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LAMINATED PLATE AND METHOD OF MANUFACTURING THE SAME

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(57) Claim

1. A laminated sheet consisting of a metal substrate defining parts that are to be highly processed in comparison to parts of the metal substrate that are to be lightly processed, and an oriented thermoplastic resin film laminated on said metal substrate, wherein a degree of crystal orientation of said resin film is varied in a planar direction in order that a highly crystal oriented part of said resin film is set to the lightly processed part of said laminated sheet, and a lightly crystal oriented part of said resin film is set to said highly processed part of said laminated sheet.

2. A laminated sheet for can manufacturing consisting of a metal substrate and an oriented thermoplastic resin film laminated on said metal substrate, wherein a part of the metal substrate which is to be formed into a can bottom is laminated with resin film which is highly crystal oriented.

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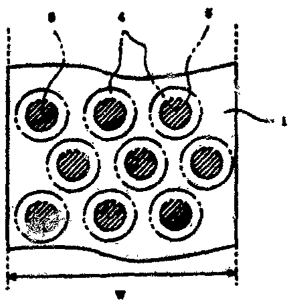


(57) Abstract

In the laminated plate according to the present invention, the degree of orientation of crystals in a covering film of a synthetic resin varies in a predetermined pattern, and the occurrence of delamination is minimized in a side wall portion, requiring a high degree of processing, of a can, a bottom portion, requiring a low degree of processing, of a can having a high denting resistance. In the laminated plate manufacturing method according to the present invention, a distribution pattern of the degree of orientation of crystals in a resin film is also set arbitrarily when the resin film is laminated on a metal plate.

（５７）要約

本発明のラミネート板は、被覆合成樹脂フィルムの結晶配向度が所定のパターンで変化しており、加工の程度が高い缶側壁部ではデラミネーションを抑制すると共に、加工の程度が低い缶底部では耐デンティング性が高い。

また、本発明のラミネート板の製造法は、金属板に樹脂フィルムをラミネート加工するときに同時に樹脂フィルムの結晶配向度の分布パターンを任意に設定する。

LAMINATED SHEET AND MANUFACTURING METHOD THEREOF

Technological field

This invention concerns laminated sheet and a manufacturing method therefor. The invention has been especially developed for beverage or food cans and the efficient manufacturing method of such cans.

Background technology

A two piece can which consists of the can body combined with the bottom lid is used for the food can or the beverage can. Those cans are formed from a metal substrate such as a cold rolled steel sheet, an aluminium sheet or tinplate. Those cans are usually coated by various resin coating in order to prevent the metal from being dissolved into the contents and to improve its corrosion resistance and durability.

The abovementioned two-piece can is occasionally formed by means of drawing the laminated sheet which is produced by laminating the resin film to the metal substrate. Such laminated sheet should endure the drawing, the ironing or the stretching processing.

Therefore, the laminated sheet is produced by a method of laminating the resin film without using adhesive (Japanese Patent Application No. TOKU-KOU-SHO 60-47103) or by a method of laminating a polyester film which is coated with epoxy resin together with curing agent, etc. (e.g. Japanese ---

Application NO. TOKU-KOU-SHO 63-13829 or No. TOKU-KAI-HEI 1-249331).

One of the required can performances is denting resistance in the drawn and formed can. There must be impact resistance of the film when the dent is caused and also resistance to cracking of the film.

The present Applicant has proposed to use the steel sheet covered with bi-axially oriented or un-oriented polyester resin film which has a specified intrinsic viscosity as a material of the laminated can (Japanese Patent Application No. TOKU-KAI-HEI 4-224936).

Above-mentioned bi-axially oriented polyester resin film improves the strength and the denting resistance because the crystalline structure is highly oriented (the molecule is highly oriented). However, Such a polyester film doesn't have enough adhesion to the metal substrate. Therefore it peels off easily during drawing process or ironing process.

In order to solve such problems, the resin film is laminated to the metal substrate which is heated in advance. As a result, the crystal orientation of the film on the side of metal substrate decreases to some degree. And, adhesion and bonding improve.

So this is a method of giving the inclination in the direction of thickness of the film concerning crystal orientation. However, the denting resistance of the can decreases when crystal orientation of the film decreases too much and it causes a problem concerning the durability of the can.

In order to improve adhesion, it has been proposed that the film of laminated sheet be partially heated especially for the high adhesion required part just before the drawing process (Japanese Patent Application No. TOKU-KAI-HEI 4-118121). However, it is difficult to control and maintain the film temperature within the range from the glass transition temperature to the temperature of the re-crystallisation.

It is an object of the invention, at least in the preferred embodiment, to overcome or substantially ameliorate at least one of the disadvantages of the prior art.

According to a first aspect of the invention there is provided a laminated sheet consisting of a metal substrate defining parts that are to be highly processed in comparison to parts of the metal substrate that are to be lightly processed, and an oriented thermoplastic resin film laminated on said metal substrate, wherein a degree of crystal orientation of said resin film is varied in a planar direction in order that a highly crystal oriented part of said resin film is set to the lightly processed part of said laminated sheet, and a lightly crystal oriented part of said resin film is set to said highly processed part of said laminated sheet.

According to a second aspect of the invention there is provided a laminated sheet for can manufacturing consisting of a metal substrate and an oriented thermoplastic resin film laminated on said metal substrate, wherein a part of the metal substrate which is to be formed into a can bottom is laminated with resin film which is highly crystal oriented.

According to a third aspect of the invention there is provided a method of manufacturing the laminated sheet as described above including the steps of; heating said metal substrate, putting a highly crystal oriented resin film on said metal substrate, and pressing said resin film and said metal substrate to adhesion by a laminating roll, wherein a means having a prescribed cooling pattern which sets to only said lightly processed part of said laminated sheet is provided, and said metal substrate or said laminated sheet is cooled by said prescribed cooling pattern.

According to a fourth aspect of the invention there is provided a method of manufacturing the laminated sheet as described above including, the steps of; heating said resin film, then varying the temperature of said resin film in the planar direction by a means having a prescribed cooling pattern, and pressing said resin film and said metal substrate to adhesion by said laminating roll.

According to a fifth aspect of the invention there is provided a method of manufacturing the laminated sheet as described above consisting of; heating said resin film, then varying the thickness of said resin film by a means having a prescribed pattern, and pressing said resin film and said metal substrate to adhesion by said laminating roll.

According to a sixth aspect of the invention there is provided a product manufactured from a laminated sheet consisting of metal substrate laminated with an oriented thermoplastic resin film, wherein lightly crystal oriented resin film is laminated to a part of said metal substrate which is to be heavily processed in said product, and highly crystal oriented resin film is laminated to a part of said metal substrate which is to be lightly processed in said product.

