of 5 % was evaluated as O and the existence of the difference at a significance level of 5 % was evaluated as X.

The measurement of flavor component absorption rate was carried out in accordance with a method described in NIPPON SHOKUHIN KOGYO GAK SHI, Vol.34, No.5, pp.267-273, 1987. That is, a model solution (1 % of citric acid) prepared by adding orange flavor (a mixture of 10 ppm of each of myrcene, a-terpinene, d-limonene, y-terpinene, pcymene, and 2-carene) was filled into a test can which was double seamed and kept at 20°C for 10 days. Thereafter, the flavor component was collected from the coating on the inside surface of the can body, concentrated and subjected to gas chromatography to obtain an absorption ratio (amount of the flavor component in the film/amount of the flavor component in the solution) from the solution before filling. The collection, concentration and analysis methods of the flavor component were based on the above document. A d-limonene distribution rate of less than 2 % was evaluated as 0 and that of 2 % or more as X.

7. Evaluation of filled can storage test

100 test can bodies were filled with Coca Cola light (carbonated drink) in accordance with a specified method, covered with an end, kept at 37°C for 6 months and opened. The area of under film corrosion (to be abbreviated as UFC) on the inside surface of the can body was measured and iron ions dissolved into the contents were measured by atomic absorption analysis to calculate the average amount of dissolution. A UFC area of 0 to 10 mm$^2$ was evaluated as 0 and that of more than 10 mm$^2$ as X.

8. Measurement of crystallinity of crystalline polyester resin coating

The crystallinity of the crystalline polyester resin coating was measured in accordance with the method described in SEN-I GAKKAISHI, Vol.33, No.10, pp.780-788, 1977. Specifically, the distribution of X-ray diffraction scattering intensity is separated according to the contributions from crystal and non-crystal phases and calculated as an integrated intensity ratio with respect to a Bragg angle.

9. Measurement of Tg, total elongation (to be abbreviated as EL hereinafter) and IV of the resin coating before forming

After the resin coating was peeled off the metal plate, Tg and EL (elongation) of the resin coating were measured by conventional means. IV was measured at 25°C in o-chlorophenol.

10. Measurement of the average thickness of the tin coating film on the inside wall of the can body and average thickness of the organic resin coating on the inside wall of the can body

The average thickness of the tin coating on the inside wall of the can body was obtained by averaging measurement values obtained by peeling off the organic resin from the inside surface of a wall portion of the can body (a 30 to 80 mm portion from the bottom of the can body) which receives the largest ironing formation, preparing three 20 mmϕ circular samples and measuring by fluorescent X-ray spectroscopy. The average thickness of the organic resin coating on the inside wall of the can body was obtained by averaging measurement values obtained by peeling off the organic resin coating by dissolving the metal at the same site and measuring any desired 10 points with a micrometer.

Example 1-1

One side of tinplate having a thickness of 0.245 mm, temper 4 and E 2.8/2.8 was thermally coated with a 90 μm thick amorphous crystalline polyester resin (polyethylene terephthalate/isophthalate based) and quenched. Tg, EL, IV and crystallinity of the resin after coating are shown in Table 1. Using this tinplate coated with resin on one side thereof, a drawn and wall-ironed can body was prepared under the conditions shown in Table 1. Forming conditions and evaluations are shown in Table 1.

Examples 1-2 and 1-3, Comparative Examples 1-1 and 1-2

Drawn and wall-ironed can bodies were prepared in the same manner as in Example 1-1 except that the thicknesses of the organic resin coatings formed on the tinplate were 30 μm, 15 μm and 9 μm, respectively

(Examples 1-2 and 1-3 and Comparative Example 1-1).

A drawn and wall-ironed can body was prepared in the same manner as in Example 1-1 except that the thickness of the organic resin coating formed on the tinplate was 120 μm (Comparative Example 1-2). Forming conditions and evaluations are shown in Table 1. Since a flange portion peeled off at the time of forming, evaluations on flavor retention and the filled can storage test were not performed.

