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"IMPROVED METHOD OF MANUFACTURING THERMOPLASTIC RESIN FILM
OR SHEET AND APPARATUS THEREFOR"

1 This invention relates to a method of manu-
facturing a thermoplastic resin film or sheet and an
apparatus therefor, and more particularly relates,
in the manufacture of a thermoplastic resin film by
5 use of an inflation film process or T-die cast film
process, to a method of and an apparatus for cooling
wherein a cooling liquid in a form of fine mist generated
by use of an ultrasonic vibrator is used.

 Methods of manufacture of a thermoplastic
10 resin film or sheet include an inflation film process
and a T-die cast film process. In the inflation film
process, in particular, it is a well-known fact that
the method of cooling is very important and ultimately
determines the physical properties, particularly
15 optical properties of the film.

 Linear low density or medium density poly-
ethylene obtained by medium to low pressure polymeriza-
tion has attracted attention in recent years as a
resin which, by virtue of its excellent mechanical
20 strength, makes the reduction of the thickness of the
film possible and consequently contributes to the
conservation of natural resources. However, there is a
problem that a film having good transparency are
not obtained when these resins are processed by use of
25 inflation film process by air cooling which is being

- 1 used for the conventional low density polyethylene
obtained by high pressure polymerization.

In a polypropylene-type resin, there is
also a problem that a film of good transparency is
5 not obtained when the resin is processed by use of
inflation film process by air cooling.

As for a method for obtaining a film of good
transparency from the linear low density or medium
density polyethylene obtained by medium to low pressure
10 polymerization or from the polypropylene-type resin,
there is an already well-known inflation process by
water cooling. In this inflation process by water
cooling, the cooling water is allowed to flow down
along the surface of a resin bubble to contact with and
15 cool the bubble by using jointly a water cooling ring
and an air cooling ring. Since the cooling water is
directly contacted with the bubble in this process,
the bubble is cooled very rapidly and a film having
good transparency is obtained. However, there is a
20 disadvantage in this process that, since the extruder
must be set at a high place and a downward die structure
must be adopted, the apparatus becomes very complicated
and process operation is difficult. There is also
another disadvantage that, since the water drops adhered
25 on the film surface must be removed and dried effect-
ively after water cooling in order to increase the
processing speed, the process is inevitably subjected
to the restriction imposed by the drying step and

- 1 the processing speed cannot be raised sufficiently.

As a process wherein almost the same processing method is employed as that in a simple air cooling process and yet the cooling efficiency can be improved, there is publicly known the one in which the bubble is cooled with a mixed cooling medium comprising a cooling gas and a cooling liquid in a form of mist or droplets (Japanese Patent Application "Kokai" (Laid-open) No. 14,762/1975 and Japanese Patent Publication No. 24,945/1972).

Since the mist in the above process is generated by a method in which the principle of spraying or the venturi effect is applied, there are disadvantages that the particle diameters of the mist or the droplets are large (from several tens to several hundreds μ) and not uniform, and moreover the control of the concentration of the mist in the mixed cooling medium is difficult.

As the result, this process has the disadvantage that, in the processing of a thermoplastic resin by inflation by use of this method, when the mist concentration is increased in order to increase the cooling efficiency, speckled patterns due to uneven cooling appear on the film surface, impairing the optical and mechanical properties of the film. Especially, the process has the disadvantage in that the speckled patterns due to uneven cooling appear markedly particularly in the case of linear low density or medium density polyethylene obtained by medium to low pressure

1 polymerization and polypropylene type resin, and hence
the process is far from being applicable practically.

The present inventors have conducted extensive
studies to overcome these disadvantages and as the
5 result, after noticing the extremely fine particles
generated by an ultrasonic vibrator, found out that a
film can be cooled uniformly and in a high cooling
efficiency and a film showing no uneven cooling and
having excellent optical properties can be obtained by
10 cooling the bubble with a mixed cooling medium such as
air containing a cooling liquid in a form of extremely
fine particles, and that the effect is very remarkable
particularly when the process is applied to linear low
density to medium density polyethylene obtained by medium
15 to low pressure polymerization and polypropylene type
resin. This invention has been accomplished on the
basis of these findings.

