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(54) COATED METAL SHEET AND PROCESS FOR PRODUCTION THEREOF

(71) We, TORAY INDUSTRIES INC. and TOYO SEIKAN KAISHA LIMITED, both Japanese Body Corporate of No. 2-2 Muro-machi, Nihonbashi, Chuo-ku, Tokyo, Japan and No. 3-1, 1-chome, Uchisaiwai-cho, Chiyoda-ku, Tokyo, Japan respectively, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to a coated metal sheet having excellent peel resistance, adaptability to shaping process and corrosion resistance, which comprises a metal sheet coated with layer of a thermoplastic polyester resin heat-bonded to the metal substrate, and to a process for the production of such coated metal sheet.

In order to impart corrosion resistance to metallic materials, methods comprising coating surfaces of metallic materials with resin layers have heretofore been broadly adopted in the art. As typical instances of such conventional coating method, there can be mentioned a method comprising coating a solution or dispersion of a thermosetting resin such as an epoxy resin, a phenolic resin, a polyester resin or an acrylic resin in a suitable solvent on the surface of a metallic material, heating the coating to remove the solvent and effect curing of the resin layer and thus forming a resin coating on the surface of the metallic material, and a method comprising applying an adhesive composed mainly of a polyfunctional isocyanate, epoxy or phenol compound on the surface of a film of a thermoplastic resin such as a vinyl chloride resin, a polyolefin resin, a polyester resin or an acrylic resin or on the surface of a metallic material and bonding them through the adhesive layer. These conventional methods, however, are defective in various respects. For example, since a number of steps such as heating, curing and solvent removal are required for obtaining intended coated metal structures, productivity is very low. Further, since the coated resin layer is composed of a thermosetting resin having a very low elongation or such a thermosetting resin is present as the bonding layer between a thermoplastic resin layer and the metal substrate, the resulting coated metal structures are very poor in adaptability to shaping processability. Therefore, although it is possible to subject these coated metal structures to relatively simple shaping processing with a low ratio of reduction or deformation such as folding and bending, it generally is difficult to subject these coated metal structures to complicated shaping processing with a high ratio of reduction or deformation such as deep drawing and ironing.

As means for overcoming such disadvantages involved in the conventional methods, there has been proposed a method in which a coated metal structure is heated before it is deformed for shaping (see Japanese Patent Publication No. 13728/66). Even according to this method, however, it is impossible to improve the adaptability to shaping processing sufficiently.

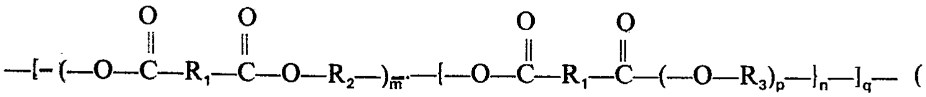
As a method which overcomes substantially the foregoing defects, a metal coating method utilizing the heat bonding technique has recently been adopted in the art, and metal structures coated with various thermoplastic resins such as polyolefine resins and vinyl chloride resins are now provided in the market. These metal structures, however, are still insufficient in various respects. For example, since the bonding between the metal substrate and the resin layer is insufficient and the mechanical properties of the resin layer are poor, when the coated metal structure is subjected to shaping processing with a high ratio of reduction or deformation, peeling and breakage of the resin layer is readily caused. Further, since the heat resistance of the coating resin layer is very low, it is difficult or substantially impossible to apply the coated metal structure to a use where the coated metal structure is exposed to high temperatures or it is subjected to a heat treatment.

It is known that a thermoplastic polyester resin composition can be used as a hot melt adhesive for metals and the like (see, for example, Japanese Patent Publication No. 4543/74 and Japanese Patent Application Laid-Open Specification No. 434/71). A polyester resin composition that is to be used in such a technique is required to have a low melting point, and the mechanical strength of this resin is low. More specifically, the properties of a thermoplastic polyester resin that is used as a hot melt adhesive are quite different from properties which must be possessed by a resin that is to be used to form a coating layer on a metal substrate. Accordingly, it has generally been considered that a thermoplastic polyester resin cannot be effectively used for coating metallic materials. Contrary to this general concept held in the art, we have found that a polyester resin having a relatively high melting point and a relatively high degree of polymerization and having a degree of crystallinity can provide a coated metal sheet having improved peel resistance, improved adaptability to shaping processing and improved corrosion resistance.

In accordance with the present invention, there is provided a metal sheet coated with a layer containing at least 70% by weight of a thermoplastic polyester resin which is heat-bonded to the surface of said metal substrate, wherein said polyester resin has a relative viscosity of 1.2 to 1.8 as measured at 25°C in o-chlorophenol at a concentration of 0.5 g/100 ml a tack point (as hereinafter defined) not lower than 130°C, and a degree of crystallinity of up to 30%.