According to another aspect of the invention there is provided a can manufactured from a laminated sheet consisting of metal substrate laminated with an oriented thermoplastic resin film, wherein a degree of crystal orientation of said resin film at a part of the metal substrate corresponding to the can bottom is higher than that at a part of the metal substrate corresponding to the can wall.

This invention as implemented in the preferred embodiment provides a laminated sheet for a can, which laminated sheet has excellent denting resistance and adhesion. That laminated sheet improves the denting resistance of the part where considerable denting is likely to occur such as can bottom etc., and also improves the adhesion of the film to the metal substrate in the other parts. Furthermore, that laminated sheet can be simply formed into cans and the damage at the time of circulation is small and durability is high.

A preferred embodiment of the invention will now be described, by way of example only, with reference to the accompanying drawings in which:

Figure 1 is projected drawing which shows one example of the laminated sheet of the present invention.

Figure 2(a) is a magnified cross section of the laminated sheet and Figure 2(b) is an expanded cross section which shows other example of the laminated sheet of the present invention.

Figure 3 is an explanation drawing which shows the transition of X-ray diffractive intention which corresponds to the degree of crystal orientation of the laminated film.

Figure 4(a) - (d) are projected drawings which show the example of the blank present invention, respectively.

Figure 5(a) - (c) pattern of the are the process charts of the method of producing the drawing can from the laminated sheet shown in Figure 1.

Figure 6(a) is the lengthwise cross section which shows laminated can produced by the method shown in Figure 5 and Figure 6(b) is the lengthwise cross section of the additionally formed laminated can.

Figure 7 is a process chart which shows an example of the manufacturing method of the laminated sheet of the present invention.

Figure 8 is a front view which shows an example of the heating roll used for the manufacturing the laminated sheet of the present invention.

Figure 9 is a cross section which shows an example of the cooling roll used for the manufacturing method of the laminated sheet of the present invention.

Figure 10 is a cross section which shows an example of the ruminating roll used for the manufacturing of the laminated sheet of the present invention.

Figure 11 is a perspective drawing of the cooling roll shown in Figure 9.

Figure 12 is a A-A line cross section of Figure 11.

Figure 13 is a process chart which shows another example of the manufacturing method of the laminated sheet of the present invention.

Figure 14 is a process chart which shows the other example of the manufacturing method of the laminated sheet of the present invention.

Figure 15 is a magnified cross section of the resin film and the metal substrate laminated by the method shown in Figure 14.

Referring to the drawings, the laminated sheet 1 shown in figure 1 consists of the metal substrate 2 and the resin film 3 laminated on one of the surfaces of it as shown in Figure 2(a).

The laminated sheet 1 is provided in the form of a coiled strip having a constant width W.

In some cases, there can be the adhesive between the metal substrate 2 and the resin film 3.

In addition, resin film 3 can be laminated to both sides of the metal substrate as shown in figure 2(b).

The above mentioned laminated sheet 1 having constant width W is punched out into disk blank 4 to form the cup and the three disk blanks in each line are zigzagingly punched out with constant difference.

The imaginary outline of the blank pattern is shown on the laminated sheet 1.

In the center part 5 of each blank 4 (shown by hatching), which corresponds to the bottom when the blank is formed into a cup, the crystal orientation of the resin film is high. However, it is low in other parts .

The shape of blank 4 can be designed in any shape according to the final product to be formed.

For instance, as shown in Figure 4(a)-(d), the shape of high crystal orientated part corresponding to the bottom of the final cup, which is circle 5(a), oval 5(b) square 5(c) or rectangle 5(d) is designed in the blank for a cylindrical cup, oval cup, square cup or rectangular cup. In the present invention, any other shapes are available.

The thickness of the metal substrate 2 can be changed according to the kind of metal, and to the usage of the container or the container size. Generally, a metallic sheet is desirable from 0.10 to 0.50 mm in thickness and is excellent especially from 0.15 to 0.40 mm in thickness.

Various surface treated steel sheet and aluminum, etc. are used as a metal substrate.

First of all, surface treated steel sheet is explained. The surface treated steel sheet is made of cold-rolled steel sheet, which is annealed and secondly cold-rolled. The cold-rolled steel sheet is surface treated by one of the following treatment groups consisting of electrolytical chromium coating and the chromate treatment, etc.

The cold-rolled sheet is treated with one or more kinds of these surface treatments. One of the suitable surface treated steel sheet types is electrolytically chromium coated steel sheet (TFS). Especiallypreferable is one having a double layer consisting of a lower metallic chromium layer having 10 to 200 mg/m^2 of metallic chromium and an upper hydrated chromium oxide layer having 1 to 50 mg/m^2 of chromium .

In case where polyester film is laminated to it, it is preferable that the hydrated chromium oxide layer has 3 -50 mg/m^2, especially 7 - 25 mg/m^2 of metallic chromium. The laminated polyester film on the electrolytically chromium coated steel sheet is excellent in adhesion and corrosion-resistance.

One of the other surface treated steel sheet types is tinplate coated with 0.5 - 11.2 g/m^2 of tin. This tinplate should be coated with 1 to 30 mg/m2 hydrated chromium oxide formed by chromate treatment or chromate -phosphate treatment.

In addition, one of the other examples is aluminum coated steel sheet which gives aluminum plated or aluminum laminated steel sheet.

Besides pure aluminum, an aluminum alloy sheet can be used as the light metal sheet. An aluminum alloy excellent in corrosion-resistance and formability is one having 0.2 -1.5 wt % of Mn, 0.8 - 5 wt % of Mg, 1.25 - 0.3 wt % of Zn and 0.15 - 0.25 wt % of Cu.

These light metal substrates can be treated by the organic or inorganic treatment.

The above-mentioned resin film 3 is made from a molecular oriented thermoplastic resin and a higher crystal orientated one is more preferable.

The resin film should be oriented in only the lengthwise direction (uniaxial) or in the lengthwise and width direction (bi-axial), unlike film which is formed only by drawing after being formed into extruded film.

The above-mentioned degree of crystal orientation can be measured from the intention of the peak of an X-ray diffraction pattern. Moreover, it is possible to be measured optically by an Abbe refractometer.

The method by which the degree of the crystal orientations is calculated from the peak height of X-ray diffraction pattern is shown as follows. Concretely, (100) plane parallel to the film surface is scanned by means of X rays and the diffracted intensity is measured. And the crystal orientation is calculated as the ratio of the diffracted intensity of X-ray to that of before lamination.

The laminated film of the present invention should have more than 90% of crystal orientation at the place corresponding to the bottom of the can and have about 5% of crystal orientation at the other parts.

Figure 3 shows the transition of the degree of crystal orientation.

When X-rays are continuously scanned to part 5 (where crystal orientation is high) which corresponds to the bottom along arrow A, the diffraction intensity of X-ray is obtained as shown in figure 3.

That is, the degree of the crystal orientation of the film becomes about 95% in part 5 which corresponds to the bottom, and it is about 5% in the other parts.