Thus, according to the present invention,
in the manufacture of a thermoplastic resin film or
20 sheet, there is provided a method of cooling a
thermoplastic resin film or sheet characterized by
cooling at least one surface of the film or sheet
extruded from a die effectively and uniformly with
a mixed cooling medium comprising a cooling liquid
25 in a form of mist having particle diameters of 10 μ
or less generated by use of an ultrasonic vibrator and
a cooling gas such as air, and there is also provided
an apparatus for cooling a thermoplastic resin film or

1 sheet comprising a mechanism for straightening the flow
of the cooling gas or the mixed cooling medium, a built-
in device for generating mist from a cooling liquid
with an ultrasonic vibrator arranged at the upstream
5 or downstream side of said straightening mechanism,
and a chamber with a slit outlet for mixing uniformly the
cooling liquid generated in the form of mist with a cooling
gas and blowing the mixed cooling medium effectively and
uniformly against the film or sheet of molten thermo-
10 plastic resin.

The first feature of the present invention
is that a thermoplastic resin film or sheet having
excellent optical properties can be obtained with a
simple and basically almost the same apparatus as that
15 used widely in a conventional air cooling process, with-
out using a complicated apparatus as is used in a
water cooling process.

The second feature of the present invention
is that, respecting particularly to linear low density
20 or medium density polyethylene obtained by medium to
low pressure polymerization, a film or sheet having
excellent optical properties can be obtained by applying
this method of cooling whereas a film having good
transparency could not be obtained by the conventional
25 air cooling process.

The third feature of the present invention
is that, when the present method of cooling is applied
with respect to polypropylene type resin in particular,

1 an equally excellent transparency to that obtained by
a water cooling process can be obtained with a simple
and basically almost the same apparatus as that used
widely in a conventional air cooling process, without
5 using a complicated apparatus as is used in a water
cooling process.

The fourth feature of the present invention
is that, because of using the cooling liquid in a form
of mist having very fine and uniform particle size,
10 speckled patterns due to uneven cooling hardly appear
on the surface even when the mist concentration is raised
substantially, and a thermoplastic resin film or sheet
having excellent optical properties can be obtained
without lowering the cooling efficiency even in high
15 speed processing.

The features described above are the advantages
of the present invention as compared with the prior
arts.

The present invention will be described in
20 detail below.

The cooling liquid in a form of mist mentioned
in the present invention is preferably as fine as
possible in size, i.e. in sizes of 10 μ or
less, more preferably 5 μ or less, in terms of a
25 particle diameter. When the particle size is large,
speckled patterns due to uneven cooling are likely to
appear on the film surface. The mist generated by the
use of an ultrasonic vibrator consists, from the principle

1 of generating the mist, of fine particles of sizes of
1 μ or less in general. On the other side, when a
method of spraying or a sprayer-type apparatus is
employed, there is the disadvantage that the particle
5 diameters are not uniform and in a larger size range
of from several tens to several hundreds μ , while, when
a steam method is employed there is the disadvantage that,
though the diameters of mist particles can be made
considerably smaller, the temperature of the mist itself
10 is high.

The concentration of the mist of the cooling
liquid contained in the mixed cooling medium is prefer-
ably 5% by weight or less in the case of air and water
mist. When the concentration is higher than 5%, the
15 film surface tends to be tacky and uneven cooling is
likely to occur. On the other hand, a too low concent-
ration is unfavorable because of the lowering of cooling
efficiency.

As the cooling liquid to be contained in the
20 mixed cooling medium, water is usually used satis-
factorily. But a small amount of a surface active
agent may be added thereto for the purpose of applying
it as an antistatic agent onto the film surface or
preventing the appearance of speckled patterns.

25 The surface active agents that may be used
include various surface active agents such as anionic,
nonionic, cationic and amphoteric ones.

As for the method of blowing the mixed cooling

1 medium containing the cooling liquid in a form of mist,
the cooling gas is mainly blown uniformly against the
bubble surface from an outlet slit arranged along the
inner periphery of a cooling apparatus having a built-in
5 mist generating device. But it is also possible to
provide newly an additional air cooling ring at the
upper or lower position of said cooling apparatus and
to let air flow out at a high speed from the air cooling
ring to induce the cooling gas containing the cooling
10 liquid in a form of mist to flow out by the venturi
effect of high speed flow of air. In this instance, the
outlet slit of the newly provided air cooling ring
and the slit of said cooling apparatus are preferably
placed as closely as possible.

15 As the thermoplastic resin of the present
invention, there should be understood all extrusion
moldable resins such as high and low density polyethylene,
polypropylene, polyvinyl chloride, polystyrene, poly-
amide and polyester.

