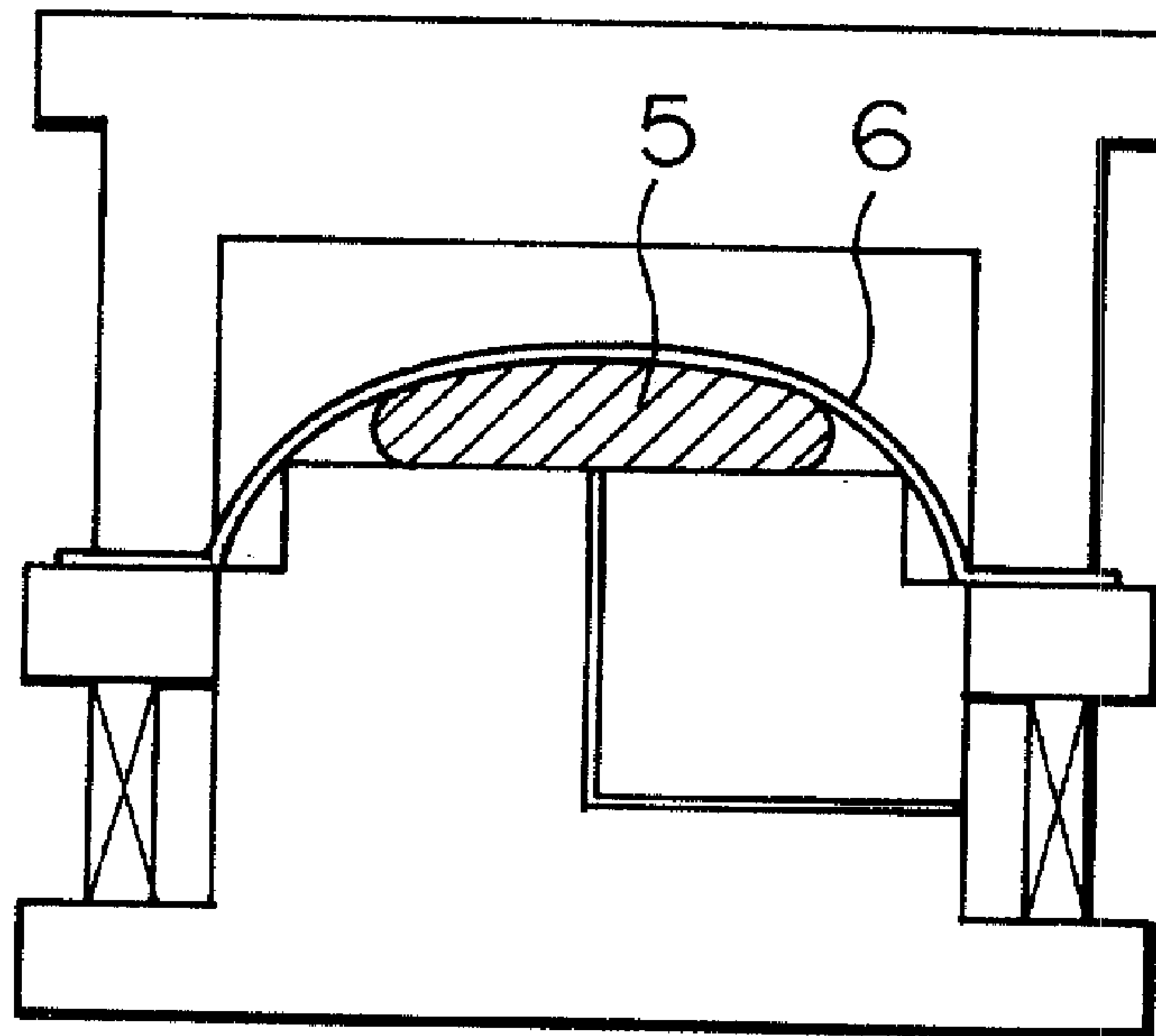




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(72) Inventeurs/Inventors:
Usui, Nobuhiro, JP;
Matsumoto, Masahito, JP;
Higashi, Kenichi, JP;
Harada, Hiroyuki, JP
(73) Propriétaire/Owner:
SUMITOMO CHEMICAL COMPANY, LIMITED, JP
(74) Agent: MARKS & CLERK

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(54) Title: MULTILAYER MOLDED ARTICLES AND PROCESS FOR PRODUCING THE SAME



(57) Abrégé/Abstract:

A multilayer molded article comprising a skin and a substrate consisting of a polypropylene resin composition having a crystallization rate of 45 second or less, said skin being integrally adhered to the substrate. Said multilayer molded article can be produced by feeding a skin material and a molten polypropylene resin composition having a crystallization rate of 45 second or less between a pair of upper and lower molds, molding the molten polypropylene resin composition in the molds with simultaneous adhering of the skin material to the surface of the molded resin composition and then cooling the molten resin composition to solidify the same. Said multilayer molded article has a small deformation degree without the soft feeling of the skin material being impaired.