Example 2-1

One side of a tinplate having a thickness of 0.245 mm, temper 4 and E 2.8/2.8 was thermally coated with a 30 μm thick biaxially oriented crystalline polyester resin film (polyethylene terephthalate/isophthalate based) and the retention time at 230°C was adjusted so that the crystallinity of the polyester resin film on the laminated tinplate (before forming) reached 2%. Thereafter, the laminated tinplate was quenched. Tg, EL, IV and crystallinity of the resin after coating are shown in Table 1. Using this tinplate coated with the resin on one side thereof, a drawn and wall-ironed can body was made. Forming conditions and evaluations are shown in Table 1.

Example 2-2, Comparative Examples 2-1 and 2-2

Drawn and wall-ironed can bodies were prepared in the same manner as in Example 2-1 except that the crystallinities of the polyester resins of the laminated plates (before forming) were 5 %, 9 % and 24 %, respectively (Example 2-2, Comparative Examples 2-1 and 2-2). Forming conditions and evaluations are shown in Table 1.

Example 3-1

One side of a tinplate having a thickness of 0.245 mm,, temper 4 and E 2-8/2-8 was thermally coated with a 30 μm thick amorphous crystalline polyester resin (polyethylene terephthalate/isophthalate based) and quenched. At this point, the copolymerization ratio of isophthalic acid was changed to set Tg to 65°C, and a drawn and wall-ironed can body was made using this tinplate. Forming conditions and evaluations are shown in Table 1.

Example 3-2, Comparative Examples 3-1 and 3-2

Drawn and wall-ironed can bodies were prepared in the same manner as in Example 3-1 except that the Tgs of the polyester resins were 58°C (isophthalic acid copolymer), 54°C (sebacic acid copolymer) and 48°C (adipic acid copolymer) (Example 3-2, Comparative Examples 3-1 and 3-2). Forming conditions and evaluations are shown in Table 1.

A drawn and wall-ironed can body was prepared as Comparative Example 3-3 in the same manner as in Example 3-1 except that a 3 μm thick thermosetting resin was coated on one side of a tinplate (inside surface), dried and baked (half-cured), thermally coated with a 30 μm thick amorphous crystalline polyester resin and quenched. Forming conditions and evaluations are shown in Table 1.

A drawn and wall-ironed can body was prepared as Comparative Example 3-4 in the same manner as in Example 3-1 except that the resin to be thermally coated on one side of the tinplate was a polyester resin (polyethylene terephthalate/isophthalate based) having no thermal crystallizability. Forming conditions and evaluations are shown in Table 1.

Example 4-1

One side of a tinplate having a thickness of 0.245 mm, temper 4 and E 2.8/2.8 was thermally coated with a 30 μm thick amorphous crystalline polyester resin (polyethylene terephthalate/isophthalate based) and quenched. The total elongation of this resin coating was set to 285 % by changing the copolymerization ratio. Using this tinplate coated with the resin on one side thereof, a drawn and wall-ironed can body was made. Forming conditions and evaluations are shown in Table 1.

Example 4-2, Comparative Example 4-1

Drawn and wall-ironed can bodies were prepared as Example 4-2 and Comparative Example 4-1 in the same manner as in Example 4-1 except that the total elongations of the polyester resins were 133 % and 3 %, respectively. Forming conditions and evaluations are shown in Table 1.

Example 5-1

One side of a tinplate having a thickness of 0.245 mm, temper 4 and E 2.8/2.8 was thermally coated with a 30 μm thick biaxially oriented crystalline polyester resin film (polyethylene terephthalate/isophthalate based), maintained at a temperature of 230°C so that the crystallinity of the polyester resin on the laminated plate (before forming) reached 5%, and quenched. Using this tinplate coated with the resin on one side thereof, a drawn and wall-ironed can body was made. Forming conditions and evaluations in Table 1.

Example 5-2, Comparative Examples 5-1 and 5-2

Drawn and wall-ironed can bodies were prepared as Example 5-2 and Comparative Example 5-1 and 5-2 in the same manner as in Example 5-1 except that the IVS of the polyester resins after lamination were 0.68, 0.63 and 0.56, respectively. Forming conditions and evaluations are shown in Table 1.