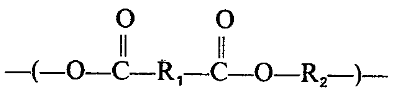
The thermoplastic polyester resin that is used in accordance with the present invention may be a homopolyester, copolyester or polyester-ether derived from, as dibasic acid component, at least one aromatic or aliphatic dicarboxylic acid such as terephthalic acid, isophthalic acid, phthalic acid, naphthalene-dicarboxylic acid, azelaic acid, sebacic acid, adipic acid or dodecane-dicarboxylic acid and, as diol component, at least one aliphatic or alicyclic glycol such as ethylene glycol, diethylene glycol, polyethylene glycol, propylene glycol, 1,4-butane diol, polytetramethylene glycol, 1,6-hexane diol, 1,10-decane diol, neoptentyl glycol or 1,4-cyclohexane diol. Thermoplastic polyester resins derived from a dicarboxylic acid component containing at least 45 mole% of terephthalic acid and an aliphatic diol component, especially one containing at least 45 mole% of 1,4-butane diol, are particularly preferred because they provide resin layers having good mechanical properties and good crystallinity characteristics. These polyester resins must have such a high strength that even when the resulting coated metal sheet is shaped, the coating layer is deformed in such a way as to follow the flow of the metal surface during deformation of the metal and no breakage or crack forms in the resin coating. In order to obtain a resin coating having such high strength, it is necessary to use a thermoplastic polyester resin having a relative viscosity of 1.2 to 1.8, especially at least 1.25, as measured at 25°C in o-chlorophenol at a concentration of 0.5 g/100 ml. If the relative viscosity is higher than 1.8, the film-forming property and heat-bonding characteristic of the thermoplastic polyester resin are degraded.

The polyester preferably is composed of recurring units of the formula:



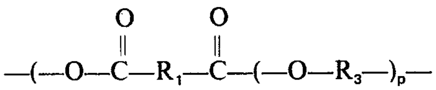
$$-[-(-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-O-R_2-)_m-[-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-(-O-R_3)_p-]_n-]_q- \quad (1)$$

wherein R_1 is a divalent hydrocarbon group (preferably at least 45 mole%, especially at least 60 mole%, of the units represented by R_1 are p-phenylene groups); R_2 and R_3, which may be the same or different, are each a divalent aliphatic hydrocarbon group (preferably at least 45 mole%, especially at least 55 mole%, of the groups represented by R_2 and R_3 are tetramethylene groups), p and q are each at least 1, and m and n are each 0 or at least 1, with the proviso that when one of m and n is 0, the other must be at least 1. (In this formula the units



$$-(-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-O-R_2-)-$$

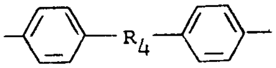
are for convenience referred to as (A) units and are ester units and the units



$$-(-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-(-O-R_3-)_p-$$

are for convenience referred to as (B) units and are ester units when p is 1 or ester-ether units when p is 2 or more).

As the divalent hydrocarbon group R_1 in the above general formula, there can be mentioned, for example, linear and branched alkylene groups having 2 to 13 carbon atoms, cycloalkylene groups having 4 to 12 carbon atoms and arylene groups having 6 to 15 carbon atoms. In view of the corrosion resistance, extraction resistance and mechanical properties of the coating resin layer, it is preferred that the divalent hydrocarbon group R_1 be wholly composed of an arylene group such as mentioned above, but up to 55 mole% of the total units represented by R_1 can be alkylene or cycloalkylene groups such as mentioned above. As the arylene group, in addition to a p-phenylene group, there can be mentioned o- and m-phenylene groups, a naphthylene group and groups represented by the following formula:



in which R_4 is a direct single bond or a divalent bridging group such as —O—, —CH_2—, —$CH(CH_3)$—, —$C(CH_3)_2$— or —NH—.

Alkylene groups having 2 to 13 carbon atoms can be mentioned as the alkylene groups R_2 and R_3, and among them, linear alkylene groups are preferred. Preferably not more than 55 mole% of the total units represented by R_2 and R_3 are groups other than alkylene groups, for example aliphatic hydrocarbon groups containing an aromatic or saturated ring such as an o-xylene group, a m-xylene group, a p-xylene group or a 1,4 dimethylenecyclohexylene group as an interposing group.

The units derived from the diol component may be contained in the polyester in any of the following 3 states. Namely, (a) all the units from the diol component are connected to units derived from the dibasic acid component so that all the diol component provides ester recurring unit; (b) all the units from the diol component are in the form of ester-ether recurring units; and (c) a part of the units from the diol component are in the form of ester recurring units and the remainder are in the form of ether-ester recurring units.

With (a) above, the recurring number n of the ester-ether unit is zero or the number p in the ester-ether unit is 1 in the above general formula (1), and the polyester is a homopolyester (derived from a single dibasic acid component and a single diol component) or copolyester (derived from at least two dibasic acid components and/or at least two diol components) containing solely ester recurring units (A). Preferred examples of such homopolyesters and copolyesters are poly(tetramethylene terephthalate), poly(propylene terephthalate), poly-tetramethylene/ethylene terephthalate), poly(tetramethylene terephthalate/isophthalate), poly(tetramethylene/ethylene terephthalate/isophthalate) and poly(tetramethylene/ethylene terephthalate/hexahydroterephthalate).

With (b) above, no ester units (A) are present and the polyester is a polyester-ether composed solely of ester-ether units (B). It is preferred in this case that p should be such that the average molecular weight of a polyethylene glycol of the formula $H-(-O-R_3-)_p-OH$ be from 200 to 4000, especially from 400 to 2000. Preferred examples of such polyester-ethers are poly(oxytetramethylene terephthalate), poly(oxyethylene terephthalate), poly(oxytetramethylene/oxyethylene terephthalate) and poly(oxytetramethylene/oxyethylene terephthalate/isophthalate).

