(12) PATENT (11) Application No. AU 199725216 B2
(19) AUSTRALIAN PATENT OFFICE (10) Patent No. 711378

(54) Title
Metallic sheet covered with polyester resin film and having high workability, and method of manufacturing same

(51)[6] International Patent Classification(s)
B32B 015/08

(21) Application No: 199725216 (22) Application Date: 1997.04.10

(87) WIPO No: WO97/37846

(30) Priority Data

| (31) Number | (32) Date | (33) Country |
|---|---|---|
| 8-112127 | 1996.04.10 | JP |

(43) Publication Date : 1997.10.29
(43) Publication Journal Date : 1998.01.08
(44) Accepted Journal Date : 1999.10.14

(71) Applicant(s)
Toyo Kohan Co., Ltd.

(72) Inventor(s)
Hiroyuki Iwashita; Fumiko Gotoh; Atsuo Tanaka

(74) Agent/Attorney
BALDWIN SHELSTON WATERS,Level 21,60 Margaret Street,SYDNEY NSW 2000

世界知的所有権機関

PCT OPI DATE 29/10/97 APPLN. ID 25216/97
AOJP DATE 08/01/98 PCT NUMBER PCT/JP97/01242

AU9725216

(51) 国際特許分類6
B32B 15/08

A1

(11) 国際公開番号 WO97/37846

(43) 国際公開日 1997年10月16日(16.10.97)

(21) 国際出願番号 PCT/JP97/01242

(22) 国際出願日 1997年4月10日(10.04.97)

(30) 優先権データ
特願平8/112127 1996年4月10日(10.04.96) JP

(71) 出願人（米国を除くすべての指定国について）
東洋鋼鈑株式会社(TOYO KOHAN CO., LTD.)[JP/JP]
〒100 東京都千代田区霞が関一丁目4番3号 Tokyo, (JP)
(72) 発明者；および
(75) 発明者／出願人（米国についてのみ）
岩下寛之(IWASHITA, Hiroyuki)[JP/JP]
後藤文子(GOTOH, Fumiko)[JP/JP]
田中厚夫(TANAKA, Atsuo)[JP/JP]
〒744 山口県下松市東豊井1296番地の1
東洋鋼鈑株式会社 技術研究所内 Yamaguchi, (JP)
(74) 代理人
弁理士 太田明男(OHTA, Akio)
〒100 東京都千代田区霞が関一丁目4番3号
東洋鋼鈑株式会社内 Tokyo, (JP)

(81) 指定国 AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ARIPO特許 (GH, KE, LS, MW, SD, SZ, UG), ユーラシア特許 (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), 欧州特許 (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI特許 (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).

添付公開書類
国際調査報告書

(54)Title: **METALLIC SHEET COVERED WITH POLYESTER RESIN FILM AND HAVING HIGH WORKABILITY, AND METHOD OF MANUFACTURING SAME**

(54)発明の名称 高加工性ポリエステル樹脂フィルム被覆金属板およびその製造方法

**(57) Abstract**

A metallic sheet covered with a polyester resin film, having a high workability and applicable to use requiring a severe working such as drawing, drawing and ironing, thin wall drawing, and ironing after thin wall drawing, and a method of manufacturing the same. A metallic sheet heated above a fusing point of a polyester resin is contacted with a polyester resin film, a pair of laminate rolls are used to clamp the both therebetween to effect compression-bonding and covering, during which time the metallic sheet is cooled at a cooling rate of at least 600 °C/sec., whereby the metallic sheet covered with the polyester resin film has an actual stress of 3.0 to 15.0 kg/mm producing a true strain of 1.0 measured at 75 °C on the polyester resin film after covering.

(57) 要約

本発明は、絞り加工、絞りしごき加工、薄肉化絞り加工、さらに、薄肉化絞り加工後しごき加工が施されるような、厳しい加工が施される用途に適用可能な、極めて高い加工性を有するポリエステル樹脂フィルム被覆金属板およびその製造方法を提供することを目的とする。

このため本発明のポリエステル樹脂フィルム被覆金属板は、ポリエステル樹脂の融点以上の温度に加熱された金属板にポリエステル樹脂フィルムを接触させ1対のラミネートロールを用いて両者を鋏みつけて圧着して被覆し、その際に金属板を 600℃/秒以上の冷却速度で冷却することにより、被覆後のポリエステル樹脂フィルムの75℃において測定する 1.0の真歪みをもたらす真応力が 3.0〜15.0 kg/mm$^2$であることを特徴とする。