Wherever the film thickness of the formed can is in the range of 5 to 20 μm, the resin film having crystal orientation previously mentioned can have excellent heat resistance, strength and permeation resistance. Therefore, the resin film should be one which can be crystal oriented (molecularly oriented) and be suitably oriented by heating, drawing, redrawing and ironing.

The following resins can be used as the film material of the present invention, for example, an olefin resin such as polyethylene, polypropylene, and ethylene propylene copolymer, ethylene acrylic ester copolymer and ionomer.

Also available are polyester resins such as polyethylene terephthalate, polybutylene terephthalate, ethylene terephthalate/isophthalate copolyester, ethylene terephthalate/adipate copolyester, ethylene terephthalate/sebacate copolyester and butylene terephthalate/ isophthalate copolyester; polyamide resins such as nylon 6, nylon 66, nylon 11 and nylon 12; polyvinyl chloride; polyvinylidene chloride; polycarbonate resins such as poly-p-xyleneglycol biscarbonete, poly-dioxydiphenyl ethane carbonate, poly-dioxdiphenyl 2,2-propane carbonate, poly dioxydiphenyl 1,1-ethane carbonate, high nitrile resins such as acrylonitrile-butadiene copolymer with the high content of nitrile, acrylonitrile-styrene copolymer, polystyrene copolymer etc., which satisfy preceding conditions.

In the present invention, all the above-mentioned resins can be used.

An especially suitable resin film is one consisting of polyester, which mainly comprises the recurring unit of ethylene terephthalate, and is bi-axially oriented.

Polyester resin should be the one in which 75-95% recurring consists of ethylene terephtalate units and 5-25% remainder consists of units of another ester.

Other acid components than terephthalic acid which can be used are phthalic acid, isophthalic acid, succinic acid, azelaic acid, adipic acid, sebacic acid, dodecanic acid, diphenyl carboxylic acid, 1,4 cyclophexane dicarboxylic acid, trimellitic anhydride acid and one or more kinds of these acids .

Other alcohol components which can be used are saturated polyhydric alcohol such as 1,4 butanediol, 1,5 pentanediol, 1,6 hexanediol, propyleneglycol, polytetramethyceneglycol, trimethylene glycol, triethylene glycol, neopentylglycol, 1,4 cyclohexanedimethanol, trimethylolpropane, pentaerythritol, and one or more kinds of these alcohols .

The ester unit, except ethylene telephthalate, can be any acid component and any polyhydric alcohol except the combination of the ethylen telephthalate and ethylene glycol.

Copolyester can be made from the above acid component and a polyhydric alcohol.

These copolyester resin can be produced by blending copolymerized polyester with ethylene terephthalate, melting them and then copolymerizing them by transesterification.

When the polyester resin film of which intrinsic viscosity, IV value, is about 0.50 to 0.70 is used, the laminated metallic sheet has excellent denting resistance in the body part of drawn and stretch formed can of the present invention.

The polyester resin can have added to it stabilizer, antioxidant, anti-static, pigment, filler for lubricating, and corrosion inhibitor as occasion demands.

Although it is not particularly restricted, suitable thicknesses of the polyester film used in the present invention are 5 to 50 μm. When the thickness of the film is 5 μm or less, the laminating process is remarkably difficult and sufficient corrosion resistance after forming cannot be obtained. Also, when the thickness becomes 50 μm or more, the cost of the can is more expensive than conventional cans coated with epoxy resin.

When an adhesive agent is between the metallic substrate 2 and the resin film 3, the laminated sheet has excellent adhesion and corrosion resistance. This adhesive agent also has excellent adhesion to the resin film. This adhesive consists of epoxy resin and curing agent resin such as phenol resin, amino resin, acrylic resin, vinyl resin, and urea resins. The suitable adhesive is an epoxy phenol coating, a vinyl chloride vinyl resin, or an organosol coating which consists of copolymerized vinyl chloride resin and epoxy resin.

The thickness of the adhesive layer should be 0.1 - 5 μm.

As shown in figure 2(b), when the resin film 3 is laminated on both sides of the metal substrate, the outer side resin film can be pigmented. This pigment conceals the metallic color of substrate and stabilizes the blank holder force to privent a metal substrate from wrinkling in drawing or redrawing.

The inorganic pigment is as follows:

Inorganic white pigments such as rutile type or anatase type titanium dioxide, zinc dioxide, and gross white.

White pigments such as perlite, precipitated sulphuric perlite, calcium carbonate, gypsum, precipitated silica, aerosil, talc, burned or non-burned kaolin, barium carbonate, alumina, white synthetic or natural mica, synthetic calcium silicate and magnesium carbonate.

Black pigments such as carbon black and magnetite, etc.

Red pigments such as Indian red, etc.

Yellow pigments such as sienna, etc.

Blue pigments such as ultramarine and cobalt blue, etc.,

Five to 500% by weight of these pigments can be blended for film resin. Especially, it is preferable to be blended at the rate of 10-300% by weight.

In the above laminated sheet 1, the resin film 3 is marked to detect the higher crystal oriented part 5 in order to laminate the resin film 3 separating the higher crystal oriented part (5) and lower oriented part. The high orientated part 5 is detected by this mark and punched out into the disk blank 4 as shown in figure 5(a).

The punched blank 4 is drawn by die and punch, and is formed into the temporary metallic cup 9 which has the bottom 7 with fixed diameter and sidewall 8 with fixed height as shown in figure 5(b).

The metallic cup 9 is redrawn several times and finally becomes the laminated can 10 which has fixed height and the diameter shown in figure 5(c) ((c) of chart 5).

The higher crystal orientated part 5 corresponds to the whole bottom 11 and the lower sidewall part 10 of this laminated can. This is shown by that the oblique lined part is extending even to the can sidewall in figure 5(c) (figure 5(c)-12).

Figure 6(a) shows the distinction of each of the areas. The area indicated by R1 corresponds to the higher crystal oriented part 5 in laminated sheet 1 shown in figure 6(a). The area shown with R2 corresponds to the lower crystal oriented part.

The laminated can shown in figure 6(a) is an example of laminated can of the present invention. The laminated can 10 is domed at the bottom and the domed part 10A is formed as shown in figure 6(b). In addition, the laminated can is trimmed, printed, cured, necked, and flanged, and shaped into the final laminated can.

In case of producing the drawn and ironed can, the laminated can is formed by ironing the drawn or redrawn cup. In ironing as mentioned above, the side wall 10b is severely processed. Because that part has the lower crystal oriented resin film, the film adheres well to the metallic substrate. Therefore, laminated film is not easily de-laminated.

The bottom 10a and its marginal part often knock against other cans in transport. That part has higher crystal orientated resin film and has excellent denting resistance. Therefore, cracks are not easily caused on the resin film in the inner wall.