With (c) above, in general formula (1), both m and n are at least 1, and p is at least 2. In this case, the manner of connection of ester units (A) and ester-ether units (B) is not particularly critical. In other words, a polyester of this type may be a block copolymer represented by the following formula:

$$(A)_m-(B)_n,$$

$$(A)_m-(B)_n-(A)_m,$$

$$(B)_n-(A)_m-(B)_n,$$

or

$$-(A)_m-(B)_n-(A)_m-(B)_n-$$

or a random copolymer represented by the following formula:

A–A–A–B–A–A–B–B–B

In this specification, the use of 1 mole of a polyester glycol of formula $H—(—O—R_3—)_p—OH$ in preparing a polyester is expressed as use of p moles of the glycol of formula $HO—R_3—OH$.

Suitable examples of copolyesters of this type are tetramethylene terephthalate/polyoxytetramethylene terephthalate, tetramethylene terephthalate/polyoxyethylene terephthalate, ethylene terephthalate/polyoxytetramethylene terephthalate, tetramethylene terephthalate/polyoxytetramethylene terephthalate, tetramethylene terephthalate/polyoxytetramethylene terephthalate/polyoxyethylene terephthalate, polytetramethylene terephthalate/polytetramethylene glycol block copolymers, polytetramethylene terephthalate/polytetramethylene glycol/polyethylene glycol block copolymers and polytetramethylene terephthalate/polypropylene glycol/polytetramethylene glycol/polyethylene glycol block copolymers.

In the present invention, the polyester layer can contain a single polyester or can be a blend of two or more polyesters.

In the present invention, in order to further improve the coated metal sheet or further improve surface characteristics of the resin layer, it is possible to incorporate into the resin layer a resin other than the polyester resin in an amount of up to 30% by weight of the total weight of the resin layer. As such an auxiliary resin, there can be mentioned, for example, polyolefin resins such as polyethylene, ethylene-vinyl acetate copolymers, saponified ethylene-vinyl acetate copolymers, grafted ethylene-vinyl acetate copolymers, ethylene-acrylic acid copolymers, metal salts of ethylene-acrylic acid copolymers, polypropylene and modified propylene polymers, vinyl resins such as polystyrene, copolymers of styrene with another vinyl monomer, homopolymers and copolymers of acrylic acid esters and homopolymers and copolymers of methacrylic acid esters, polyamide resins, and epoxy resins of the bisphenol A type. These resins may be used singly or in the form of mixtures of two or more of them. Moreover, in order to enhance the thermal stability, weatherability and flame resistance, it is possible to incorporate known additives effective for these improvements into the thermoplastic polyester resin layer in the present invention.

The tack point (T_1) of the polyester resin layer coated on the metal sheet is very important for the shapability or processability of the resulting coated metal structure. The tack point (T_1) should be at least 130°C, especially at least 150°C, and preferably is not higher than 250°C, especially not higher than 240°C.

The tack point is the temperature at which the polyester resin layer begins to adhere to the metal substrate heated and is determined by placing a polyester resin film on a metal sheet and heating the metal sheet while applying a pressure of 100 g/cm^2 to the film. The lowest temperature at which the film is fusion-bonded to the metal sheet is recorded and this temperature is defined as the tack point. When the polyester has a definite melting point (which is determined as the endothermic peak in differential thermal analysis) as with a crystalline polymer, this tack point corresponds substantially to the temperature of the rising portion of the endothermic peak. When the polyester does not show a definite melting point as with an amorphous polymer, the tack point corresponds substantially to the softening point as measured according to the ring and ball method (JIS K-2531).

If a polyester resin layer having a tack point lower than 130°C is used to prepare a coated metal sheet, then in shaping processing such a coated sheet, for example by deep drawing, the operation efficiency is drastically lowered when parting the resulting shaped article from a shaping mold. Further, the resin layer adheres to the mould and peeling is often caused.

When the tack point is higher than 250°C, thermal degradation of the polymer can take place when it is heat-bonded to the metal sheet, and a long time is required for fusion bonding or cooling of the polyester, resulting in reduction of the operation efficiency at the coating step. Moreover, a polyester having such a high tack point is ordinarily inferior with respect to the processability of the coating. The tack point of a thermoplastic polyester resin to be used in the present invention can be adjusted within the above-mentioned range by selecting appropriately the kind of the dicarboxylic acid component or diol component in the recurring units of the polyester or choosing an appropriate combination of these two components. Namely, in the present invention, it is preferred that constituents of the thermoplastic polyester resin be selected so that the tack point of the resin layer is from 130°C to 250°C.

In view of the peel resistance between the coating layer and metal sheet and the processability and corrosion resistance of a coated metal sheet, it is very important that the coating layer of the thermoplastic polyester resin heat-bonded to the metal sheet has a degree of crystallinity in the range of 0% to 30%.

When a cylindrical metal vessel having a drawing ratio of 2.0 is formed from a coated metal sheet by deep drawing, if the flow state of the metal surface is observed by a scanning electron microscope, it is seen that deformation of the metal is relatively small in the bottom portion of the vessel, but the flow of the metal surface gradually increases from the side face of the vessel toward the top thereof and the extent of flow is extremely large in the vicinity of the top end of the vessel. When a coated metal sheet is subjected to processing in the same manner as described above, it is observed that the surface of the resin layer in contact with the metal surface or the entire resin layer follows the flow of the metal surface. If the degree of crystallinity of the polyester resin layer of the coated sheet is higher than 30%, during the above deformation large strains appear and partial peeling of the resin layer is caused or the resin layer is easily peeled off when a slight shock is given to the resulting shaped article while it is actually used. Accordingly, it is necessary that the degree of crystallinity of the polyester resin layer of the coated metal sheet should be from 0% to 30%. If the degree of crystallinity of the polyester resin layer of the metal sheet is within this range, the interlaminar peel resistance, shaping processability and corrosion resistance of the coated metal sheet are remarkably improved.