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ABSTRACT OF THE DISCLOSURE:

A multilayer molded article comprising a skin and a substrate consisting of a polypropylene resin composition having a crystallization rate of 45 second or less, said skin being integrally adhered to the substrate. Said multilayer molded article can be produced by feeding a skin material and a molten polypropylene resin composition having a crystallization rate of 45 second or less between a pair of upper and lower molds, molding the molten polypropylene resin composition in the molds with simultaneous adhering of the skin material to the surface of the molded resin composition and then cooling the molten resin composition to solidify the same. Said multilayer molded article has a small deformation degree without the soft feeling of the skin material being impaired.

1 BACKGROUND OF THE INVENTION

This invention relates to a multilayer molded article comprising a skin and a substrate consisting of a polypropylene resin composition having a specific
5 crystallization rate.

Multilayer molded articles comprising a skin and a substrate consisting of a resin such as polypropylene or the like have been much used in a wide field such as automobile interior parts, household
10 electric appliances and the like from the viewpoint of economy, light weight, and good moldability.

Such multilayer molded articles are produced, as described in, for example, USP 5,154,872, by feeding a molten thermoplastic resin between a pair of male and
15 female molds in which a skin material has already been placed, clamping the two molds to mold the molten resin in the molds and simultaneously adhere the skin material to the surface of the molded resin, and then cooling the molten resin to solidify the same.

20 However, when molded articles are produced by known processes, the resulting multilayer molded articles are sometimes deformed, and this deformation not only makes appearance bad but also causes troubles in the course of production of a final article from the
25 multilayer molded articles, whereby the production

1 efficiency is remarkably affected.

In order to prevent such deformation from being caused, it is effective to apply a sufficient pressure during the clamping of the molds in the molding
5 process and then sufficiently cool the molten resin; however, this process has such problems that it requires a long molding cycle and hence is inferior in productivity, or the soft feeling of the skin material is lost in the resulting molded article. Thus, the above
10 process is not practical.

SUMMARY OF THE INVENTION

Under such circumstances, the present inventors have made extensive research on producing a multilayer molded article, the deformation of which is
15 small, without adversely affecting the productivity and appearance of the product, and have, as a result, found that this object can be achieved by using as a substrate resin a polypropylene resin composition having a crystallization rate not greater than a certain value.

20 In one aspect, this invention provides a multilayer molded article comprising a skin and a substrate consisting of a polypropylene resin composition having a crystallization rate of 45 second or less, said skin being integrally adhered to the surface of the
25 substrate.

In another aspect, this invention provides a process for producing a multilayer molded article

1 comprising a skin and a substrate consisting of a
thermoplastic resin, which process comprises feeding a
skin material and a molten thermoplastic resin as a
substrate material between a pair of upper and lower
5 molds, molding the molten resin in the molds with
simultaneous adhering of the skin material to the sur-
face of the molded resin, and then cooling the molten
resin to solidify the same, characterized in that the
thermoplastic resin is a polypropylene resin composition
10 having a crystallization rate of 45 second or less.

BRIEF DESCRIPTION OF THE DRAWINGS

Figs. 1A to 1C show an outline of a press-
molding apparatus which is an embodiment of producing
the present multilayer molded article and also show the
15 successive steps of the present molding process.

Fig. 2 is a partial view of a multilayer
molded article in which d shows a deformation degree.

DETAILED DESCRIPTION OF THE INVENTION

20 The thermoplastic resin used as a substrate
material in this invention is a polypropylene resin
composition obtained by adding an appropriate amount of
a crystallization rate-controlling agent (referred to
hereinafter as a nucleating agent) to a polypropylene
25 resin such as a conventional propylene homopolymer or
copolymer or a resin composition consisting of the
polypropylene resin, a stabilizer and other compounding

1 agents such as inorganic filler and the like to control
the crystallization rate of the polypropylene resin
composition to 45 second or less, preferably 35 second
or less.

5 In this invention, it is very important to use
a polypropylene resin composition having a crystalliza-
tion rate adjusted to 45 second or less, preferably 35
second or less. When a polypropylene resin composition
having a crystallization rate of more than 45 second is
10 used, the deformation degree of the molded article
obtained is great and the purpose of this invention
cannot be achieved.