Because the bottom 10a is less processed, de-lamination is not caused even if the laminated film is highly oriented. Therefore, whole can has excellent durability.

Next, the manufacturing method of the laminated sheet which has higher and lower crystal orientation in the laminated film of the present invention is explained through the figure 7 to 15.

Figure 7 shows a heating roll 21 to heat metal substrate 2 as strip. A pair of laminating rolls 22 are arranged below the heating roll 21 in order to laminate the metal substrate 2 and two resin film 3 which locate both side of the metallic substrate. A water bath 23 is arranged below the pair of laminating rolls 22 to quench the laminated sheet.

After being uncoiled from the uncoiler, the metal substrate 2 is heated by the heating roll 21 and turned downwardly.

In addition, the metal substrate 2 runs through between the couple of laminating rolls 22 and enters the water bath 23 for quenching. The resin film 3 is supplied from the above part of laminating roll 22 and is laminated to the metallic substrate 2 by the pair of laminating rolls 22. The heating roll 21 of the above-mentioned laminating facility has the shape shown in figure 8.

The heating pipes 24 are arranged in the heating roll 22 to circulate the heating medium such as heated water or oil in the direction of the roll axis. Those heating pipe 24 are not passed through area Z which corresponds to the higher crystal orientated part in the laminated sheet 1 shown in figure 1. That is, heating pipe 24 which penetrates from a left axis 25 to the right axis 26 of heating roll 21 passes the vicinity of surfaces of heating roll 21 except area Z. The heating pipe 24 passes the center part of the heating roll 21 in area Z and the heat conduction is intercepted by a heat insulator.

A cooling pipe which sends cooling water to area Z can be arranged. When the metallic substrate 2 is heated by above heating roll 21, the temperature of metal substrate is raised except in the part contacting area Z. Therefore, the crystal orientation of the film decreases at all parts except the part contacting area Z when resin film 3 is laminated on the heated metal substrate 2 and is passed through laminating rolls 22.

Moreover, the crystal orientation of the film contacting the area Z is kept near in original orientation. Therefore, the higher crystal oriented circular part 5 is partially formed on the laminated sheet 1, and the other area has the lower crystal orientation.

In order to produce the disk blank pattern when the higher crystal oriented part 5 is zigzagingly arranged as shown in figure 1, area Z on the opposite side of the heating roll 21 shown in figure 8 must be located with constant difference in the direction of the roll axis.

The surface temperature of the above-mentioned heating roll 21 is different according to the material and the thickness of resin film 3. For instance, in using bi-axially oriented polyester film, the higher temperature part is about 210 - 260°C and area Z is about 170 - 230°C.

The laminating speed is about 150 m/min in the case of the general laminating method.

An induction heating roll, heating pipe roll or jacket heating roll can be used as heating roll which heats metal substrate 2.

The cooling roll 27 shown in figure 9 partially cools the metal substrate 2 which is uniformally heated by the above-mentioned heating roll 21. The cooling roll 27 is arranged on the both sides or one side of the metallic substrate 2 below the heating roll 21 as shown in figure 7. The cooling roll 27 is made of the high heat conductivity metal such as aluminum.

A projecting part 28 is arranged on the cooling roll 27 under the uniform pattern. This projecting part 28 contacts to the metal substrate 2 which has been heated by the heating roll 21, and cools it. In the case of using this cooling roll 27, the heating roll 21 can be the one which heats whole area of the metal substrate 2. The pattern of projecting part 28 is the same as the area shown in figure 8.

Such cooling rolls 27 can also cause the desired temperature distribution on the surface of the metal substrate 2. And the degree of the crystal orientation of the resin film 3 laminated to the metal substrate 2 can be changed in the direction of the plane.

Figure 10 shows the case where the laminating roll 22 has an insulating part 29 and cooling part 30 on itself. Such insulating part 29 can be composed of a rubber lining of the same type as in a general laminating roll. The cooling part 30 can be composed of an exposed metallic part 31 of the center of the roll. The cooling part 30 and insulating part 29 have a continuously smooth and cylindrical surface. The metallic part 31 in the laminating roll 22 can have a cavity 32 and cooling medium such as cooling water flows in it.

The cooling roll 27 shown in Figure 9 can be given the rubber lining same as laminating roll 22 and the surface temperature of it can be partially changed.

Figure 11 shows the perspective drawing of the cooling roll 27 shown in figure 9 (or laminating roll shown in figure 10) to indicate the projecting part 28 (or the cooling part 30) clearly. The circular projecting part 28 (or the cooling part 30) is arranged according to the specified pitch P (see figure 12). The lines of these projecting parts 28 are zigzagingly arranged with constant difference in the direction of the roll axis.

The metal substrate 2 is partially cooled by the cooling roll 27. This metal substrate 2 and resin film 3 are laminated by the pair of laminating rolls 22, and are formed to the laminating sheet 1 as shown in figure 1. The imaginary line 33 in figure 11 indicates the outline drawing of the laminating roll which is covered with rubber. All parts except the projecting part 28 are insulated by means of the lining rubber.

Figure 12 shows A - A line cross section of figure 11. The projecting part 28 (or cooling part 30) is composed of the cylindrical projection surroundedby tapered face 34. The diameter D of the projecting part 28 is decided according to the diameter of the bottom of the laminated can produced by above-mentioned method.

In the case where the diameter of the blank is 179 mm, for instance, the diameter D of the projecting part 28 is 65 mm. For instance, the pitch P is assumed 310 mm. The height H of the projecting part 28 is about 3 to 5 mm.

Figure 13 shows another example, and laminating roll 22 is the same as a conventional one. The laminating roll 22 is partially cooled by the cooling roll 35. The metal substrate 2 and resin film 3 are laminated by partially cooled laminating rolls. The construction of the cooling roll 35 is the same as those shown in figure 11 - 12. The projecting part 35a to cool is arranged on the surface of the cooling roll 35.

In above examples, the metal substrate 2 is partially heated by heating roller and partially cooled by the cooling roll before laminating. Or higher and lower temperature parts are formed on the metal substrate in laminating by laminating roll 22.

The imaginary outline S in figure 13 shows the another example, and it indicates that the laminated sheet 1 is partially cooled just after laminating. At that time, the cooling roll used is the same as above cooling roll 28 .

All examples mentioned above indicate the common method to change the temperature of the metal substrate or laminated sheet partially and consequently the distribution of the crystal orientation of the laminated resin film changes in the planar direction.

Figure 14 shows the outline to produce the laminated sheet with same property by means of partially changing the thickness of the resin film 3 . Before laminating, the resin film 3 is heated by preheating roll 36 in advance and runs through the pair of pattern rolls 37 which have the projecting or depressing parts . As a result, the thick part 38 and the thin part 39 are formed in the resin film 3 as shown in figure 15. When such a resin film 3 and metal substrate 2 are laminated by conventional laminated roll, the thick part 38 of the film is not heated sufficiently , so that the thick part

38 of the film has the higher crystal orientation. On the contrary, the crystal orientation of the thin part 39 of the film decreases because that part reaches a high temperature.