When the coated metal sheet is used to prepare a container for canned food, it is often subjected to a heat treatment for outer surface printing or inner surface coating or at the step of filling with food or the sterilization step subsequent to the filling step. In this case, the degree of crystallinity of the polyester resin layer is ordinarily increased. In shaped articles prepared from the coated metal sheet of the present invention, it is preferred that the degree of crystallinity of the polyester resin layer be maintained at a level lower than 50%, especially lower than 40%, even after such heat treatment.

The degree of crystallinity referred to herein is a value determined according to the following procedures.

(1) The X-ray diffraction intensity of the resin layer is measured within a range of $2\theta=5$ to 40.

(2) A point of $2\theta=10$ and a point of $2\theta=35$ are connected by a straight line, and this line is designated as the base line.

(3) A substantially amorphous sample of a polyester resin having the same composition as that of the polyester resin layer is formed by a method comprising melting the polyester resin and throwing the melt into the liquid nitrogen or other appropriate method, and the X-ray diffraction intensity of the sample is measured in the same manner as described in (1) above.

(4) A gentle curve is drawn by connecting portions of the crystal diffraction peaks appearing on the diffraction curve obtained in (1) above so that it has a shape similar to the shape of the diffraction intensity curve obtained in (3) above.

(5) An area Ia surrounded by the base line obtained in (2) above the curve obtained in (4) above and an area Ic surrounded by the curve obtained in (4) above and the diffraction intensity curve obtained in (1) above are measured.

(6) The degree of crystallinity (DC) is defined as follows:

$$DC=\frac{Ic}{Ia+Ic}\times 100$$

As means for adjusting the degree of crystallinity of the polyester resin layer in the coated metal structure to 0 to 30%, there may be adopted, for example, (a) a method in which the rate of crystallization of the polyester resin layer heat-bonded to the metal substrate is adjusted so that the resulting degree of crystallinity is controlled at a level not higher than 30%, (b) a method in which a copolyester is used for formation of the resin layer and the kinds of copolyester-constituting components or copolymerization ratios thereof are adjusted so that a highest attainable degree of crystallinity is 30% or lower, and (c) a method in which several polyester resins differing in crystallinity characteristics are blended so that a highest attainable degree of crystallinity is 30% or lower. The foregoing methods may be adopted in combination. At any rate, when a polyester resin shaped in advance into a film is bonded to a metal sheet, it is preferred that the film be in the undrawn state or the degree of orientation by drawing be low. When a film having a degree of orientation enhanced by drawing is used, the degree of crystallinity heat-bonded to a metal sheet is often higher than 30% and no good results are obtained. When the degree of crystallinity of the polyester resin layer is adjusted according to the above method (a), the desired adjustment is accomplished by controlling the cooling conditions at the cooling step subsequent to the heat-bonding step. Still further, it is possible to adjust the degree of crystallinity of the polyester resin layer at a desirable level by incorporating a suitable crystallizing agent or plasticizer in the starting polyester resin.

The material of the metal sheet that is used in the present invention is not particularly critical in the present invention. For example, there can be used an untreated steel sheet (black sheet), a steel sheet chemically or electrochemically treated with phosphoric acid or a chromic acid, a tin free steel sheet, a chromium-coated steel sheet, a zinc-coated steel sheet, an aluminum-coated steel sheet, an iron sheet, an aluminum sheet, a chromium-coated aluminum sheet, a copper-plated steel sheet or a tin-coated steel sheet. Various steel and aluminum sheets are especially preferred as the metal sheet. These metal sheets, in general, are used after they have been sufficiently degreased. These metal sheets may be subjected to a surface treatment such as acid washing, oxidizing and reducing treatments according to need.

The method for formation of the coated metal sheet of the present invention is not particularly critical. However, in general, it is preferred to adopt a film lamination method comprising shaping a polyester resin into a film according to known procedures and heat-bonding the film to the metal sheet and an extrusion lamination method comprising extruding a melt of a polyester resin on a metal sheet to thereby form a coating directly on the metal sheet. If desired, there may be adopted a method in which a primer of the thermo-setting type or an anchoring agent of the isocyanate type is coated on the polyester resin film or metal sheet and the polyester resin film is heat-bonded to the metal sheet. The heat bonding temperature (T_2) is determined depending on the tack point (T_1) of the polyester resin, and in general, the heat bonding is carried out at a temperature in the range of from T_1 to (T_1+130)°C, preferably from (T_1+20)°C to (T_1+100)°C.

In preparing the coated metal sheet of the present invention, it is preferred that a coated metal sheet to which a thermoplastic polyester resin layer is heat-bonded be quenched so that the degree of crystallinity of the polyester resin layer is in the range of 0 to 30%. Known means may be adopted for this quenching operation. For example, there can be adopted a method in which a cooling medium such as cooling water is sprayed on the coated metal sheet, a method in which the coated metal sheet is dipped in a cooling medium such as cooling water, and a method in which the coated metal sheet is passed through quenching rollers. These methods may be adopted in combination. In order to control the degree of crystallinity of the polyester resin layer below 30%, it is preferred to quench the resin layer of the coated metal sheet from the hot bonding temperature [$T_2=T_1$ to T_1+130°C, especially T_1+20 to T_1+100°C] to a level lower than 70°C, especially a level lower than 50°C, within 60 seconds.