**参考情報**

PCTに基づいて公開される国際出願のパンフレット第一頁に記載されたPCT加盟国を同定するために使用されるコード

AL アルバニア
AM アルメニア
AT オーストリア
AU オーストラリア
AZ アゼルバイジャン
BA ボズニア・エルツェゴビナ
BB バルバドス
BE ベルギー
BF ブルギナ・ファソ
BG ブルガリア
BJ ベナン
BR ブラジル
BY ベラルーシ
CA カナダ
CF 中央アフリカ共和国
CG コンゴー
CH スイス
CI コート・ジボアール
CM カメルーン
CN 中国
CU キューバ
CZ チェッコ共和国
DE ドイツ
DK デンマーク
EE エストニア
ES スペイン
FI フィンランド
FR フランス
GA ガボン
GB 英国
GE グルジア
GH ガーナ
GM ガンビア
GN ギニア
GR ギリシャ
HU ハンガリー
ID インドネシア
IE アイルランド
IL イスラエル
IS アイスランド
IT イタリア
JP 日本
KE ケニア
KG キルギスタン
KP 朝鮮民主主義人民共和国
KR 大韓民国
KZ カザフスタン
LC セントルシア
LI リヒテンシュタイン
LK スリランカ
LR リベリア
LS レソト
LT リトアニア
LU ルクセンブルグ
LV ラトヴィア
MC モナコ
MD モルドヴァ共和国
MG マダガスカル
MK マケドニア旧ユーゴスラヴィア共和国
ML マリ
MN モンゴル
MR モーリタニア
MW マラウイ
MX メキシコ
NE ニジェール
NL オランダ
NO ノルウェー
NZ ニュー・ジーランド
PL ポーランド
PT ポルトガル
RO ルーマニア
RU ロシア連邦
SD スーダン
SE スウェーデン
SG シンガポール
SI スロヴェニア
SK スロヴァキア共和国
SL シエラレオネ
SN セネガル
SZ スワジランド
TD チャード
TG トーゴ
TJ タジキスタン
TM トルクメニスタン
TR トルコ
TT トリニダード・トバゴ
UA ウクライナ
UG ウガンダ
US 米国
UZ ウズベキスタン
VN ヴィェトナム
YU ユーゴスラビア
ZW ジンバブエ

[Abstract]

[Objective]

The present invention produces a polyester resin covered metal sheet having extremely excellent formability, which can be available for uses in which severe forming is practiced such as drawing, drawing and ironing, and drawn and stretch forming as well as the composite forming consisting of drawn and stretch forming followed by ironing, and a production method thereof.

[Means for attaining objective]

A polyester resin film is contacted to a metal sheet heated to a temperature of more than the melting temperature of the polyester resin, and covered on the metal sheet pinching and press laminating both members of the film and the metal sheet, followed by cooling the metal sheet at the cooling rate of more than 600 ℃ at the laminating process, which produces a metal sheet covered with polyester resin film in which true stress of 3.0 to 15.0 $kg/mm^2$ causing true strain of 1.0 measured at 75 ℃ after covering.

[Title] Polyethylene terephthalate resin covered metal sheet having excellent formability and production method thereof.

[Technological field]

The present invention relates to polyester resin covered metal sheet having remarkably excellent formability, which is applicable to heavily formed use such as drawing, drawing and ironing, drawing and stretch forming, and ironing after drawing and stretch forming, and production method thereof.

[Background of invention]

Metal containers such as beverage can or battery container are formed by drawing, drawing and ironing, drawing and stretch forming, or ironing after drawing and stretch forming with the object of material reduction and extension of inside measurement by reduction of wall thickness of container. These metal containers are generally coated to give corrosion resistance for content or printed after being coated to show content. However, a metal sheet previously covered with organic resin is tried to apply to above-mentioned heavily formed use with a view to reduce coating cost and to eliminate environmental pollution caused by dispersing of solvent during coating operation. And cans formed of metal sheet covered with organic resin has already been placed on sale in beverage can market.

In the organic resin covered metal sheet applied to the above-mentioned heavily formed use, a biaxially oriented film, which is manufactured by biaxial elongation of a thermoplastic polyester resin and subsequent heat-setting of it, is heat bonded to a metal sheet. When the mechanical characteristics of these biaxially oriented films are measured using a tensile tester, the general characteristic of large yield strength and small elongation (elongation after fracture). In case where such a biaxially oriented film is laminated on a metal sheet with adhesive but without heat bonding in order not to destroy the biaxial orientation and the laminate is formed by severe forming described above, the resin film is fractured or numerous cracks are generated in the portion that is heavily formed because of the small elongation. Furthermore, in case where the adhesion is poor, the resin film is peeled off when the laminate is formed. For this reason, in the organic resin covered metal sheet for the use of the above-described severe forming, the biaxial orientation of the film that the film had before the lamination is partially or entirely lost by the heat caused when the film is heat bonded to the metal sheet in the lamination of the biaxially oriented film on the metal sheet using heat bonding method. As a result, the yield strength of the film after being laminated on the metal sheet is decreased and the elongation is improved, which prevents peeling-off or fracture of the film, or the generation of film cracks in the forming operation. On the other hand, On the other hand, the film without orientation has so large permeability that the content permeates the film and corrodes the metal substratum, and furthermore, it has faults that coarse spherlites are generated in the film by post heating during the operation of printing which shows the content or the like and cracks are easily caused in the film by falling of container or collision of each container.