20 Among these, polypropylene is preferred for
having the advantage that, although it is usually
processed by water cooling inflation, an equally
excellent transparency to that obtained in a water
cooling inflation process can be obtained when the
25 method and apparatus of the present invention are
applied to the processing apparatus by air cooling
inflation conventionally used widely in inflation
processing of polyethylene and the like.

1 The polypropylene type resins which can be
used include various resins such as propylene homo-
polymer, propylene-ethylene random copolymer and
propylene-ethylene block copolymer. Among these,
5 propylene homopolymer and propylene-ethylene random
copolymer are particularly preferred.

The melt index of said polypropylene type
resin is preferably 0.3 to 20 g/10 minutes, and more
preferably 0.5 to 15 g/10 minutes.

10 A melt index of below the lower limit is
unfavorable because the surface of molten resin extruded
from the die tends to be rough, and a film or sheet
having good transparency is hardly obtained.

A melt index of above the upper limit is
15 unfavorable because the melt tension of molten resin
extruded from the die is too small, and stable processing
is difficult.

As the linear low density or medium density
polyethylene obtained by medium to low pressure poly-
20 merization mentioned as a preferable resin in the
present invention, there should be understood an ethylene-
 α -olefin copolymer which is obtained by copolymerizing
ethylene with an α -olefin having 3 to 18 carbon atoms
under a medium to low pressure by use of a transition
25 metal catalyst. The α -olefins which are a component
to be copolymerized with ethylene are compounds re-
presented by the general formula $R-CH=CH_2$ (wherein R
denotes an alkyl group having 1 to 16 carbon atoms) and

1 include, for example, propylene, butene-1, pentene-1,
hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-
methylpentene-1, 4-methylhexene-1, 4,4-dimethylpentene-1,
etc. Among these α -olefins, those having 4 or more
5 carbon atoms are preferred, and particularly butene-1,
pentene-1, hexene-1, octene-1 and 4-methylpentene-1
are preferred from the points of monomer availability,
copolymerizability and the quality of the copolymer
obtained. It is also possible to use two or more of
10 these α -olefins jointly.

The linear low density or medium density
polyethylene to be used in the present invention has
a density of preferably 0.910 to 0.940 g/cm³, and
more preferably 0.915 to 0.935 g/cm³.

15 A density of higher than 0.940 g/cm³ is
unfavorable because a film having good transparency
is not obtained even when the cooling apparatus of
the present invention is employed. A density of lower
than 0.910 g/cm³ is unfavorable because only a tacky
20 film is obtained.

The melt index (MI) of said linear low
density or medium density polyethylene is preferably
0.1 to 5 g/10 minutes, more preferably 0.3 to 4 g/10
minutes, and most preferably 0.5 to 3 g/10 minutes.

25 A melt index of less than 0.1 g/10 minutes
is unfavorable because a rough pattern appears distinct-
ly on the surface of the film when the molten resin
comes out of the die so that no film having good

1 transparency can be obtained.

A melt index of larger than 5 g/10 minutes is unfavorable because the mechanical strength of the film obtained is low.

5 The melt flow ratio (hereinafter abbreviated as MFR), which is a measure to indicate the molecular weight distribution of said linear low density or medium density polyethylene, is preferably 15 to 40, and more preferably 20 to 37.

10 An MFR of less than 15 is unfavorable because the polymerization is practically difficult. An MFR of larger than 40 is unfavorable because a film having good transparency can be hardly obtained.

As to said linear low density or medium
15 density polyethylene, it need not be limited to a pure ethylene- α -olefin copolymer. It may as well be a resin blended with a small amount (about 20% by weight) of a high molecular compound such as a low density polyethylene obtained by high pressure polymerization.
20 It may also be optionally incorporated with various additives conventionally used in the arts such as antioxidant, lubricant, antistatic agent, light stabilizer, antiblocking agent, coloring pigment, etc.

This invention will be illustrated in more
25 detail referring to the drawings in the followings, but it is not limited thereto so long as the scope of the invention is obeyed.

In the attached drawings, Fig. 1 is a

1 longitudinal sectional view illustrating an embodiment of the present invention, the numerical in the figure indicating the following apparatus respectively:

- 1 ... circular die, 2 ... bubble, 3 ... guide plate,
5 4 ... take-off roll, 5 ... cooling apparatus,
6 ... cooling liquid, 7 ... ultrasonic vibrator,
8 ... feed water pipe, 9 ... drain pipe,
10 ... vacant space.