The thickness of the coating layer is varied depending on the desired degree of coating and the intended use of the coated metal sheet, but in general, it is preferred that the thickness of the polyester resin coating in the state applied on the surface of the metal sheet be 1 to 100 μ, especially 5 to 60 μ.

In the so prepared coated metal sheet of the present invention, the polyester resin coating is tightly bonded to the metal sheet and the surface condition is very good. The coated metal sheet may be used directly in the as-prepared form. Since the adaptability of the coated metal sheet of the present invention to shaping processing is excellent as pointed out hereinbefore, it can be conveniently subjected to various shaping processings, for example, deep drawing, ironing, (i.e. thinning the walls of a deep-drawn metal article by using a die and a punch), folding, bending, flanging, beading, curling (i.e. using a curling die to bend the edges or ends of the workpiece into a form having a generally arcuate or circular cross-section), crimping and stamping, and it can be formed into various shaped articles such as vessels, can bodies, retortable pouches (i.e. pouches that can be sterilized in a retort at high temperatures), vessel lids, casings of electric instruments or office instruments, toys, roofing materials, wall materials and armoring and inner lining materials of vehicles or ships. These shaped articles can be used effectively in various fields.

The coated metal sheet of the present invention is characterized in that since the thermoplastic polyester resin constituting the resin layer is heat-bonded to the metal sheet and the degree of crystallinity of this resin layer is controlled within the specific range, severe processing conditions can be applied to the coated metal sheet and even after they have been subjected to shaping processing conducted under severe conditions, excellent adhesion (peel resistance) of the resin coating and excellent corrosion resistance of the metal sheet can be retained.

By virtue of the above characteristic properties, the coated metal sheet of the present invention can be effectively used as a material for various vessels and containers. In this case, the coated metal sheet is formed into a vessel or container according to known means so that the thermoplastic polyester resin coating layer is located at least on the inner surface of the vessel or container.

For example, the coated metal sheet of the present invention can be conveniently used as a metal blank for production of can bodies. In this case, the coated metal sheet of the present invention is cut into a blank prescribed can body size, the cut blank is fed to a can making machine and shaped into a roll, and both the side edges of the blank are heat-bonded in the lapped state. Since the thermoplastic polyester resin used in the present invention has excellent heat bondability, formation of side seams by heat bonding can be accomplished very easily. This heat bonding can readily be performed by heating in advance facing side portions of the blank at a temperature causing softening of the thermoplastic polyester resin and pressing the heated side portions of the blank together whilst cooling.

The so prepared can is subjected to flanging or beading according to known means and it is then double-seamed with a can lid to form a final can body.

Instead of the above-mentioned lap bonding method, there may be adopted a method in which facing side portions of the blank are bonded through a lock seam or a combination of a lock seam with a lap seam. In each case, the coated polyester resin layer per se can be used as a hot melt adhesive, or other hot melt adhesive or a synthetic rubber type sealing material or hot curing type adhesive may be applied from the outside and used for bonding.

The coated metal sheet of the present invention can be shaped into a side seamless container according to known means. In this case, the coated metal sheet is subjected to deep drawing in at least one stage between a drawing die and a punch to form a can body comprising a side wall portion having no seam and a bottom integrated seamlessly with the side wall portion, and if desired, the side wall portion of the resulting can body is subjected to ironing to elongate it. Thus, a side seamless container can be prepared from the coated metal structure of the present invention.

Since the coated metal sheet of the present invention is excellent in its adaptability to shaping processing, it can be subjected to such deep drawing treatment that the drawing ratio (R_D) defined by the following formula:

$$R_D = \frac{D}{d}$$

wherein D is the minimum diameter of a blank of the coated metal sheet to be processed and d is the minimum diameter of a punch, is from 1.1 to 3.0, especially from 1.2 to 2.8, and it can also be subjected to such ironing treatment that the ironing ratio (R_1) defined by the following formula:

$$R_1 = \frac{t_0 - t_1}{t_0} \times 100$$

wherein t_0 stands for the thickness of the metal blank before ironing and t_1 stands for the thickness of the metal plate after ironing, is 10 to 50% after one-stage ironing and is 10 to 80% after completion of ironing.

The so prepared container comprises a side wall portion having no seam and a bottom portion seamlessly integrated with the side wall portion. The thickness of the bottom is substantially the same as the thickness of the coated metal sheet used as the blank. When only drawing is performed, the thickness of the side wall portion is substantially the same as the thickness of the coated metal sheet used, and when both drawing and ironing are carried out, the thickness of the side wall portion is smaller than that of the coated metal sheet used. This side seamless vessel may further be subjected to doming, necking-in and beading according to need and then to flanging, whereby a can body which can be double-seamed with a can lid or closure is formed.

Further, since the coated metal sheet of the present invention is excellent in its adaptability to shaping processing, it can easily be shaped into various vessel lids and closures, for example, crown caps, screw caps, twist-off caps, peelable caps and can lids. In each case, advantages as mentioned above with respect to formation of containers are similarly attained. Especially, when the coated metal sheet of the present invention is used for formation of can lids, processing for attaching an opening mechanism such as an easy open end can easily be performed while retaining the excellent corrosion resistance. This is another advantage attained by the present invention.