Therefore, in the metal sheet covered with polyester resin film having biaxial orientation applied to the above-mentioned heavily formed use, the elongation after fracture of the film before being laminated on the metal sheet is defined in the preferable range (Laid open Japanese patent Hei 1-249331), or the range of the orientation coefficient which shows the degree of the biaxial orientation before being laminated on the metal sheet, or the preferable range of the elongation after fracture and the tensile strength of the film are defined (Laid open Japanese patent Hei 2-74030).

However, the values of the elongation after fracture, or the elongation after fracture and the tensile strength of the film disclosed in Laid open Japanese patent Hei 1-249331 and Laid open Japanese patent Hei 2-74030 are those before the film is laminated on the metal sheet.

In case where such a biaxially oriented resin film is laminated on a metal sheet using heat bonding method, the biaxial orientation is destroyed, which makes the value of the elongation after fracture and the tensile strength change. Therefore, The films after lamination laminated on the different conditions may not have favorable biaxial orientation and favorable elongation and tensile strength of the film, and the polyester resin film covered metal sheet disclosed in Laid open Japanese patent Hei 1-249331 and Laid open Japanese patent Hei 2-74030 cannot be favourably formed in some cases.

## SUMMARY OF THE INVENTION

According to a first aspect of the invention there is provided a metal sheet covered with polyester resin film having orientation wherein said polyester resin film having orientation, obtained from said metal sheet covered with polyester resin film rejecting metal sheet alone by chemical dissolution, has true stress of 3.0 to 15.0 $kg/mm^2$ measured at 75°C, corresponding to true strain of 1.0, in the mechanical characteristics.

Preferably, the polyester resin is polyethylene terephthalate resin. More preferably, the polyethylene terephthalate resin is a polyethylene terephthalate resin having low temperature crystallization temperature of 130 to 165°C, even more preferably 140 to 155°C.

Alternatively, the polyester resin is a copolyester resin mainly consisting of ethylene terephthalate recurring unit, a copolyester resin mainly consisting of butylene terephthalate recurring unit, or a blended copolyester resin consisting of at least 2 of these resins, or a double layered polyester resin consisting of a laminate of at least 2 of these resins.

In a method of producing any one of the above-mentioned metal sheet covered with polyester resin film the metal sheet is cooled by a nip formed by a couple of laminating roll at the cooling rate of 600°C/second or more when said polyester resin film is contacted to said metal sheet heated to a temperature more than the melting temperature of said polyester resin and both members are pinched and pressed into a laminate by said couple of laminating roll.

Advantageously, at least in a preferred form, the present invention may provide a polyester resin film covered metal sheet having extremely excellent formability which can be applied to severely formed use such as drawing, drawing and ironing, drawing and stretch forming, or ironing after drawing and stretch forming.

[The best manner to practice the present invention]

The present invention is a metal sheet covered with polyester resin film manufactured in the manner in which the metal sheet is cooled by a couple of laminating roll at the cooling rate of 600 ℃/second or more when the polyester resin film having orientation is contacted to one side or both sides of the metal sheet heated to a temperature more than the melting temperature of the polyester resin and both members are pinched and pressed into a laminate by the couple of laminating roll, wherein the polyester resin film is heat bonded to the metal sheet, so that the polyester resin film obtained from the metal sheet covered with the polyester resin film rejecting metal sheet alone by chemical dissolution, has true stress of 3.0 to 15.0 kg/mm $^2$ measured at 75 ℃, corresponding to true strain of 1.0, in the mechanical characteristics. The polyester resin used in the present invention is preferably polyethylene terephthalate, one having low temperature crystallization temperature of 130 to 165 ℃ in particular, or copolyester resin consisting of ethylene terephthalate and ethylene isophthalate. The lamination of such a polyester resin film on a metal sheet using the above-described heat bonding method enables to prevent peeling-off of the film, fracture of the film and occurrence of film cracks during the forming in the severe forming use, destroying a part of or whole biaxial orientation by heat conducted from the metal sheet when the film is heat bonded to the metal sheet, decreasing yield strength of the film after the lamination and improving elongation of it.