Table 1

| | Type of resin | F | G | H | J | K | L | M | N | O | Diameter | Rate | Evaluation | P | | Q | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Dissolution of Fe (ppm) | UFC | R | S |
| Example 1-1 | A | 30 | 0.9 | 100 | 74 | 0.85 | 212 | 0 | Yes | 4.5 | 206 | 0.81 | 0 | 0.0 | ○ | ○ | ○ |
| Example 1-2 | A | 10 | " | 100 | " | " | " | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 1-3 | A | 5 | " | 92 | " | " | " | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 1-1 | A | 3 | " | 78 | " | " | " | | " | " | " | " | " | 10.3 | X | ○ | X |
| Comparative Ex. 1-2 | A | 40 | " | 100 | " | " | " | " | " | " | " | " | 36 | - | - | - | - |
| Example 2-1 | A | 10 | " | 100 | " | " | 276 | 2 | " | " | " | " | 0 | 0.0 | ○ | ○ | ○ |
| Example 2-2 | A | " | " | 95 | " | " | 329 | 5 | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 2-1 | A | " | " | 81 | " | " | 254 | 9 | " | " | " | " | " | 3.5 | X | ○ | X |
| Comparative Ex. 2-2 | A | " | " | 68 | " | " | 191 | 24 | " | " | " | " | " | 16.2 | X | ○ | X |
| Example 3-1 | A | " | " | 100 | 64 | | 336 | 0 | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 3-2 | A | " | " | 85 | 55 | | 280 | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 3-1 | B | " | " | 72 | 53 | | 383 | " | " | " | " | " | " | 9.0 | X | X | X |
| Comparative Ex. 3-2 | C | " | " | 64 | 48 | | 411 | " | " | " | " | " | " | 7.9 | X | X | X |
| Comparative Ex. 3-3 | D | " | " | 73 | 74 | | 246 | " | " | " | " | 0.40 | " | 11.3 | X | ○ | X |
| Comparative Ex. 3-4 | E | " | " | 79 | 68 | | 3 | " | " | " | " | 0.81 | " | 2.5 | X | X | X |
| Example 4-1 | A | " | " | 100 | 78 | | 285 | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 4-2 | A | " | " | 100 | 72 | | 133 | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 4-1 | A | " | " | 77 | 70 | | 3 | " | " | " | " | " | " | 4.0 | X | ○ | X |
| Example 5-1 | A | " | " | 100 | 78 | | 308 | 5 | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 5-2 | A | " | " | 100 | 71 | | 352 | " | " | " | " | " | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 5-1 | A | " | " | 83 | 70 | 0.63 | 295 | " | " | " | " | " | " | 5.3 | X | ○ | X |

Notes on Table 1

(Notes) Reference letters A to S in the Table stand for the following:-

A: copolymer of isophthalic acid and PET

B: copolymer of sebacic acid and PET

C: copolymer of adipic acid and PET

D: thermoset resin (adhesive layer) + copolymer of isophthalic acid and PET

E: copolymer of isophthalic acid and PET having no thermal crystallizability

F: average thickness of organic resin coating on inside surface of can body (μm)

G: average thickness of tin coating on inside surface of can body (g/m$^2$)

H: effective coverage rate of tin on inside surface of can body (rate of a portion having a tin mass of 0.1 g/m$^2$ or more)

J: Tg of resin coating before forming (°C)

K: IV of resin coating before forming (dl/g)

L: EL of resin coating before forming (%)

M: crystallinity of resin coating before forming (%)

N: cooling immediately after final ironing step

O: approach angle of ironing die (1)

P: evaluation of corrosion resistance

Q: evaluation of flavor retention

R: absorption of flavor component

S: flavor sensory test

UFC: under film corrosion

diameter: inside diameter of top of necked can body

rate: coverage rate of iron-tin alloy

evaluation: evaluation on peeling-off of flange portion

In Comparative Example 1-2, peeling-off at a flange portion occurred. Continuous forming was impossible because of poor strippability from the punch sleeve. Comparative Examples 6-1 and 6-2