As will be apparent from the foregoing illustration, the coated metal sheet of the present invention can easily be formed and processed into various containers and vessels differing in the shape, and even after such forming processing, the adhesion (peel resistance) of the coating and the corrosion resistance of the metal sheet can be maintained at high levels. Moreover, when foods or the like are filled in such containers, the coating-constituting components are not extracted by the contents and the effect of retaining flavors of the contents is prominently excellent. Furthermore, these characteristics are not lost during severe post treatments such as high-temperature sterilization. Because of the excellent heat bondability of the coating of the coated metal sheet of the present invention, a finishing treatment such as fusion bonding of a printed film can easily be performed.

The present invention will now be described in detail by reference to the following Examples.

Example 1

A 30 μ thick film composed of a poly(tetramethylene terephthalate) having a relative viscosity of 1.55 as measured at 25°C in o-chlorophenol at a concentration of 0.5 g/100 ml and a tack point of 224°C, which had a degree of crystallinity of 12%, was heat-bonded under the conditions indicated in Table 1 to a 0.17 mm thick cold-rolled steel sheet, the surface of which had been sufficiently degreased by using trichloroethylene. A part of the resin layer of the resulting coated steel sheet was sampled and the relative viscosity and degree of crystallinity were measured. The coated steel sheet was subjected to a drawing test at a drawing ratio of 1.9 by using a drawing mold for forming a can body having an inner diameter of 50 mm so that the resin layer was located inside. The resulting can body was subjected to a salt spray test for 5 days according to the method of JIS Z-2371. Measurement results and test results are shown in Table 1.

Coating methods A to E mentioned in Table 1 are as follows:

Coating Method A:

The film was preliminarily bonded under a pressure of 1.5 Kg/cm^2 by means of a roller to the steel sheet pre-heated to 240°C, and then, the steel sheet was heated at 260°C for 30 seconds to completely bond the film to the steel sheet. Then, the coated steel sheet was cooled for 6 seconds by liquid N_2.

Coating Method B:

The preliminary bonding and finish bonding were performed in the same manner as in the coating method A, and the coated steel sheet was cooled for 60 seconds in water maintained at 0°C.

Coating Method C:

The preliminary bonding and finish bonding were performed in the same manner as in the coating method A, and the coated steel sheet was cooled for 60 seconds in water maintained at 50°C.

Coating Method D:

The preliminary bonding and finish bonding were performed in the same manner as in the coating method A, and the coated steel sheet was naturally cooled in air.

Coating Method E:

The preliminary bonding and finish bonding were performed in the same manner as in the coating method A, and the coated steel sheet was forcibly cooled to 110°C and then naturally cooled in air.

TABLE 1

Run No.	Coating method	Properties of coating resin layer		Adaptability of coated steel plate to drawing processing	Properties of shaped articles		
					Salt spray test (for 5 days) According to JIS Z-2371	Actual application test*	
		Relative viscosity	Degree (%) of crystallinity			Rusting	Peeling of coating
1	A	1.48	0	good	no rust	not observed	not observed
2	B	1.46	17	good	no rust	not observed	not observed
3	C	1.46	27	quite good	no rust	not observed	not observed
4	D	1.45	37	bad (peeling occurred on side wall of cup)	considerable rusting and peeling	partial rust	partial peeling
5	E	1.45	33	quite bad (slight peeling occurred on side wall of cup)	no rust	spot rusting in double-seamed portion	peeling in double-seamed portion

Note

* The can body having a diameter of 50 mm was trimmed and subjected to flanging. Then, tuna flakes were filled in the resulting can body and a lid was attached to the filled can body by double seaming. The packed can was heated and sterilized at 118°C for 90 minutes and stored for 1 hour.

Example 2

A polyester resin having a relative viscosity of 1.55, and derived from, the dicarboxylic acid component, terephthalic acid (abbreviated to "TPA") and isophthalic acid (abbreviated to "IPA") at a molar ratio indicated in Table 2 and 1,4-butane diol, as the diol component, was melted and formed into a film having a thickness of 30 to 33 μ. The film was preliminarily bonded under a pressure of 2.0 Kg/cm^2 by means of a roller to a surface-cleaned cold-rolled steel sheet pre-heated to a temperature higher by 15°C than the tack point of the polyester resin, and then, the metal sheet was heated to a temperature higher by 30°C than the tack point of the polyester for 30 seconds to complete bonding. The coated steel sheet was immediately passed through water maintained at 20°C for 60 seconds to cool the coated steel sheet. A part of the resin layer was sampled and the relative viscosity and degree of crystallinity were measured to obtain results shown in Table 2. Then, the coated steel sheet was subjected to the drawing test at a drawing ratio of 1.8 by using a drawing mold for forming a can body having an inner diameter of 50 mm so that the resin layer was located outside. The resulting shaped article was subjected to the salt spray test to obtain results shown in Table 2.