The nucleating agent used for controlling the
crystallization rate includes, for example, metal salts
15 of organic acids such as aluminum p-t-butylbenzoate,
sodium bis(4-t-phenyl)phosphate and the like; sorbitol
compounds such as dibenzylidenesorbitol, 1,3,2,4-di-p-
methylbenzylidenesorbitol, 1,3,2,4-di-p-ethylbenzyl-
idenesorbitol and the like. However, any nucleating
20 agent can be used as far as it can adjust the crystal-
lization rate to 45 second or less.

The crystallization rate may be varied depend-
ing upon the kind of nucleating agent, the polypropylene
resin composition used and the like, and hence, the
25 amount of the nucleating agent is appropriately deter-
mined depending upon the various conditions. Thus, the
amount of the nucleating agent is not critical. For
example, when aluminum p-t-butylbenzoate is used as the

1 nucleating agent, it is added so that the proportion of
this compound becomes 0.05-0.3% by weight based on the
weight of the polypropylene resin composition.

The term "crystallization rate" used herein
5 means a value obtained by melting the polypropylene
resin composition, subjecting the same to isothermal
crystallization at 130°C and measuring the time required
for crystallization of 1/2 of the total amount of the
resin to be crystallized by means of a differential
10 scanning calorimeter (DSC).

The polypropylene resin composition used in
this invention is required to have a crystallization
rate of 45 second or less, and moreover, it is suitable
that the polypropylene resin composition has a melt
15 index (MI) of 20 or more, preferably 30 or more, from
the viewpoint of effecting the molding of the molten
resin to form a multilayer molded article at a
relatively low pressure. The upper limit of the melt
index is not critical in relation to deformation;
20 however, it is usually 200, preferably 150 from the
viewpoint of physical properties.

The term "MI" used herein means a value
obtained by measurement according to JIS K7210 (230°C,
2.16 kg).

25 The skin material used in this invention is
not critical, and various materials can be used. It
includes, for example, woven, knit and non-woven fabrics
composed of various starting materials, and sheets and

1 films of thermoplastic resins and thermoplastic elasto-
mers. These may be embossed. The skin material also
includes foams of various resins such as polyolefins,
polyvinyl chloride, polystyrene, polyurethane and the
5 like and rubber foams of cis-1,4-butadiene polymers,
ethylene-propylene copolymer and the like. The above-
mentioned materials may be used alone or in the form of
a laminate of two or more.

In the use of such a skin material, pre-
10 heating or pre-forming may be previously applied thereto
in order to adjust the tensile stress, elongation and
the like.

As far as a polypropylene resin composition
having a crystallization rate of 45 second or less is
15 used as a substrate material, the multilayer molded
article of this invention can be produced by a known,
general molding method for a thermoplastic resin which
comprises feeding a skin material and a molten thermo-
plastic resin between a pair of molds, molding the resin
20 in the molds with simultaneous adhering of the skin
material to the surface of the molded resin, and then
cooling the molten resin to solidify the same, thereby
forming a multilayer molded article consisting of a skin
and a substrate consisting of the thermoplastic resin,
25 such as a press molding method, injection molding method
or the like, and the molding method is not critical.
However, the press molding method is preferred because
substantially no strain or the like is caused.

1 An example of producing the multilayer molded
article of this invention is explained below referring
to Figs. 1A to 1C.

5 The press molding apparatus in this example
consists of a pair of upper mold (1) and lower mold (2),
as shown in Figs. 1A to 1C, and a clamper (3) which can
be moved upward and downward by means of hydraulic
pressure, pneumatic pressure, spring or the like is
arranged about the outer periphery of the lower mold (2)
10 for putting the skin material (6) on the clamper.

 The clamper (3) may be provided at its upper
end with pins (not shown) for controlling the elongation
of the skin material (6), and the control and adjustment
of elongation of the skin material are effected with
15 these pins or by adjusting the power of fastening the
skin material sandwiched in between the upper surface of
the clamper (3) and the lower surface of the peripheral
portion of the upper mold (1).

 The mold surface of the lower mold (2) is
20 provided with an opening (4) for feeding the molten
polypropylene resin composition sent through a resin
path (7). Incidentally, either one or both of the molds
may be provided, if necessary, with a piping for
cooling.