Drawn and wall-ironed can bodies were prepared as Comparative Examples 6-1 and 6-2 by drawing and wall-ironing a tinplate having a thickness of 0.245 mm, temper 4, D 6.0/2.8 and E 2.8/2.8, making the side 2.8 outside of the can body, without an organic resin coated thereon, washing and drying, spray coating with a vinyl organosolbased resin, and baking. The average tin coating mass on the inside wall of the can body and the coverage rate of the tin coating were measured, and the peeling of a flange portion, flavor retention and a filled can storage test were evaluated. The coverage rate of an iron-tin alloy was not meas red. As a result, the average tin coating masses on the inside walls of the can bodies were found to be 2.0 g/m$^2$ and 0.9 g/m$^2$, the coverage rates of tin coatings on the inside walls of the can bodies were 81% and 77%, the numbers of cans whose flange portions were peeled off were 0, the amounts of iron dissolution were 2.7 ppm and 6.5 ppm, UFC evaluations were all X and flavor sensory test evaluations were all X, respectively. In the filled can storage test, perforation leakage from a double seamed area was observed in 5 and 9 out of 100 can bodies, respectively.

Example 7-1

Side 6.0 (inside of the can body) of a tinplate having a thickness of 0.245 mm, temper 4 and D 6.0/2.8 was thermally coated with a 30 μm thick amorphous crystalline polyester resin (polyethylene terephthalate/isophthalate based) and quenched. Using this coated tinplate, a drawn and wall-ironed can body was made. Forming conditions and evaluations are shown in Table 2.

Examples 7-2 and 7-3, Comparative Examples 7-1 and 7-2

Drawn and wall-ironed can bodies were prepared in the same manner as in Example 7-1 except Example 7-2 used a tinplate having D 4-5/2.8 (1-5 is the inside of the can body), Example 7-3 and Comparative Examples 7-1 and 7-2 had tin coatings on the one side (inside) of the tinplate of 0.6 g/m$^2$, 0.3 g/m$^2$ and 0.0 g/m$^2$ , respectively, and those on the other side (outside) of 2.8. Forming conditions and evaluations are shown in Table 2.

Comparative Example 8

A drawn and wall-ironed can body was prepared as Comparative Example 8 in the same manner as in Example 1-2 except cooling was not carried out just after the final wall-ironing step. A cup could not formed due to poor strippability from punch sleeve after wall-ironing.

Example 9-1

A drawn and wall-ironed can body was prepared in the same manner as in Example 1-2 except a wall-ironing die (to be abbreviated as ID hereinafter) having an approach angle of 21 was used in first, second and third wall-ironing steps. Forming conditions and evaluations are shown in Table 2.

Examples 9-2 and 9-3, Comparative Examples 9-1 and 9-2

Drawn and wall-ironed can bodies were prepared in the same manner as in Example 9-1 except that ID approach angles of Examples 9-2 and 9-3 and Comparative Examples 9-1 and 9-2 were 6°, 8°, 10° and 12°, respectively. Forming conditions and evaluations are shown in Table 2.

Example 10-1

One side of a tinplate having a thickness of 0.245 mm, temper 4 and E 2.8/2.8 was thermally coated with a 30 μm thick amorphous crystalline polyester resin (polyethylene terephthalate/isophthalate based) and quenched. Tg, EL, IV and crystallinity of this resin after coating are shown in Table 1. A drawn and wall-ironed cup having a cup diameter of 65.8 mm, a metal thickness of the can body wall of 80 μm and a metal thickness of a neck portion of 135 μm was formed of this tinplate coated with the resin on one side thereof by blanking to a blank diameter of 142 mm, drawing in a total draw ratio of 2.1, and carrying out three steps of wallironing so that the resin coated surface turned to the inside of the can body. The edge of a first drawn cup was subjected to a high-frequency induction heat treatment. This drawn and wall-ironed cup was trimmed to a can body height of 123 mm, washed, dried, printed on the outside surface thereof, and heated at 200°C for 30 seconds. The inner diameter of the top of the can body was necked into 57.25 mm and a flange was formed to obtain a drawn and wall-ironed can body. Forming conditions are shown in Table 2.