The surface of the laminated sheet 1 with thin or thick part of the resin film 3 is smoothed through the drawing and ironing as shown in figure 5 whereby roughness of the laminated film does not stand out.

The thickness of each part of previous resin film is decided according to the product. Usually the part subject to denting has a thickness of about 5 to 50% of the original thickness of the resin film.

Next, a concrete example and a comparison example are given and the effect of the laminated sheet of the present invention is explained.

(Example 1)

Tin free steel which was 0.175 mm in thickness and 960 mm in width was used as a metal substrate. Bi-axially oriented polyethylene terephthalate resin films were laminated to both side of that metallic substrate by the laminating apparatus as shown in figure 7. An adhesive of epoxy resin was provided between the metal substrate and the film. The thickness of the film was 25 μm and the thickness of the adhesive layer was 0.8 μm.

At the laminating, the circular low temperature parts of diameter of 80 mm were zigzagingly arranged by the pitch 131 mm on the heating roll as shown in figure 1.

The other conditions of the laminating were the same as the conventional method.

(Example 2)

In the laminating process, cooling rolls were used. The other conditions were same as example 1, and the laminated sheet was produced by means of example 2.

(Example 3)

The cooling part was arranged on the laminating roll. The other conditions were same as example 1, and the laminated sheet was produced by means of example 3.

(Comparison example 1)

A polyethylene terephthalate resin film with a high crystal orientation was laminated to and over the same metallic substrate as example 1. That laminated film had constant crystal orientation over all parts.

(Comparison example 2)

A polyethylene terephthalate with a low crystal orientation such as undrawn film was laminated to the same metal substrate as example 1. That laminated film had constant crystal orientation over all parts.

The above laminated sheet was drawn and redrawn by means of the method shown in figure 5 and was formed into the laminated can. The bottom of that can was 65 mm in diameter. Whether de-lamination occurred in the laminated can or not was evaluated by visual observation.

The denting resistance was evaluated by the following method. The laminated can was filled with water and then the was seamed on it. In addition, the packed can was dropped from a height of 15 cm.

The film crack of the dented part was evaluated by enamel rater value (ERV) measuring method. ERV measuring method is explained as follows. A brine solution of about 3% is poured into the above can after it has fallen, dented and opened. And a stainless steel stick is immersed into it as cathode.

Next, voltage of 6.3 volt's is applied between the can which is anode and the stainless steel stick cathode. At this time. in case of the metal is exposed through the crack in the film, the current flows between both poles.

The results are shown in table 1.

Table I

The degree of de-lamination	The denting resistance (ERV current value)
example 1	None 0 (insulated)
example 2	None 0 (insulated)
example 3	None 0 (insulated)
compersion example 1	
large de-lamination in upper part of can	0 (insulated)
compersion example 2	
None	1.25 mA

The cans of example 1-3 did not have any de-lamination and had excellent denting resistance as shown in table 1.

On the other hand the can of comparison example 1 had excellent denting resistance. However, a large de-lamination occurred in the upper part of the can.

Moreover, a film crack occurred remarkably in the dented part on the can of comparison example 2 though de-lamination was not generated.

The laminated resin film which uniformally has the low crystal orientation has inferior denting resistance and never de-laminated.

On the contrary, the laminated resin film which uniformally has the high crystal orientation has superior denting resistance and de-laminates at much area.

When the laminated sheet which consists of metal substrate and resin film is drawn or ironed, the extensional deformation or the shrinkage deformation in the substrate is caused according to the degree of the processing. Then, if the lightly crystal oriented part is set to the highly processed part, the laminated sheet has excellent adhesion. As a result, de-lamination is hardly caused.

As the laminated resin film was elongated with metallic substrate, the higher the crystal orientation of the film becomes, the greater the film is drawn in the processing.

On the contrary, the highly oriented part is set to the lightly processed part. As a result, the orientation of the film of the can increases in a whole can after forming. That laminated can has excellent denting resistance and corrosion resistance.

For instance, when the laminated sheet is used as a material of the two piece can, the film corresponding to the bottom of the can should have the high crystal orientation. The film in the sidewall where the degree of the processing is high should have the low crystal orientation.

When the resin film which has high crystal orientation is laminated to the metal substrate, and high and low temperature part were given to the metal substrate or laminating roll, the crystal orientation of the film which contacts with the high temperature part decreases. And the crystal orientation of the film which contacts low temperature part is kept as original.

The same effect is achieved also when the laminated sheet passes through the laminating roll cooled partially. When the temperature of the film partially changes according to fixed pattern, the same effect is achieved. The resin film which has the high orientation is preheated and the thin or thick part is formed immediately before laminating. Then the temperature of the thin part rises and the crystal orientation decreases. On the contrary, the temperature of the thick part does not rise so much and the crystal orientation is kept as original.

Industrial possibility

The laminated sheet of the present invention has the highly or lightly crystal oriented part of the resin film according to the fixed pattern.

The de-lamination of the film is suppressed and the denting resistance of the can is superior.

The laminated sheet of the present invention is for the use of can manufacture , and de-lamination of the severely processed side wall is suppressed.

Moreover the bottom of the can has excellent denting resistance.

When the resin film is laminated to the metal substrate, the pattern of the high crystal orientation of the film can be set according to the manufacturing method of the present invention.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:-

1. A laminated sheet consisting of a metal substrate defining parts that are to be highly processed in comparison to parts of the metal substrate that are to be lightly processed, and an oriented thermoplastic resin film laminated on said metal substrate, wherein a degree of crystal orientation of said resin film is varied in a planar direction in order that a highly crystal oriented part of said resin film is set to the lightly processed part of said laminated sheet, and a lightly crystal oriented part of said resin film is set to said highly processed part of said laminated sheet.

2. A laminated sheet for can manufacturing consisting of a metal substrate and an oriented thermoplastic resin film laminated on said metal substrate, wherein a part of the metal substrate which is to be formed into a can bottom is laminated with resin film which is highly crystal oriented.

3. A method of manufacturing the laminated sheet according to claim 1 or 2 including the steps of; heating said metal substrate, putting a highly crystal oriented resin film on said metal substrate, and pressing said resin film and said metal substrate to adhesion by a laminating roll, wherein a means having a prescribed cooling pattern which sets to only said lightly processed part of said laminated sheet is provided, and said metal substrate or said laminated sheet is cooled by said prescribed cooling pattern.

4. The method of claim 3, wherein the low temperature part having said prescribed cooling pattern is provided on a heating roll which heats said metal substrate.

5. The method of claim 3, wherein after being wholly heated said metal substrate is partially cooled by a cooling roll provided with said prescribed cooling pattern.