25 An explanation is made below of a specific
production method using the above-mentioned apparatus.

 In the state that the lower mold (2) and the
upper mold (1) are opened, the skin material (6) is put

1 on the upper surface of the clamper (3) (see Fig. 1A),
and the upper mold (1) is allowed to fall down to an
appropriate position as shown in Fig. 1B, after which
the molten polypropylene resin composition (5) is fed
5 between the skin material (6) and the lower mold (2)
from the resin-feeding opening (4) (see Fig. 1B).
While the molten resin is fed, or after the feeding of
the desired amount of the molten resin has been com-
pleted, the upper mold (1) is further allowed to fall
10 down to clamp the molds, whereby the molten polypro-
pylene resin composition (5) is spread in the cavity
formed by the molds and molded and simultaneously
adhered to the skin material (see Fig. 1C). After
cooling, the molds are opened and the molded article is
15 taken out.

By the above method, there can be obtained a
multilayer molded article (9) in which the skin material
(6) has been integrally and firmly adhered to the
surface of the substrate resin (8) consisting of the
20 polypropylene resin composition.

The above-mentioned apparatus and the above-
mentioned production method using the apparatus are
merely an embodiment, and the present invention is not
limited thereto.

25 In the following Examples, % and parts are by
weight unless otherwise specified.

1 Example 1

Preparation of polypropylene resin composition

	Polypropylene block copolymer (ethylene content=8.2%, MI=35)	81.9%
5	Talc (Micronwhite 5000S' manufactured by Hayashi Kasei K.K.)	18.0%
	Aluminum p-t-butylbenzoate	0.1%

To 100 parts by weight of a mixture of the these components were added as stabilizers 0.1 part of Irganox 1010 (phenol type stabilizer manufactured by Geigy) and 0.15 part of Ultrinox 626 (phosphite type antioxidant manufactured by General Electric). The resulting resin mixture was kneaded in a twin-screw kneader and pelletized to form polypropylene resin composition pellets. Incidentally, a small amount of 2,5-dimethyl-2,5-di(t-butylperoxy)hexane was added during the kneading to adjust the MI to 40. The crystallization rate of the polypropylene resin composition was 30.4 second.

20 Preparation of multilayer molded article

Using the press-molding apparatus shown in Figs. 1A to 1C, a multilayer molded article consisting of a skin and a substrate consisting of a polypropylene resin composition was prepared by the following press-molding method:

On the clamper (3) was put a skin material (a

1 laminate consisting of a polypropylene elastomer sheet
having a thickness of 0.5 mm and a polypropylene foam
sheet having a thickness of 3 mm and a foaming magnifi-
cation of 15) so that the foam sheet faced the clamper,
5 and thereafter, the upper mold (1) was allowed to fall
down. The polypropylene resin composition (5) was
previously melted, and the molten polypropylene resin
composition (5) was fed between the skin material (6)
and the lower mold (2) from the resin-feeding opening
10 (4) through the resin path (7).

After the desired amount of the resin had been
fed, the upper mold (1) was further allowed to fall down
to clamp the molds, and thereafter, the molded resin was
cooled.

15 The molds were opened to obtain a box-shaped
multilayer molded article (9) having a length of 2300
mm, a width of 750 mm, a depth of 100 mm and a resin
layer thickness of 3 mm.

The molding conditions were as follows:

20 Molten resin temperature: 200°C
Mold temperature: upper mold, 30°C; lower mold, 35°C
Cooling time under pressure: 40 second

The pressing pressure required for the molding
was 60 kg/cm² of unit area of the molded article
25 obtained.

The deformation degree d of the molded article

1 obtained was 4 mm. Incidentally, the deformation degree
d was evaluated by the difference of the end of the
deformed horizontal wall from its position before the
deformation (see d in Fig. 2) in the cross-section at
5 about the center portion of the molded article obtained.
The smaller the d value, the smaller the deformation
degree.

Example 2

The same procedure as in Example 1 was
10 repeated, except that the MI was adjusted to 20 during
the kneading, to obtain a multilayer molded article.

The deformation degree d of the molded article
obtained was 4 mm and the pressing pressure required for
the molding was 100 kg/cm² of unit area of the molded
15 article.

Example 3

	Polypropylene block copolymer (PD 7035 manufactured by Exxon)	81.8%
	Talc (MP 1250 manufactured by Pfizer)	18.0%
20	Aluminum p-t-butylbenzoate	0.2%

To 100 parts by weight of a mixture of these components
were added as stabilizers 0.1 part of Irganox (phenol
type stabilizer manufactured by Geigy) and 0.15 part of
Ultranox 626 (phosphite type antioxidant manufactured by
25 General Electric), and a small amount of 2,5-dimethyl-

1 2,2-di(t-butylperoxy)hexane was added to the mixture to
adjust the MI to 40. The resulting mixture was kneaded
in a twin-screw kneader and then pelletized to obtain
polypropylene resin composition pellets. The crystal-
5 lization rate of the polypropylene resin composition was
25.8 second.