[Embodiment]

Hereinafter, the present invention is explained in detail referring embodiment. At first, the polyester resin film used in the present invention is preferably that of polyethylene terephthalate biaxially oriented in the lengthwise and the widthwise directions having a low temperature crystallization temperature ranging 130 to 165 ℃ in particular, more preferably 140 to 155 ℃. A low temperature crystallization temperature is explained hereinafter. When an amorphous polyester resin such as polyethylene terephthalate which is obtained by heating it to a temperature more than melting temperature of it and quenching immediately after that is gradually heated using a differential scanning calorimeter (DSC), an exothermic peak appears in the temperature range of 100 to 200 ℃ depending resin composition. The resin of which exothermic peak appears in the higher temperature has a smaller crystallization velocity, while that appears in the lower temperature has a larger crystallization velocity. For example, the exothermic peak of polybutylene terephthalate resin on the market which is heat melted and subsequently quenched appears at about 50 ℃, while that of polyethylene terephthalate resin on the market which is heat melted and subsequently quenched appears at about 128 ℃. On the other hand, in case of ethylene terephthalate －ethylene isophthalate copolyester resin, which is used in a 2 piece can (a can of which body wall part and bottom part is formed in 1 piece) made of a metal sheet covered with a polyester resin film on the market, the exothermic peak appears at about 177 ℃.

In the present invention, a biaxially oriented film of a polyethylene terephthalate resin having a low temperature crystallization temperature exceeding 165 ℃ or less than 130 ℃ can be heat bonded to a metal sheet, however, a metal sheet covered with a polyethylene terephthalate resin having orientation structure suitable for the compatibility of adhesion and formability with permeation resistance and impact resistance can be obtained heat bonding a biaxially oriented film of a polyethylene terephthalate resin having a low temperature crystallization temperature of 130 to 165 ℃ to a metal sheet.

In the present invention, a film of any resin of polyethylene terephthalate, polybutylene terephthalate, copolyester mainly consisting of ethylene terephthalate recurring unit, or that mainly consisting of ethylene isophthalate recurring unit, that of a blended polyester resin consisting of at least 2 of these resins, or a multi layered polyester resin film manufactured by lamination of at least 2 of these resins can be available. Furthermore, in case where impact resistance is required, a film of bis－phenol A poly carbonate resin blended with the above－described polyester resin, or a multi layered resin film consisting of the uppermost and the lowermost layers of the above－described polyester resin and the intermediate layer of the bis－phenol A poly carbonate resin blended with the above－described polyester resin or the bis-phenol A poly carbonate can also be available.

The thickness of the polyethylene terephthalate resin film is preferably 5 to 50 μm, more preferably 10 to 30 μm. When a film of which thickness is less than 5 μm is heat bonded to a metal sheet, wrinkles are apt to be caused and it is extremely difficult to stably cover the film on the metal sheet. On the other hand, when using a film of which thickness is more than 50 μm, the necessary characteristics can be attained but it is not profitable to economy. A colored film, produced by adding color pigment into molten polyethylene terephthalate when the film is manufactured, can also be available.

In the present invention, it is essential that true stress measured at 75 ℃ is 3.0 to 15.0 kg/mm $^2$, corresponding to true strain of 1.0 in the mechanical characteristics of the polyester resin film obtained rejecting the metal sheet alone by chemical dissolution from the polyester resin covered metal sheet. It is the objective of the present invention that the polyester resin covered metal sheet having excellent formability is adapted to the use of severe forming such as drawing, drawing and ironing, drawing and stretch forming, and ironing after drawing and stretch forming. It is particularly essential that the polyester resin film covered on the metal sheet has excellent formability in the use of the high degree forming such as drawing and stretch forming, and ironing after drawing and stretch forming. Furthermore, these severe forming are practiced at the temperature more than glass transition temperature of the polyester resin in order to enhance the formability of the polyester resin film. In the present invention, extremely excellent formability adaptable to the use of the severe forming such as drawing and stretch forming, and ironing after drawing and stretch forming can be obtained in case where the following orientation structure after heat bonding is attained, that is the structure in which true stress is 3.0 to 15.0 kg/mm $^2$, corresponding to true strain of 1.0, is measured using tensile tester at 75 ℃ that is more than glass transition temperature of the polyester resin in the tensile characteristics of the polyester resin film obtained rejecting the metal sheet alone by chemical dissolution from the polyester resin covered metal sheet after a biaxially oriented polyester resin film is heat bonded to a metal sheet.

The manner of heat bonding of a polyester resin film to a metal sheet will be described later. Hereinafter, the measuring method of trues train and true stress of the polyester resin film peeled off from the above described polyester resin film covered metal sheet will be explained. After immersing the polyester resin film covered metal sheet into a hydrochloric acid solution, chemically dissolving the metal sheet and peeling off the polyester resin film alone, the test piece for tensile test having the width of 5 mm and the length of 50 to 60 mm is prepared. After that, the nominal stress-elongation curve is measured of the test piece using a tensile tester in the environmental temperature of 75 ℃ on the conditions of the cross head distance of 20 mm and the speed of testing rate of stressing, from which the nominal stress $\sigma_0$ and the elongation El are obtained. The elongation El can be calculated by the following formula.

$$El = 100 \times (L - L0)$$

wherein

L0 : the length of a test piece before stressing

L : the length of a test piece after stressing

true strain $\varepsilon a$ and true stress $\sigma a$ can be obtained from the following formulas, respectively.

$$\varepsilon a = \varepsilon / (1 + \varepsilon)$$

$$\sigma a = \sigma_0 / (1 + \varepsilon)$$

wherein

$\varepsilon$ : strain $\varepsilon = El / 100$

The value of true stress corresponding to true strain of 1.0 can be read in the true strain–true stress curve prepared plotting true stress and true strain obtained as described above.