6. The method of claim 3, wherein the cooling part having said prescribed cooling pattern is provided on the surface of said laminating roll.

7. The method of claim 6, wherein said cooling roll provided with said cooling part is put onto the surface of said laminating roll.

8. The method of claim 3, wherein immediately after pressing said metal substrate and said resin film to adhesion, said laminated sheet is partially cooled by said cooling roll provided with cooling part having said prescribed cooling pattern.

9. A method of manufacturing the laminated sheet according to claim 1 or 2 including the steps of; heating said resin film, then varying the temperature of said resin film in the planar direction by a means having a prescribed cooling pattern, and pressing said resin film and said metal substrate to adhesion by said laminating roll.

10. A method of manufacturing the laminated sheet according to claim 1 or 2 consisting of; heating said resin film, then varying the thickness of said resin film by a means having a prescribed pattern, and pressing said resin film and said metal substrate to adhesion by said laminating roll.

11. A product manufactured from a laminated sheet consisting of metal substrate laminated with an oriented

thermoplastic resin film, wherein lightly crystal oriented resin film is laminated to a part of said metal substrate which is to be heavily processed in said product, and highly crystal oriented resin film is laminated to a part of said metal substrate which is to be lightly processed in said product.

12. A can manufactured from a laminated sheet consisting of metal substrate laminated with an oriented thermoplastic resin film, wherein a degree of crystal orientation of said resin film at a part of the metal substrate corresponding to the can bottom is higher than that at a part of the metal substrate corresponding to the can wall.

13. A forming method of said product according to claim 11 or 12, wherein the processing intensity at the part where said crystal orientation of said resin film is high, is lighter than that at the part where said crystal orientation of said resin film is low.

14. A laminated sheet substantially as herein described with reference to any one of the accompanying drawings.

15. A method of manufacturing the laminated sheet according to claim 1 or claim 2 substantially as herein described with reference to the accompanying drawings.

16. A laminated sheet for can manufacturing substantially as herein described with reference to the accompanying drawings.

DATED this 24th day of October, 1997

TOYO KOHAN CO., LTD.

Attorney: JOHN B. REDFERN
Fellow Institute of Patent Attorneys of Australia
of SHELSTON WATERS