TABLE 2

Properties of resin layer

Run No.	TPA/IPA molar ratio in resin layer	Tack point (°C)	Degree of crystallinity (%)	Adaptability to drawing processing	Salt spray test (5 days) of shaped article according to JIS Z-2371
1	100/0	224	27	quite good	no rust
2	80/20	193	5	good	no rust
3	70/30	175	0	good	no rust
4	60/40	163	0	good	no rust
5	50/50	132	0	quite good, mold releasing property of shaped article quite bad	no rust
6	40/60	115	0	bad, resin layer adhering to mold during processing	considerable rusting, peeling

Example 3

A 35 μ thick film of a polyester derived from terephthalic acid as the dicarboxylic acid component and, as the diol component, 70 mole% of 1,4-butane diol and 30 mole% of ethylene glycol, which had a degree of crystallinity of 5% and a tack point of 220°C, was preliminarily bonded under a pressure of 2.0 Kg/cm^2 by means of a roller to a 0.35 mm thick chromic acid-treated steel sheet pre-heated to 260°C, and the steel sheet was heated at 280°C for 30 seconds to complete bonding. Then, the coated steel sheet was passed through water maintained at room temperature for 60 seconds to effect cooling. The resin layer of the resulting coated steel sheet had a relative viscosity of 1.30 and a degree of crystallinity of 5%. The coated steel sheet was subjected to drawing processing at a drawing ratio of 1.5 to obtain a can body, having a diameter of 70 mm. The shaped article was drawn again so that the diameter became 50 mm and then ironed to obtain a can body having a diameter of 50 mm. In this step, the ironing ratio was 20%. The resulting shaped article had a good appearance, and when it was subjected to the salt spray test for 5 days according to the method of JIS Z-2371, rusting was not observed at all.

This can body was trimmed and subjected to flanging, and 100% orange juice was hot-packed in the resulting can and a lid was attached according to a customary double seaming method. The packed orange juice was stored at 37°C for 6 months, and when the can was opened and the contents examined, it was found that the can had an excellent preservative effect.

Example 4

A pelletized polyester resin having a relative viscosity of 1.49 and a tack point of 140°C, derived from, as the dicarboxylic acid component, 80 mole% of terephthalic acid and 20 mole% of sebacic acid, and, as 80 mole% of 1,4-butane diol and 20 mole% of 1,6-hexane diol, was fed to an extruder having a screw diameter of 40 mm and being provided with extrusion lamination equipment, in which the extrusion temperature was maintained at 200°C. Simultaneously, a sufficiently degreased 0.34 mm thick aluminum sheet was continuously fed just below a die. Under application of a pressure of 2.0 Kg/cm^2 an extruded resin layer was press-bonded to the aluminum sheet using a pressing roller, and the coated aluminum sheet was passed through water maintained at 25°C to effect cooling. The degree of crystallinity of the resin layer of the resulting coated aluminum sheet was substantially 0%. This coated aluminum sheet was shaped into a vessel having an inner diameter of 60 mm and a height of 80 mm by subjecting the coated aluminum sheet to drawing processing so that the resin layer was located inside. The resulting shaped vessel had good properties. When the shaped article was subjected to the salt spray test in the same manner as described in the preceding Examples, no corrosion was caused on the coated surface. A liver paste was filled in the so prepared can body and a lid composed of the above coated aluminum sheet was attached to the can body by double seaming. The packed can was sterilized at 120°C and stored for 6 months. When the can was opened and the contents examined, no change was observed, and it was found that good performance was attained.

Example 5

A poly(tetramethylene terephthalate/isophthalate) resin having a tack point of 175°C derived from, as the dicarboxylic acid component, terephthalic acid and isophthalic acid in a molar ratio of 70/30 was synthesized. The relative viscosity of the polymer was 1.48.

The so prepared polyester (80 parts by weight) and 20 parts by weight of an ethylene-ethyl acrylate copolymer (ethylene/ethyl acrylate weight ratio=95/5) were melted and kneaded using an extruder. The resulting polymer chips were fed to an extruder provided with a T-die, and melted and coated on a chromic acid-treated steel sheet having a thickness of 0.22 mm, which was heated at 280°C. Then, the coated steel sheet was cooled with water. The extrusion conditions were adjusted so that the thickness of the resin layer was 50 to 55 μ. The degree of crystallinity of the resin layer was 5%.

The coated steel sheet was punched into a disc and then subjected to drawing processing. By conducting deep drawing twice, a can body having an inner diameter of 107 mm was prepared at a drawing ratio of 2.13. The resulting can body was washed with hot water, and boiled and flavored tuna was packed in the can body. A lid formed by punching the above resin coated steel plate into a disc-like form was attached to the packed can body by double seaming. The sterilization was carried out at 120°C for 90 minutes and the packed can was stored at 50°C for 2 months. When the can was opened and the contents examined, it was found that no change was caused in the contents and no rusting was observed on the can.