The thus obtained drawn and wall-ironed can body was used for the measurement of the average tin coating mass, the thickness of an organic resin coating, the coverage rate of a tin coating and he coverage rate of an iron-tin alloy, the observation of can body forming conditions, and evaluations on flavor retention and filled can storage test. Results are shown in Table 2.

Example 11-1

A drawn and wall-ironed can body was prepared in the same manner as in Example 1-2 except that a first drawn cup was subjected to a high-frequency induction heat treatment at a cup edge ultimate temperature of about 300°C for 1.0 second and the inner diameter of the top of the can body was necked into 52.4 mm (diameter 202). Forming conditions and evaluation results are shown in Table 2.

Example 11-2

A drawn and wall-ironed can body was prepared in the same manner as in Example 11-1 except that a first drawn cup was subjected to a high-frequency induction heat treatment at a cup edge ultimate temperature of about 320°C for 1.0 second. Forming conditions and evaluation results are shown in Table 2.

Example 11-3

A drawn and wall-ironed can body was prepared in the same manner as in Example 11-1 except that the tin coating mass of a tinplate which turns to the inside of the cup was 6.0 g/m$^2$. Forming conditions and evaluation results are shown in Table 2.

Example 11-4

A drawn and wall-ironed can body was prepared in the same manner as in Example 11-1 except that the tin coating mass of a tinplate which turns to the inside of the cup was 0.6 g/m$^2$. Forming conditions and evaluation results are shown in Table 2.

Comparative Example 11-1

A drawn and wall-ironed can body was prepared in the same manner as in Example 11-1 except that a first drawn cup was subjected to a high-frequency induction heat treatment at a cup edge ultimate temperature of 320°C for 1.0 second. Forming conditions and evaluation results are shown in Table 2.

Comparative Example 11-2

A drawn and wall-ironed can body was prepared in the same manner as in Example 11-1 except that the cup was not subjected to a heat treatment. Forming conditions and evaluation results are shown in Table 2.

It was understood from Examples 1-1 to 1-3, 3-1, 3-2, 7-1 to 7-3, 10-1 and 11-1 to 11-4 that, when the drawn and wall-ironed can bodies are formed of a tinplate thermally coated with a thermoplastic resin on one side thereof which turns to the inside of the can body, the thermoplastic resin on the inside surface of the can body is essentially composed of crystalline polyester resin, the average thickness of a thermoplastic resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass on the inside wall of the can body is 0.2 to 2.0 g/m$^2$, the effective average rate of tin is at least 85 %, the surface of metal, in contact with the thermoplastic resin, of a portion at least 2 mm wide from the top end of the flange is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7, corrosion resistance (dissolution of Fe, UFC, perforation corrosion resistance) and flavor retention (flavor component absorption, resin component migration) are excellent.

It is evident from Comparative Examples 6-1 and 6-2 that, when drawn and wall-ironed can bodies are formed of a tinplate without an organic coating and an organic coating is formed thereon by spray coating, the effective coverage rate of tin coating is below 85 %, and corrosion resistance and flavor retention is poor.

It is seen from Comparative Example 3-3 that, when a drawn and wall-ironed can body is formed of a tinplate coated with a thermoset resin on the inside surface of the can body and with a thermoplastic resin on the thermoset resin coating, the effective coverage rate of tin coating is below 85 %, and corrosion resistance and flavor retention are poor.

It is seen from Comparative Example 3-4 that, when the thermoplastic resin on the inside surface of the can body is essentially composed of an amorphous (having no thermal crystallizability) polyester resin, the effective coverage rate of tin coating is below 85 %, and corrosion resistance and flavor retention are poor.

It is seen from Comparative Example 1-1 that, when the average thickness of the thermoplastic resin coating on the inside wall of the can body is less than 5 μm, the effective coverage rate of tin coating is below 85 %, and corrosion resistance and flavor retention are poor.

It is understood from Comparative Example 1-2 that, when the average thickness of the thermoplastic resin coating on the inside wall Of the can body is less than 30 μm, a flange portion peels between the organic resin and the metal and can body making is impossible.