Fig. 1

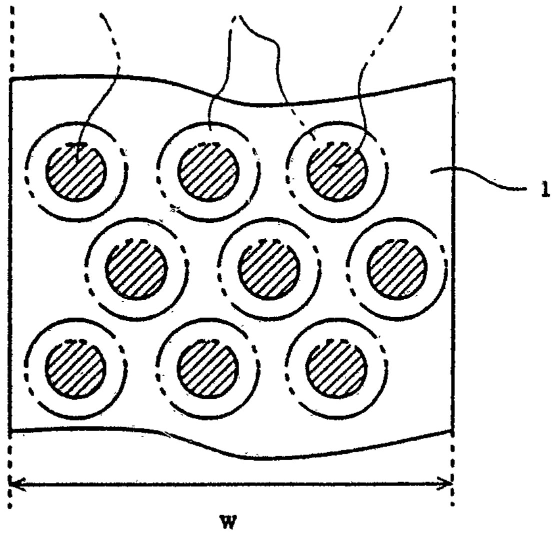


Fig. 2

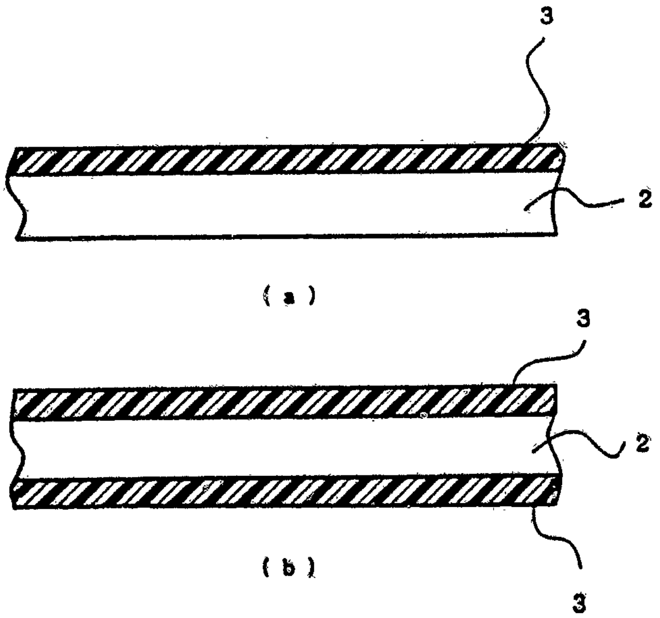


Fig. 3

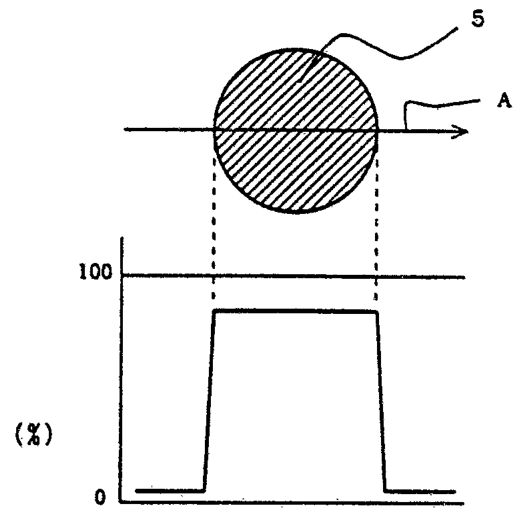


Fig. 4

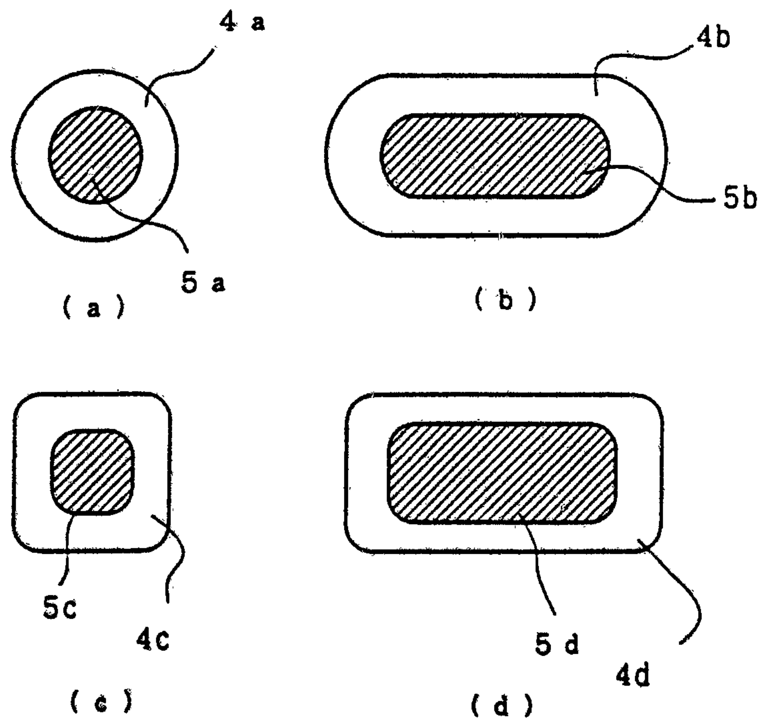


Fig. 5

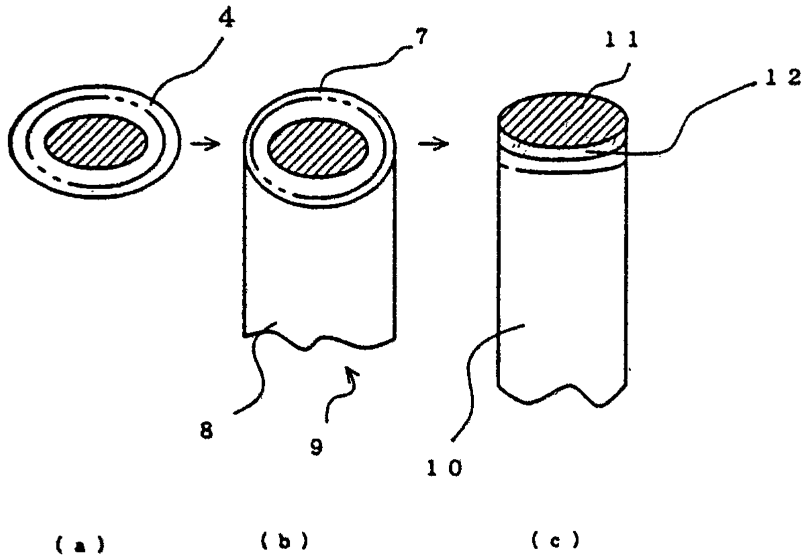


Fig. 6

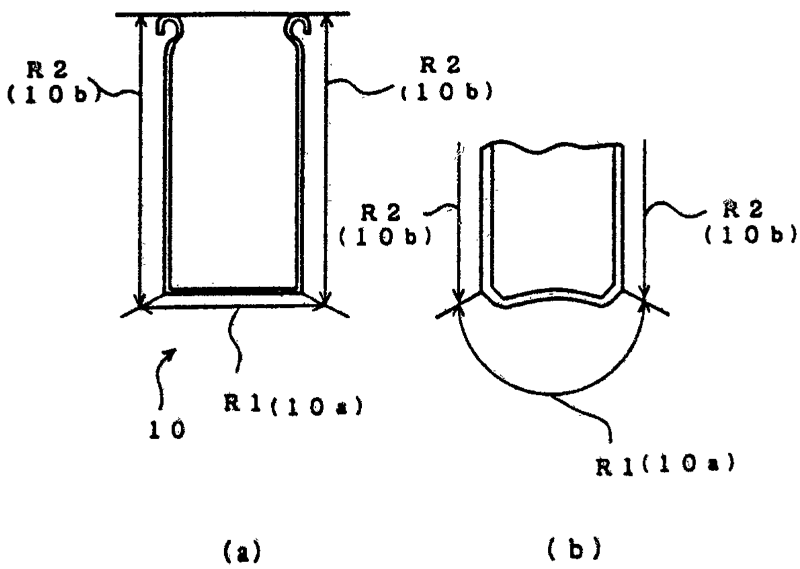


Fig. 7

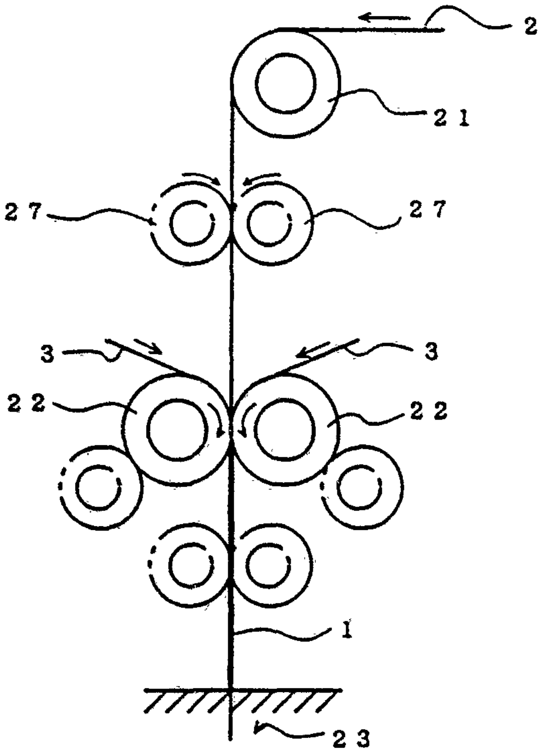
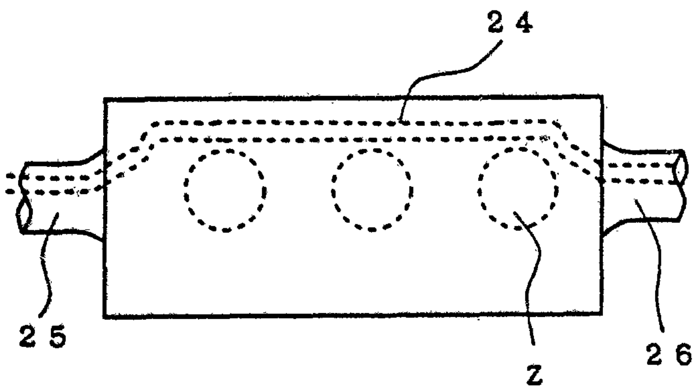
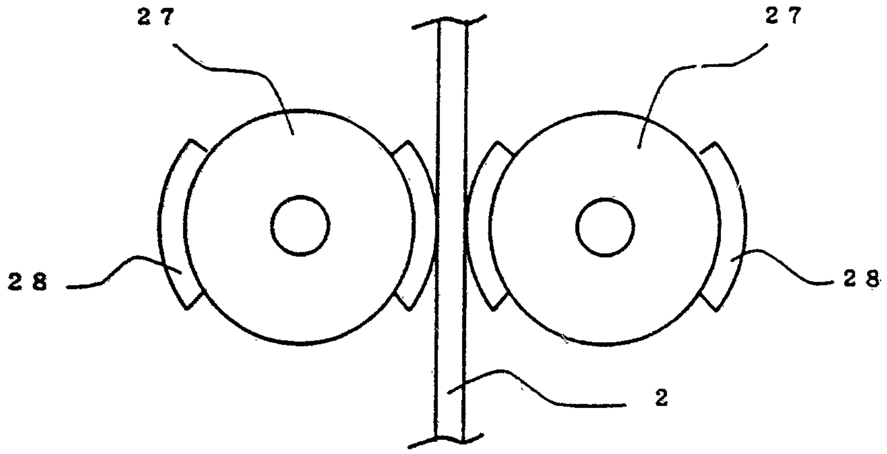