Example 6

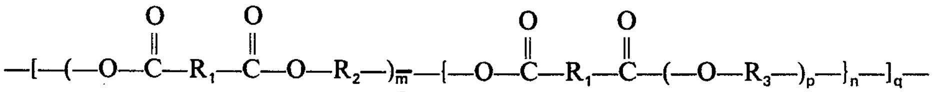
A polymer blend comprising 30% by weight of a polyester having a relative viscosity of 1.37 and a tack point of 215°C and derived from, as the dicarboxylic acid component, 80 mole% of terephthalic acid and 20 mole% of isophthalic acid, and, as the diol component, ethylene glycol and 70% by weight of a polyester having a relative viscosity of 1.53 and a tack point of 170°C and derived from, as the dicarboxylic acid component, 65 mole% of terephthalic acid and 35 mole% of isophthalic acid and, as the diol component, butylene glycol was formed into an unstretched film having a thickness of 50 μ by using an extruder in which the extrusion temperature was set at 250°C. The so prepared film was preliminarily bonded under a pressure of 2.0 Kg/cm^2 by means of a roller to a surface-cleaned chromic acid-treated steel sheet, and the steel sheet was then heated at 270°C for 40 seconds to complete bonding. The coated steel sheet was passed through water maintained at 25°C for 60 seconds to effect cooling. The degree of crystallinity of the resin layer of the resulting coated steel sheet was substantially 0%. The coated steel sheet was subjected to draw processing at a drawing ratio of 2.0 to form a can body having an inner diameter of 100 mm. Tuna flakes were packed in the resulting can body and sterilization was effected at 120°C for 120 minutes. By this treatment, the degree of crystallinity of the resin layer was increased to 35%. After the sterilization, a lid composed of the above coated steel sheet was attached to the packed can body by double seaming. The packed can was stored for 1 year. When the can was opened and the content was examined, it was found that the contents had kept in good condition and no rusting was observed of the can.

WHAT WE CLAIM IS:—

1. A metal sheet coated with a layer containing at least 70% by weight of a thermoplastic polyester resin which is heat-bonded to the surface of said metal substrate, wherein said polyester resin has a relative viscosity of 1.2 to 1.8 as measured at 25°C in o-chlorophenol at a concentration of 0.5 g/100 ml, a tack point (as hereinbefore defined) not lower than 130°C, and a degree of crystallinity of up to 30%.

2. A metal sheet according to Claim 1 wherein the metal is steel, tin-coated steel, aluminum, aluminum-coated steel, chromium-coated steel or steel chemically or electrochemically treated with chromic acid or phosphoric acid.

3. A metal sheet according to Claim 1 or 2 wherein the thermoplastic polyester is at least one thermoplastic polyester composed of recurring units of the formula:



$$-[-(-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-O-R_2-)_{\overline{m}}-\{-O-\overset{\overset{O}{\|}}{C}-R_1-\overset{\overset{O}{\|}}{C}-(-O-R_3-)_p-\}_n-]_q- \qquad (1)$$

wherein R_1 is a divalent hydrocarbon group, R_2 and R_3, which may be the same or different, are each a divalent aliphatic hydrocarbon group, p and q are each at least 1 and m and n are 0 or at least 1, with the proviso that when one of m and n is 0, the other must be at least 1.

4. A sheet according to Claim 3 wherein at least 45 mole% of the units represented by R_1 are *p*-phenylene groups.

5. A sheet according to Claim 4 wherein at least 60 mole% of the units represented by R_1 are *p*-phenylene groups.

6. A metal sheet according to Claim 3 wherein the thermoplastic polyester is poly(tetramethylene terephthalate), poly(tetramethylene/ethylene terephthalate), poly(tetramethylene terephthalate/isophthalate), poly(ethylene terephthalate/isophthalate), poly(ethylene/p-hexahydroxylylene terephthalate) or poly(tetramethylene/polyoxytetramethylene terephthalate).

7. A metal sheet according to any one of the preceding claims wherein the layer comprises a blend of at least 70% by weight of the thermoplastic polyester resin and up to 30% by weight of another thermoplastic resin.

8. A metal sheet according to Claim 1 substantially as described in any one of the Examples.

9. A shaped article formed from a metal sheet as claimed in any one of the preceding claims.

10. A shaped article according to Claim 9 in the form of a can.

11. A shaped article according to Claim 9 in the form of a metal closure.

12. A shaped article according to Claim 9 which is a container formed from a blank of the metal sheet by drawing or drawing and ironing and which comprises a side wall portion having no seam therein and a bottom portion seamlessly integrated and connected with said side wall portion.

13. A container according to Claim 12 wherein the thickness of the coating layer is from 1 μ to 100 μ.

14. A container according to Claim 12 or 13 wherein the coating layer is present at least on the inner surface of the container.

15. A process for the production of a coated metal sheet as claimed in any one of Claims 1 to 8 which comprises heat-bonding to the surface of a metal sheet a film containing at least 70% by weight of the thermoplastic polyester resin at a temperature (T_2) higher than the tack point (T_1) of the thermoplastic polyester resin but not higher than (T_1+130)°C and quenching the coated metal sheet so that the temperature of the resin layer is lowered from said temperature (T_2) to a level lower than 70°C within 60 seconds, thereby to control the degree of crystallinity of the resin layer to within the range from 0% to 30%.

16. A process according to Claim 15 wherein the heat bonding temperature (T_2) is from (T_1+20)°C. to (T_1+100)°C.

17. A process according to Claim 15 or 16 wherein the coated metal sheet is quenched with cooling water.

18. A process according to Claim 15 substantially as described in any one of the Examples.

19. A process for the production of a seamless container as claimed in any one of Claims 12 to 14 which comprises deep drawing the blank of the coated metal sheet in at least one stage between a die and a punch, thereby to form a can body comprising said side wall portion and bottom portion.

20. A process according to Claim 19 wherein the can body formed by deep drawing is then subjected to ironing in at least one stage between a die and a punch thereby to elongate the side wall portion.

21. A process according to Claim 19 wherein the blank of the coated metal sheet is subjected to deep drawing under such conditions that the drawing ratio (R_D), defined by the formula:

$$R_D = \frac{D}{d}$$

wherein D is the minimum diameter of the blank of the coated metal sheet before deep drawing and d is the minimum diameter of the punch, is from 1.1 to 3.0.

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