It is understood from Comparative Examples 7-1 and 7-2 that, when the average tin coating mass on the inside wall of the can body is less than 0.2 g/m$^2$, the effective coverage rate of tin coating is below 85 %, and corrosion resistance and flavor retention are poor.

It is understood from Comparative Examples 1-1, 2-1, 2-2, 3-1 to 3-4, 4-1, 5-1, 5-2, 6-1, 6-2, 7-1, 7-2, 9-1, 9-2, 11-1 and 11-2 that, when the effective coverage rate of tin coating is below 85 %, corrosion resistance and flavor retention are poor.

It is understood from Comparative Example 11-1 that, when the temperature of the high-frequency induction heating treatment of the cup edge is low, the coverage rate of the iron-tin alloy is below 0.7 and peeling at the flange portion occurs. As a result, a can body which can be subjected to a filled can storage test cannot be made.

It is understood from Comparative Example 11-2 that, when the cup is not subjected to a heat treatment, the coverage rate of the iron-tin alloy is below 0.7 and peeling at the flange portion occurs. As the result, a can body which can be subjected to a filled can storage test cannot be made.

It is understood from Comparative Examples 11-1 and 11-2 that, when the coverage rate of the iron-tin alloy is below 0.7, peeling at the flange portion occurs and a can body cannot be made.

It is understood from Comparative Example 8 that, when cooling is not carried out immediately after the final ironing step, strippability from the punch sleeve is poor and continuous can body forming is impossible.

It is evident from Examples 2-1, 2-2, 3-1, 3-2, 4-1, 4-2, 5-1, 5-2, 9-1 to 9-3 and 11-1 to 11-4 and Comparative Examples 2-1, 2-2, 3-1, 3-2, 4-1, 5-1, 5-2, 8, 9-1, 9-2, 11-1 and 11-2 that a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention, which is formed of a tinplate thermally coated with a thermoplastic resin on the side thereof which turns to the inside of the can body, wherein the thermoplastic resin on the inside surface of the can body is essentially composed of a crystalline polyester resin (having thermal crystallizability), the average thickness of the thermoplastic resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass on the inside wall of the can body is 0.2 to 2.0 g/m$^2$, the effective coverage rate of tin coating is at least 85 % and the surface of a metal of an inner portion at least 2 mm wide from the top end of the flange of the can body is coated with an iron-tin alloy, can be produced when the crystalline polyester resin, a main component of the thermoplastic resin on the inside surface of the can body has a Tg of at least 55°C, an IV of at least 0.65, a crystallinity before forming of 5 % or less, and a total EL of at least 100 %, a cup is formed by at least a single drawing, the portion at least 2 mm wide from the top end of the flange of the can body is subjected to a heat treatment, the cup is redrawn if necessary, the approach angle of an ironing die is 2 to 81, and cooling is carried out immediately after the final ironing step.