Fig. 8



F i g. 9



F i g. 10

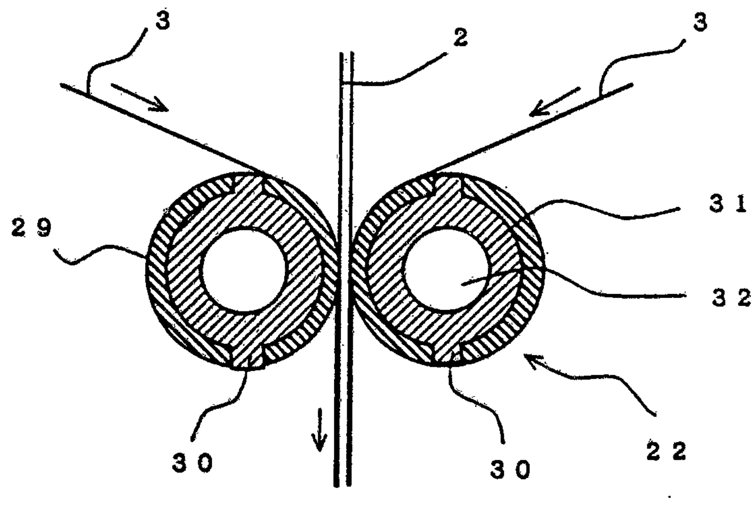


Fig. 11

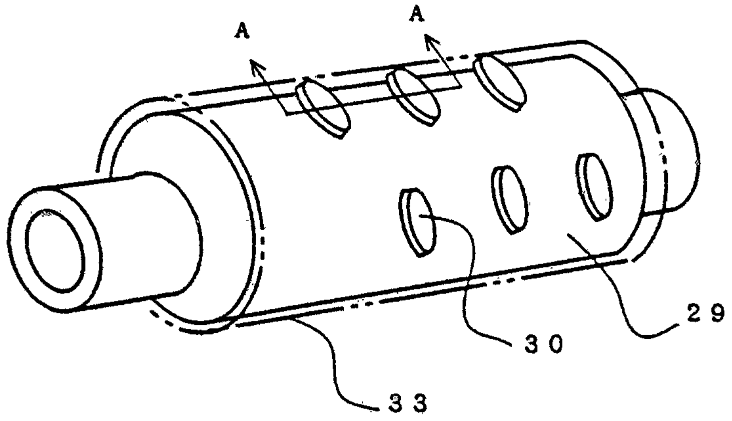


Fig. 12

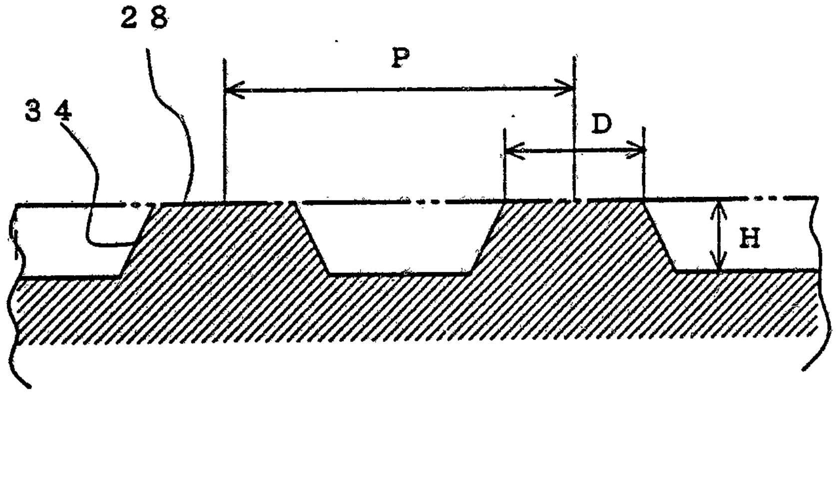


Fig. 13

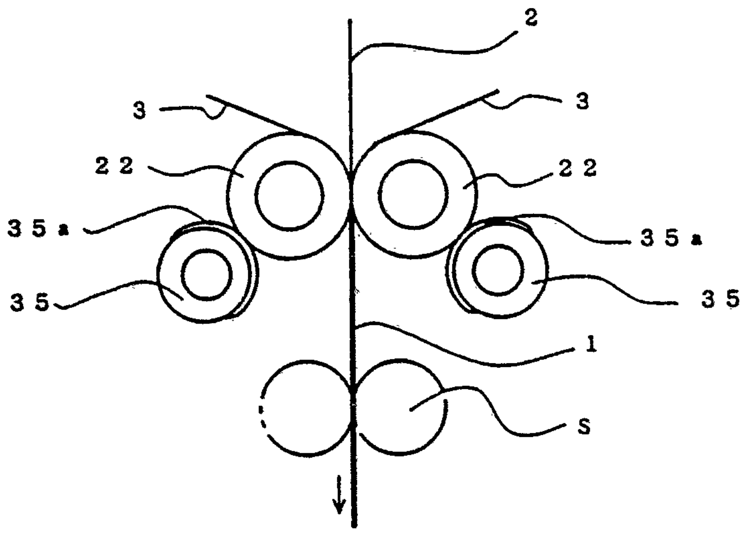


Fig. 14

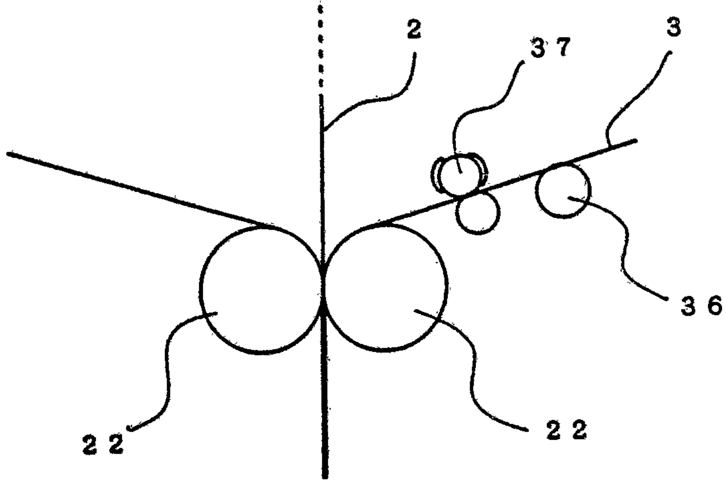


Fig. 15