In the present invention, true stress of 3.0 to 15.0 kg/mm $^2$ corresponding to true strain of 1.0 obtained as described above is preferable. In the case where true stress is less than 3.0 kg/mm $^2$, uniform forming can not be practiced in the drawing because the friction coefficient between resin film and the blank holder or forming tool such as the punch becomes extremely high and the severe unevenness is caused on the resin film and the metal sheet. Furthermore, the permeation resistance of the resin film is extremely decreased, which causes the corrosion of the metal sheet in some cases where the resin film covered metal sheet is formed into a drawn can and the content is packed in it and then storaged for a certain period of time, that is unfavorable. On the other hand, in case where true stress exceeds 15.0 kg/mm $^2$, the resin film is peeled off or numerous cracks are generated in the film when the severe forming such as drawing and stretch forming or ironing after drawing and stretch forming is practiced, and the metal sheet can not completely be covered with the resin film.

Furthermore, in case where the adhesion after forming of the above-mentioned polyester resin film having the orientation to a metal sheet is not enough or in case where the lamination of one of these polyester resin film alone can not attain the enough corrosion resistance and impact resistance, the following methods are required that a polyester resin film is laminated on a metal sheet after a thermosetting adhesive such as phenol-epoxy adhesive is coated on a surface of the metal sheet and dried, or the polyester resin film on which surface to be laminated to a metal sheet is previously coated with the thermosetting adhesive and dried is laminated on the metal sheet. However, the laminating method intervening of the adhesive is unfavorable except in case of necessity since it needs extra cost and it also needs a measure to counter environmental pollution by the solvent contained in the adhesive.

Next, a metal sheet used for a polyethylene terephthalate covered metal sheet of the present invention will be explained. A surface treated strip or sheet of steel or aluminum alloy is used as a metal sheet. In case where a steel sheet is used, it is not necessary to define the chemical composition of the steel as far as the aforementioned severe forming can be practiced. The low carbon steel sheet having a thickness of 0.15 to 0.30 mm is preferably used. In order to produce excellent adhesion after forming of polyethylene terephthalate film to a steel sheet, it is more preferable to use a steel sheet having a coating of hydrated chromium oxide, a double layered coating consisting of a lower layer of metallic chromium and an upper layer of hydrated chromium oxide in particular, on the surface, that is tin free steel (TFS). And the steel sheet having a plating of one metal selected from tin, nickel or aluminum, a double layered plating or an alloy plating of more than one metal selected from those 3 metals, and further having the above-mentioned double layered coating is also available. In case where an aluminum alloy sheet is used, it is not necessary to define the chemical composition of the aluminum alloy as far as the aforementioned severe forming can be practiced as with the case of the steel. The aluminum alloy sheet of JIS 3000 series or 5000 series is preferably used with a view to economy and formability. It is more preferable to use an aluminum alloy sheet which is surface treated by known method such as the electrolytical treatment or the dipping treatment in the chromic acid solution, the etching in the alkali solution or acid solution, or the anodic oxidization. In case where the above-mentioned double layered coating consisting of a lower layer of metallic chromium and an upper layer of hydrated chromium oxide is formed on the sheet of steel or aluminum, the coating weight of the hydrated chromium oxide is preferably 3 to 50 $mg/m^2$ as chromium, more preferably 7 to 25 $mg/m^2$ as chromium, on the point of adhesion after forming of the covering resin film. It is unnecessary to define the coating weight of the metallic chromium, however, it is preferably 10 to 200 $mg/m^2$, more preferably 30 to 100 $mg/m^2$, on the point of corrosion resistance after forming and adhesion after forming of the covering resin film.

Further next, the covering method of the polyester resin film of the present invention will be explained below.

The covering method is consisting of

heating a metal strip continuously supplied from a means of the metal strip supply to the temperature range above the melting temperature of the polyester resin by a heating mean,

contacting a biaxially oriented film of polyester resin supplied from a means of the film supply on one side or both sides of the metal strip, putting them together between a couple of laminating roll,

pinching and pressing them, and quenching immediately after that. In the series of these process, the film of polyester resin is heated by heat conducted from the metal strip, the polyester resin at the contacting portion with the metal strip melts, and the biaxial orientation of the film is more lost in the portion nearer to the contacting portion with the metal strip, while the biaxial orientation of the film is more retained in the portion nearer to the uppermost surface free from contacting with the metal strip since the uppermost surface of the film, opposite from the contacting surface with the metal strip, contacts to the laminating roll which cools the film. The orientation structure of the film after covered on the metal strip changes into more preferable one controlling the cooling rate immediately after lamination determined by the temperature of the metal strip and the laminating roll, the period of time during the metal strips contacting to the laminating roll, which corresponds to the feeding speed of the metal strip, and the length of the contacting portion of the resin covered metal sheet with the laminating roll (nip : determined by diameter of the laminating roll and the elasticity modulus of the roll). The higher temperature of the metal strip and the laminating roll, the greater feeding speed of the metal strip and the shorter the nip length, the greater the film is heated and the more the biaxial orientation of the whole film is lost.