In the same manner as in Example 1, the poly-
propylene resin composition pellets thus obtained were
subjected to molding treatment to obtain a multilayer
10 molded article.

The deformation degree d of the molded article
was 3 mm and the pressing pressure required for the
molding was 60 kg/cm² of unit area of the molded article
obtained.

15 Example 4

The same procedure as in Example 1 was
repeated, except that a polypropylene block copolymer
having an ethylene content of 4.5% and an MI of 50 was
substituted for the polypropylene resin, to obtain a
20 polypropylene resin composition having an MI of 40.
The crystallization rate of the polypropylene resin
composition obtained was 25.8 second.

In the same manner as in Example 1, the
polypropylene resin composition was subjected to molding
25 treatment to obtain a multilayer molded article.

The deformation degree d of the multilayer
molded article obtained was 2.5 mm, and the pressing

1 pressure required for the molding was 60 kg/cm² of unit
area of the molded article obtained.

Comparative Example 1

5	Polypropylene block copolymer (PD 7035 manufactured by Exxon)	82%
	Talc (Micronwhite 5000S' manufactured by Hayashi Kasei K.K.)	18%

To 100 parts by weight of a mixture of these components
were added as stabilizers 0.1 part of Irganox 1010
10 (phenol type antioxidant manufactured by Geigy) and 0.15
part of Ultrinox 626 manufactured by General Electric),
and a small amount of 2,5-dimethyl-2,5-di(t-butyl-
peroxy)hexane was added to the mixture to adjust the MI
of the mixture to 40. The resulting mixture was kneaded
15 in a twin-screw kneader and then pelletized to obtain
polypropylene resin composition pellets. The crystal-
lization rate of the polypropylene resin composition was
57.6 second.

In the same manner as in Example 1, the poly-
20 propylene resin composition pellets were subjected to
molding treatment to obtain a multilayer molded article.

The deformation degree d of the multilayer
molded article was 7 mm and the pressing pressure
required for the molding was 60 kg/cm² of unit area of
25 the molded article obtained.

1 Comparative Example 2

Polypropylene block copolymer (PD 7035 manufactured by Exxon)	78%
Talc (MP 1250 manufactured by Pfizer)	22%

5 To 100 parts by weight of a mixture of these components
were added as stabilizers 0.1 part of Irganox (phenol
type stabilizer manufactured by Geigy) and 0.15 part of
Ultranox 626 (phosphite type antioxidant manufactured by
General Electric), and a small amount of 2,5-dimethyl-
10 2,5-di(t-butylperoxy)hexane was added to the mixture to
adjust the MI to 40. The resulting mixture was kneaded
in a twin-screw kneader and then pelletized to obtain
polypropylene resin composition pellets. The crystal-
lization rate of the polypropylene resin composition was
15 58.8 second.

In the same manner as in Example 1, the poly-
propylene resin composition pellets were subjected to
molding treatment to obtain a multilayer molded article.

The deformation degree d of the multilayer
20 molded article obtained was 8 mm and the pressing
pressure required for the molding was 60 kg/cm² of unit
area of the molded article obtained.

According to the present invention, a poly-
propylene resin composition having a specific crystal-
25 lization rate is used as the substrate resin, and this
enables one to obtain a multilayer molded article having
a small deformation degree without impairing the soft

1 feeling of the skin material by the known molding method
without any special modification being applied thereto.
Since the deformation degree of the molded article thus
obtained is small, the appearance is good, and final
5 products can be easily obtained using the multilayer
molded article as the starting material.

THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. A multilayer molded article comprising a skin and a substrate consisting of a polypropylene resin composition having a crystallization rate of 45 second or less, said skin being integrally adhered to the surface of the substrate.
2. A multilayer molded article according to Claim 1, wherein the polypropylene resin composition has a melt index of 20 or more.
3. A multilayer molded article according to Claim 1 or 2, wherein the polypropylene resin composition has a crystallization rate of 35 second or less.
4. A multilayer molded article according to Claim 1, 2 or 3, wherein the crystallization rate is a value obtained by melting the polypropylene resin composition, subjecting the polypropylene resin composition to isothermal crystallization at 130°C and measuring the time required for crystallizing 1/2 of the total amount of resin to be crystallized by means of a differential scanning calorimeter.
5. A process for producing a multilayer molded article comprising a skin and a substrate consisting of a thermoplastic resin, which process comprises feeding a skin material and a molten thermoplastic resin between a pair of upper mold and lower mold, molding the molten resin in the molds with simultaneous adhering of the skin material to the surface of the molded resin, and then cooling the molten resin to solidify the same,

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characterized by using a polypropylene resin composition having a crystallization rate of 45 second or less as the thermoplastic resin.