Table 2

| | Type of resin | F | G | H | J | K | L | M | N | O | Dia-meter | Rate | Evalu-ation | P | | Q | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | | | | | | Dissolution of Fe (ppm) | UFC | R | S |
| Example 7-1 | A | 10 | 2.0 | 100 | 74 | 0.85 | 212 | 0 | " | " | 206 | 0.71 | 0 | 0.0 | ○ | ○ | ○ |
| Example 7-2 | A | " | 1.5 | 100 | " | " | " | " | " | " | " | 0.90 | " | 0.0 | ○ | ○ | ○ |
| Example 7-3 | A | " | 0.2 | 97 | " | " | " | " | " | " | " | 0.95 | " | 0.0 | ○ | ○ | ○ |
| Comparative Ex. 7-1 | A | " | 0.1 | 53 | " | " | " | " | " | " | " | 1.00 | " | 5.4 | X | ○ | X |
| Comparative Ex. 7-2 | A | " | 0.0 | 0 | " | " | " | " | " | " | " | - | " | 7.8 | X | ○ | X |
| Comparative Ex. 8 | A | " | 0.9 | - | " | " | " | " | No | " | - | - | - | - | - | - | - |
| Example 9-1 | A | " | " | 100 | " | " | " | " | Yes | 2 | 206 | 0.81 | 0 | 0.0 | ○ | ○ | ○ |
| Example 9-2 | A | " | " | 100 | " | " | " | " | " | 6 | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 9-3 | A | " | " | 95 | " | " | " | " | " | 8 | " | " | " | 0.0 | Δ | ○ | X |
| Comparative Ex. 9-1 | A | " | " | 73 | " | " | " | " | " | 10 | " | " | " | 6.8 | X | ○ | X |
| Comparative Ex. 9-2 | A | " | " | 65 | " | " | " | " | " | 12 | " | " | " | 8.3 | X | ○ | X |
| Example 10-1 | B | " | " | 100 | " | " | " | " | " | 4.5 | " | " | " | 0.0 | ○ | ○ | ○ |
| Example 11-1 | C | " | " | " | " | " | " | " | " | " | 202 | " | " | " | ○ | ○ | ○ |
| Example 11-2 | D | " | " | " | " | " | " | " | " | " | " | 0.92 | " | " | ○ | ○ | ○ |
| Example 11-3 | E | " | " | " | " | " | " | " | " | " | " | 0.71 | " | " | ○ | ○ | ○ |
| Example 11-4 | A | " | " | 97 | " | " | " | " | " | " | " | 0.95 | " | " | ○ | ○ | ○ |
| Comparative Ex. 11-1 | A | " | " | 100 | " | " | " | " | " | " | " | 0.57 | 7 | - | - | - | - |
| Comparative Ex. 11-2 | A | " | " | " | " | " | " | " | " | " | " | 0.46 | 53 | - | - | - | - |

Notes on Table 2

(Notes) Reference letters A to S in the Table stand for the following:-

A: copolymer of isophthalic acid and PET

B: copolymer of sebacic acid and PET

C: copolymer of adipic acid and PET

D: thermoset resin (adhesive layer) + copolymer of isophthalic acid and PET

E: copolymer of isophthalic acid and PET having no thermal crystallizability

F: average thickness of organic resin coating on inside surface of can body (μm)

G: average thickness of tin coating on inside surface of can body ($g/m^2$)

H: effective coverage rate of tin on inside surface of can body (rate of a portion having a tin mass of 0.1 $g/m^2$ or more)

J: Tg of resin coating before forming (OC)

K: IV of resin coating before forming (dl/g)

L: EL of resin coating before forming (%)

M: crystallinity of resin coating before forming (%)

N: cooling immediately after final ironing step

O: approach angle of ironing die (0)

P: evaluation on corrosion resistance

Q: evaluation on flavor retention

R: absorption of flavor component

S: flavor sensory test

UFC: under film corrosion

diameter: inside diameter of top of necked can body

rate: coverage rate of iron-tin alloy

evaluation: evaluation on peeling-off from flange portion

In Comparative Examples 11-1 and 11-2, peeling-off at a flange portion occurred due to poor forming and can body making conditions. In Comparative Example 8, peeling-off at neck and flange portions occurred. Strippability from the punch sleeve was poor and continuous can body forming was impossible.

This invention relates to a drawn and wall-ironed can body which is unknown in the prior art, wherein the tin coating mass is 0.2 to 2.0 $g/m^2$, a thermoplastic resin coating having a thickness of 5 to 30 μm is formed on the surface of the tinplate, the effective coverage rate of the tin coating is at least 85 %, the surface of a metal of a portion at least 2 mm wide from the top end of the flange is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least

0.7. This invention has an excellent effect of improving the corrosion resistance and flavor retention of the can.

## Claims

1. A drawn and wall-ironed can body having excellent corrosion resistance and flavor retention, which is formed of tinplate coated with a thermoplastic resin at least on one side thereof which becomes the inside of the can body, wherein the thermoplastic resin is essentially composed of a crystalline polyester resin, the average thickness of the resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass is 0.2 to 2.0 $g/M^2$, the effective coverage rate of the tin coating is at least 85 %, the surface of the metal of the inner portion at least 2 mm wide from the top end of the flange of the can body is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7.