In the above-mentioned covering method of the present invention, the most preferable orientation structure after the lamination, in which the biaxial orientation of the film is more lost in the portion nearer to the contacting portion with the metal strip, while it is more retained in the portion nearer to the uppermost free surface not contacting with the metal strip, can be obtained controlling the cooling rate immediately after the lamination and cooling at the rate of more than 600 ℃/second. In case of the cooling rate of less than 600 ℃/second, the metal strip is not enough cooled and the film is excessively heated, which causes the biaxial orientation is lost to larger extent and improves formability, but reduces the impact resistance when the resin covered metal sheet is heated after forming.

In the present invention, a thermosetting resin such as an epoxy resin can be intervened between the film and the metal strip when the above-described polyester resin film is heat bonded to a metal sheet.

Hereinafter, the present invention is explained more in detail referring embodiment.

(Example)

The strip of TFS (amount of metallic chromium : 110 mg/m 2 , the amount of chromium hydroxide : 14 mg/m 2 as chromium) having thickness of 0.18 mm and temper of DR-10 continuously supplied from the means of metal strip supply was heated to temperatures shown in Table 1 to 3 contacting to some heating rolls, contacted on both sides with the various biaxially oriented polyester resin films shown below supplied from the film supplying roll. After that, both members were laminated, pinched and bonded together between a couple of laminating roll having temperatures shown in Table 1 to 3, and then quenched at the cooling rates shown in Table 1 to 3. The cooling rate after the heat bonding was controlled changing the nip length using laminating rolls having several diameters. The laminated biaxially oriented polyester resin films were the biaxially oriented films having thickness of 25 $\mu$ m manufactured from polyethylene terephthalate resin having various low temperature crystallization temperatures shown in Table 1 to 3 (hereinafter shown as PET), copolyester resin consisting of 88 mole % of ethylene terephthalate and 12 mole % of ethylene isophthalate (hereinafter shown as PETI), blended resin consisting of polyethylene terephthalate resin and polybutylene terephthalate resin blended at the weigh ratio of 1 : 0.6 (hereinafter shown as PET+PBT), and that having thickness of 25 $\mu$ m (thickness of lower layer film : 20 $\mu$ m, that of upper layer film : 5 $\mu$ m) manufactured from blended resin consisting of copolyester resin composed of 94 mole % of ethylene terephthalate and 6 mole % of ethylene isophthalate and polybutylene terephthalate resin blended at the weigh ratio of 0.8 : 1 as the lower layer, and copolyester resin consisting of 88 mole % of ethylene terephthalate and 12 mole % of ethylene isophthalate as the upper layer (hereinafter shown as PES/PETI).

Various polyester resin films were obtained immersing parts of the metal sheets covered with the above-described polyester resins into hydrochloric acid solution and dissolving TFS substratum alone and then they were made into test pieces for tensile test having width of 5 mm and length of 50 to 60 mm. These test pieces were tested using tensile tester in the environmental temperature of 75 ℃ on the condition of the cross head distance of 20 mm and the stress rate of 200 mm/minute. In these manners, the nominal stress – elongation curves were measured, true strains – true stress curves were calculated, and the values of true stress corresponding to true strain of 1.0 at 75 ℃ were obtained.

In addition, the resin covered metal sheets produced on the same laminating condition as those used for the above-mentioned measurement of the film properties were formed in the manner described below.

At first, the resin covered metal sheets were punched out into circular blanks having a diameter of 160 mm and then they were formed into drawn cans having a diameter of 100 mm. After that, they were formed into redrawn cans having a diameter of 80 mm by redrawing. These redrawn cans were formed into drawn and stretch formed and ironed cans having a diameter of 66 mm by a composite forming consisting of simultaneous drawn and stretch forming and ironing. This composite forming was practiced on the conditions that

the clearance between drawing portion, which corresponds to the upper edge part of the can, and ironing portion was 20 mm,

curvature radius in a corner of dies for redrawing process was 1.5 times of the thickness of the resin covered metal sheet,

the clearance between the redrawing dies and the punch was 1.0 time of the thickness of the resin covered metal sheet, and

the clearance between the ironing portion of the redrawing dies and the punch was 50 % of the thickness of the resin covered metal sheet. After that, the upper edge part of the can was trimmed off by a known method, then they were practiced by necked-in forming and flange forming.