6. A process for producing a multilayer molded article comprising a skin and a substrate of a thermoplastic resin, which process comprises feeding a skin material between an unclosed pair of upper and lower molds, allowing the upper mold to fall down to an appropriate position, feeding a molten thermoplastic resin between the skin material and the lower mold, allowing the upper mold to further fall down while feeding the molten thermoplastic resin or after completion of feeding the predetermined amount of the molten thermoplastic resin, thereby clamping the upper and lower molds to mold the molten thermoplastic resin in the molds and simultaneously adhere the skin material to the surface of the molded resin, and then cooling the molten resin to solidify the same, characterized by using, as the thermoplastic resin, a polypropylene resin composition having a crystallization rate of 45 second or less.

7. A process according to Claim 5 or 6, wherein the polypropylene resin composition has a melt index of 20 or more.

8. A process according to Claim 5, 6 or 7, wherein the polypropylene resin composition has a crystallization rate of 35 second or less.

9. A process according to Claim 5, 6 or 7,

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wherein the crystallization rate is a value obtained by melting the polypropylene resin composition, subjecting the polypropylene resin composition to isothermal crystallization at 130° and measuring the time required for crystallizing 1/2 of the total amount of resin to be crystallized by means of a differential scanning calorimeter.

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FIG. 1A

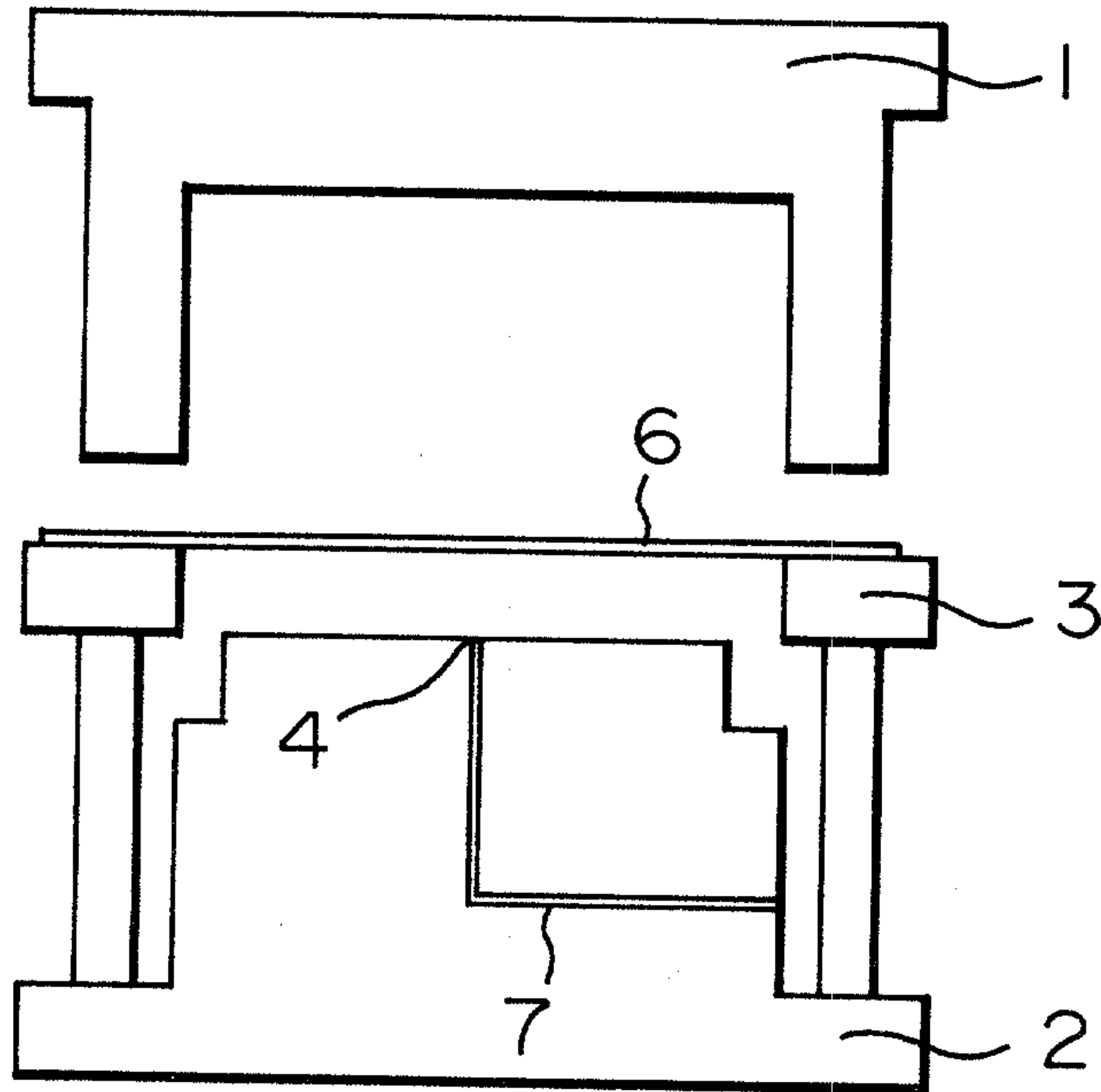
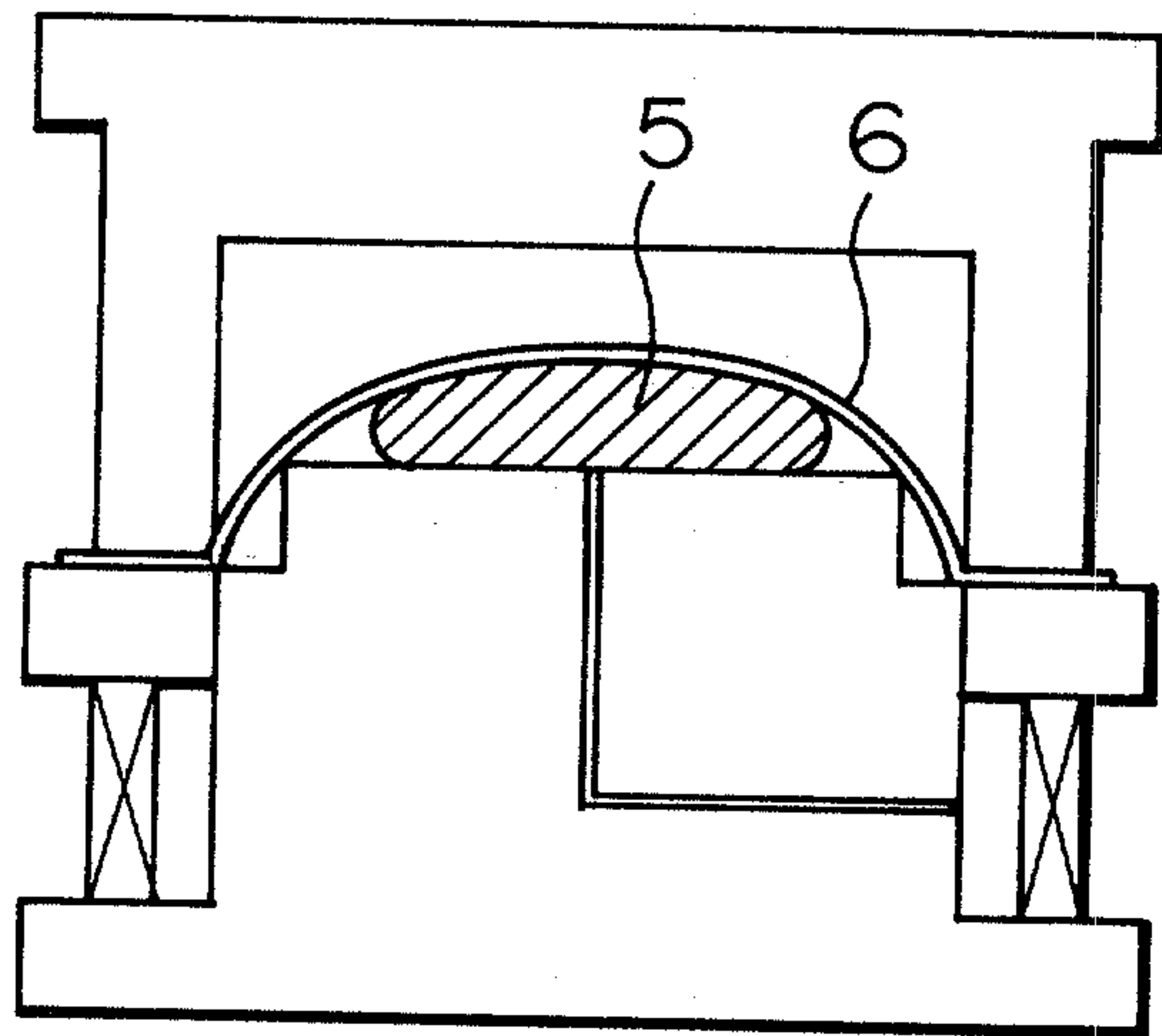