2. A drawn and wall-ironed can body having excellent corrosion resistance and flavor retention according to claim 1, wherein said crystalline polyester resin which is a main component of the coating resin has a glass transition temperature (Tg) of at least 55°C and an intrinsic viscosity (IV) of at least 0.65.

3. A drawn and wall-ironed can body having excellent corrosion resistance and flavor retention according to claim 1 or 2, wherein the effective coverage rate of the tin is a value indicative of the rate of portions having a tin coating mass of at least 0.1 $g/m^2$.

4. A drawn and wall-ironed can body having excellent corrosion resistance and flavor retention according to any one of claims 1 to 3, wherein the coverage rate of the iron-tin alloy is a value C obtained from the expression $C = A/(A + B)$ wherein A is the amount of tin contained in the alloy present on the 2 mm area from the top end of the flange and B is an amount of free tin present in the same area.

5. A method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention, wherein the average thickness of a resin coating on the inside wall of the can body is 5 to 30 μm, the average tin coating mass is 0.2 to 2.0 $g/m^2$, and the effective coverage rate of the tin coating is at least 85 %, the surface of the metal of the inner portion at least 2 mm wide from the top end of the flange of the can body is coated with an iron-tin alloy, and the coverage rate of the iron-tin alloy is at least 0.7, the method comprising the steps of:

   forming a thermoplastic resin coating which is essentially composed of a crystalline polyester resin, has a crystallinity of 5 % or less, a thickness of 15 to 90 μm, a total elongation of at least 100 %, a Tg of at least 55°C and an intrinsic viscosity (IV) of at least 0.65 on the surface of the tinplate having a tin coating mass of 0.4 to 6.0 $g/M^2$, which becomes the inside surface of the can body,
   making a cup by at least a single drawing of the thermoplastic resin coated tinplate,
   heating the portion of the drawn cup which becomes at least 2 mm wide from the top end of the flange of the can body,
   redrawing if necessary,
   ironing the wall of the cup with a punch and ironing dies having an approach angle of 2 to 8°, and cooling immediately after the final ironing step.

6. A method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention according to claim 5, wherein the temperature of the tin coating formed on the inside surface of the cup is maintained lower than 232°C at the time of forming, and the temperature of the tin coating on the inside surface of the neck portion and the flange portion is maintained lower than 232°C by quenching immediately after the final ironing step.

7. A method for producing a drawn and wall-ironed can body having excellent corrosion resistance and flavor retention according to claim 5 or 6, wherein the thermoplastic resin coating essentially composed of a polyester resin is oriented and crystallized in the step of drawing, wall-ironing and heating.

European Patent Office

# EUROPEAN SEARCH REPORT

Application Number
EP 96 30 4119

| DOCUMENTS CONSIDERED TO BE RELEVANT | | | |
|---|---|---|---|
| Category | Citation of document with indication, where appropriate, of relevant passages | Relevant to claim | CLASSIFICATION OF THE APPLICATION (Int.Cl.6) |
| A | EP-A-0 432 497 (NIPPON STEEL CORP ;MITSUI PETROCHEMICAL IND (JP)) 19 June 1991<br>* the whole document *<br>--- | 1,5 | B05D7/14 |
| A | DE-A-38 36 858 (TOYO KOHAN CO LTD) 10 May 1990<br>* the whole document *<br>--- | 1,5 | |
| A | PATENT ABSTRACTS OF JAPAN<br>vol. 013, no. 485 (M-887), 6 November 1989<br>& JP-A-01 192545 (NIPPON STEEL CORP), 2 August 1989,<br>* abstract *<br>--- | 1 | |
| A | DATABASE WPI<br>Section Ch, Week 8542<br>Derwent Publications Ltd., London, GB;<br>Class A92, AN 85-259471<br>XP002013087<br>& JP-A-60 172 637 (KISHIMOTO A) , 6 September 1985<br>* abstract *<br>--- | 1 | TECHNICAL FIELDS SEARCHED (Int.Cl.6) |
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The present search report has been drawn up for all claims

| Place of search | Date of completion of the search | Examiner |
|---|---|---|
| THE HAGUE | 11 September 1996 | Brothier, J-A |

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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