The peeling-off of the resin layer at the wall portion of the thus produced can body was evaluated by the method described below. And further, the impact resistance of the resin film on the inside of the can body was evaluated by the method described below.

(I) Peeling-off of the resin layer from the can wall portion

The degree of peeling-off of the resin layer from the can wall portion of the inside and outside of the produced can body was observed by the naked eye and evaluated based on the following standard.

◎ : no peeling-off

○ : slightly peeled off but no problem for practical use

△ : heavily peeled off

× : peeled off at the whole upper portion of the can body

(II) Impact resistance of the resin film on the inside of the can body

At first, water was packed in the produced can and the rid was corked. Then, the can was fallen on the bottom down from a height of 15 cm. After it was opened and the water was taken out, 3 % sodium chloride solution was packed and a rod of stainless steel as a cathode was immersed in it. After that, a voltage about 6.3 volts was charged between the cathode and the can body as an anode. At this voltage charging, in case where even if the metal substratum under the resin layer is slightly exposed, a current flows. The degree of the metal expose was evaluated by the current value (mA). The results of the evaluation were shown in Table 4 to 6 in accompany with the values of true stress corresponding to true strain of 1.0 measured at 75 ℃.

Table 1

Characteristics of polyester resins and laminating conditions (1)

| Sample number | Resin film | | Covering conditions of resin film | | |
|---|---|---|---|---|---|
| | Resin composition | L.T.C.* temperature (° C) | Heating temperature of metal sheet (° C) | Temperature of laminating (° C) | Cooling rate after lamination (° C/sec) |
| 1 | PET | 128 | 310 | 150 | 587 |
| 2 | PET | 128 | 280 | 150 | 637 |
| 3 | PET | 128 | 270 | 150 | 650 |
| 4 | PET | 128 | 280 | 150 | 637 |
| 5 | PET | 128 | 290 | 150 | 619 |
| 6 | PET | 128 | 300 | 150 | 603 |
| 7 | PET | 128 | 310 | 150 | 587 |
| 8 | PET | 130 | 290 | 150 | 619 |
| 9 | PET | 140 | 270 | 150 | 650 |
| 10 | PET | 140 | 280 | 150 | 637 |

Remarks : L.T.C.* Low temperature crystallization

Table 2

Characteristics of polyester resins and laminating conditions (2)

| Sample number | Resin film | | Covering conditions of resin film | | |
|---|---|---|---|---|---|
| | Resin composition | L.T.C.* temperature (° C) | Heating temperature of metal sheet (° C) | Temperature of laminating (° C) | Cooling rate after lamination (° C/sec) |
| 11 | PET | 140 | 290 | 150 | 619 |
| 12 | PET | 140 | 300 | 150 | 603 |
| 13 | PET | 140 | 310 | 150 | 587 |
| 14 | PET | 155 | 270 | 150 | 650 |
| 15 | PET | 155 | 280 | 150 | 637 |
| 16 | PET | 155 | 290 | 150 | 619 |
| 17 | PET | 155 | 300 | 150 | 603 |
| 18 | PET | 155 | 310 | 150 | 587 |
| 19 | PET | 165 | 290 | 150 | 619 |
| 20 | PETI | 177 | 245 | 120 | 655 |

Remarks : L.T.C.* Low temperature crystallization

Table 3

Characteristics of polyester resins and laminating conditions (3)

| Sample number | Resin film | | Covering conditions of resin film | | |
|---|---|---|---|---|---|
| | Resin composition | L.T.C.* temperature (°C) | Heating temperature of metal sheet (°C) | Temperature of laminating (°C) | Cooling rate after lamination (°C/sec) |
| 21 | PET+PBT | 140 | 290 | 150 | 619 |
| 22 | PES/PETI | 140 | 300 | 150 | 603 |

Remarks : L.T.C.* Low temperature crystallization

Table 4

Evaluation result of properties of resin covered metal sheet (1)

| Sample number | True stress corresponding to true strain of 1.0 measured at 75 °C (kg/mm²) | Evaluation of covered metal sheet | | Item |
|---|---|---|---|---|
| | | Peeling-off of film (by naked eye) | Impact resistance (mA) | |
| 1 | 2.1 | ◎ | 0.95 | Comp.Ex.# |
| 2 | 13.9 | ○ | 0.01 | Example |
| 3 | 17.2 | × | unmeasured | Comp.Ex.# |
| 4 | 14.7 | ○ | 0.00 | Example |
| 5 | 10.2 | ○ | 0.00 | Example |
| 6 | 3.4 | ◎ | 0.09 | Example |
| 7 | 2.3 | ◎ | 0.85 | Comp.Ex.# |
| 8 | 9.3 | ◎ | 0.00 | Example |
| 9 | 16.5 | △ | 0.00 | Comp.Ex.# |
| 10 | 14.3 | ○ | 0.00 | Example |