FIG. 1B



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FIG. 1C

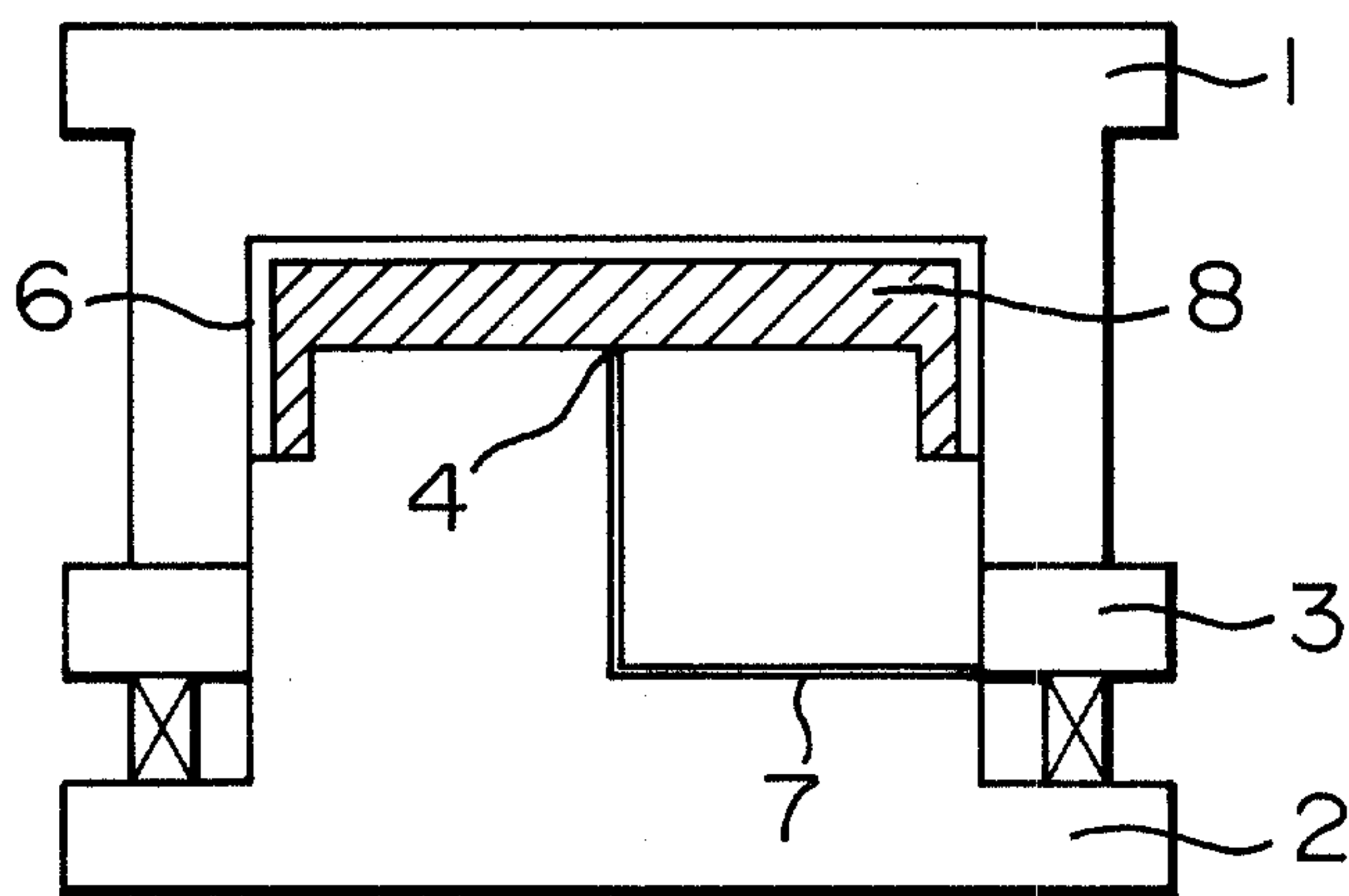


FIG. 2