Remarks : Comp.Ex.# Comparative Example

Table 5

Evaluation result of properties of resin covered metal sheet (2)

| Sample number | True stress corresponding to true strain of 1.0 measured at 75 °C (kg/mm²) | Evaluation of covered metal sheet | | Item |
|---|---|---|---|---|
| | | Peeling-off of film (by naked eye) | Impact resistance (mA) | |
| 11 | 9.1 | ◎ | 0.00 | Example |
| 12 | 3.4 | ◎ | 0.08 | Example |
| 13 | 2.6 | ◎ | 0.53 | Comp.Ex.* |
| 14 | 16.8 | △ | 0.00 | Comp.Ex.* |
| 15 | 14.4 | ○ | 0.00 | Example |
| 16 | 9.4 | ◎ | 0.00 | Example |
| 17 | 3.3 | ◎ | 0.09 | Example |
| 18 | 2.1 | ◎ | 0.49 | Comp.Ex.* |
| 19 | 8.9 | ◎ | 0.00 | Example |
| 20 | 14.7 | ◎ | 0.00 | Example |

Remarks : Comp.Ex.* Comparative Example

Table 6

Evaluation result of properties of resin covered metal sheet (3)

| Sample number | True stress corresponding to true strain of 1.0 measured at 75 °C (kg/mm $^2$) | Evaluation of covered metal sheet | | Item |
|---|---|---|---|---|
| | | Peeling-off of film (by naked eye) | Impact resistance (mA) | |
| 21 | 11.3 | ◎ | 0.01 | Example |
| 22 | 7.5 | ◎ | 0.00 | Example |

Remarks : Comp.Ex. = Comparative Example

As can be seen in Table 4 to 6, the metal sheet covered with a polyester resin film having true stress of 3.0 to 15.0 kg/mm$^2$ corresponding to true strain of 1.0 measured at 75°C has excellent adhesion after forming and impact resistance.

[Effect of invention]

The polyester resin film covered metal sheet of the present invention, in which the polyester resin film having orientation obtained rejecting metal sheet alone from the polyester resin film covered metal sheet by chemical dissolution has true stress of 3.0 to 15.0 kg/mm$^2$ corresponding to true strain of 1.0 measured at 75°C in the mechanical property, is produced contacting the above-described polyester resin film to a metal sheet heated to a temperature of more than the melting temperature of the above-described polyester resin, pinching and press bonding both members with a couple of laminating roll, and cooling the metal sheet at the cooling rate of more than 600°C/second in this laminating process with a nip formed in the above-described laminating roll. The thus produced polyester resin film covered metal sheet can reconcile adhesion after forming and impact resistance of the polyester resin film and can be adapted to the use of severe forming such as drawing, drawing and ironing, and drawing and stretch forming as well as ironing after drawing and stretch forming.

Although the invention has been described with reference to specific examples it will be appreciated to those skilled in the art that the invention may be embodied in many other forms.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A metal sheet covered with polyester resin film having orientation, wherein said polyester resin film having orientation, obtained from said metal sheet covered with polyester resin film rejecting metal sheet alone by chemical dissolution, has true stress of 3.0 to 15.0 kg/mm$^2$ measured at 75°C, corresponding to true strain of 1.0, in the mechanical characteristics.

2. The metal sheet covered with polyester resin film according to claim 1, wherein polyester resin is polyethylene terephthalate resin.

3. The metal sheet covered with polyester resin film according to claim 2, wherein said polyethylene terephthalate resin is a polyethylene terephthalate resin having low temperature crystallization temperature of 130 to 165°C.

4. The metal sheet covered with polyester resin film according to claim 3, wherein said polyethylene terephthalate resins a polyethylene terephthalate resin having low temperature crystallization temperature of 140 to 155°C.

5. The metal sheet covered with polyester resin film according to claim 1, wherein polyester resin is a copolyester resin mainly consisting of ethylene terephthalate recurring unit, a copolyester resin mainly consisting of butylene terephthalate recurring unit, or a blended copolyester resin consisting of at least 2 of these resins, or a double layered polyester resin consisting of a laminate of at least 2 of these resins.

6. A production method of the metal sheet covered with polyester resin film according to any claim 1 to 5, wherein said metal sheet is cooled by a nip formed by a couple of laminating roll at the cooling rate of 600°C/second or more when said polyester resin film is contacted to said metal sheet heated to a temperature more than the melting temperature of said polyester resin and both members are pinched and pressed into a laminate by said couple of laminating roll.

7. A metal sheet covered with a polyester resin film having an orientation substantially as herein described with reference to any one of the embodiments of the invention as illustrated in the accompanying examples.

DATED this 11th Day of May 1999

TOYO KOHAN CO. LTD

Attorney: CAROLINE M. BOMMER
Fellow Institute of Patent Attorneys of Australia
of BALDWIN SHELSTON WATERS