Fig. 2 is a longitudinal sectional view illustrating another embodiment of the present invention, the numerals 1-10 in the figure indicating the same as in Fig. 1 respectively and 11 indicating a control valve for gas flow.

In Fig. 1, the molten thermoplastic resin is extruded upward through a circular extrusion die connected to an extruder (not shown in the figure). The bubble 2, after being quenched with the second air ring, is take off with a take-off unit comprising a guide plate 3 and a take-off roll 4.

20 The cooling apparatus arranged above the circular die 5 is shaped in a ring form along the outer periphery of the bubble 2 and has the following structure: inside the cooling apparatus and near the outlet of a cooling gas such as compressed air, is provided a
25 tank to be filled with a cooling liquid 6 having a large specific heat such as water, several to ten-odd ultrasonic vibrators being arranged along the periphery of a circle at the bottom of said tank. The feed of

1 the cooling liquid 6 is supplied via the feed pipe 8,
and excess liquid is discharged via the drain pipe 9
while said discharge being controlled to keep a proper
liquid level. The fine mist of the cooling liquid
5 generated with the ultrasonic vibrators and having
a particle diameter of about 1μ is mixed uniformly
with a cooling gas supplied under pressure with a
blower and the like, and then blown upwards from the
outlet of a circular ring against the bubble. As for
10 the method of uniform mixing, a vacant space 10 may
be provided or a baffle plate or the like may be
adopted. The blowing angle is not restricted specifical-
ly, but is generally in the range of 45 to 60° up-
wards. There may be provided a mechanism which makes
15 the stepwise or continuous control of the amount of the
mist of the cooling liquid generated possible. For
example, an electric circuit which makes it possible
to change the number of ultrasonic vibrator at work
is incorporated, the amount of mist generated per one
20 vibrator is controlled, or the generated mist is control-
led with a damper or the like before being mixed with
the cooling gas. But the mechanism is not limited to
these examples.

In Figure 1, the cooling gas such as air, supplied
25 under pressure with a blower or the like, is straightened
with a straightening device and then mixed in the vacant
space 10 with the cooling liquid in a form of mist generat-
ed with ultrasonic vibrators and is exhausted from

1 the opening 5a to the outside of the apparatus to be
blown against the outer surface of the running bubble.
In the course of this step, since the cooling liquid
in a form of mist vaporizes while adhering to or
5 colliding against the bubble surface uniformly, the
bubble is cooled very effectively by the latent heat
of vaporization of the cooling liquid.

As the secondary effect, the temperature of
the cooling gas such as air is lowered with the cooling
10 liquid in a form of mist, so that the cooling effect
for the bubble is further increased.

Another example of the embodiment of the
present invention is illustrated in Fig. 2.

In Fig. 2, the explanation for respective
15 unit is almost the same as that in Fig. 1. The only
different point is that the apparatus in Fig. 2 has
a structure such that a control valve 11 for gas flow
is provided and the compressed air can be led to another
route in order to make it possible to control the
20 velocities of the mixed cooling medium accompanied
with generated mist and of the cooling gas at will.

The apparatus thus far described has a
structure of mixing the mist generated with the ultrasonic
vibrator at the downstream side of straightened cooling
25 gas. But the object of the present invention can be
attained also by mixing said mist with a cooling gas
before the cooling gas is straightened.

It is needless to say that the method of

1 cooling a thermoplastic resin film and the apparatus
therefor of the present invention are not limited to
those of the inflation film process described above
concretely, but can be applied also to an air knife
5 in a T-die cast film processing and to all other
cases where a thermoplastic resin film is cooled by
an air cooling method.

By use of the method of cooling and the ap-
paratus therefor of the present invention, a thermo-
10 plastic resin film having excellent optical properties
can be obtained even in higher speed processing with
a simple and basically almost the same apparatus as
that used widely in a conventional air cooling process,
without using a complicated apparatus such as, for
15 example, that for an inflation film process by water
cooling. Particularly when the method and the apparatus
of the present invention are applied to linear low
density or medium density polyethylene obtained by
medium to low pressure polymerization, they give very
20 remarkable effects, so that they have a large economic
advantage in that a film can be obtained in a reduced
thickness while keeping good transparency and strength,
and are of great practical value.

The definitions of physical properties used
25 in the present invention are shown below.

(1) Density: The method specified in JIS-K-6760
is applied.

1 (2) Melt index (MI):

For polyethylene type resin, the method specified in ASTM-D1238 condition E is applied.

5 For polypropylene type resin, the method specified in ASTM-D1238 condition L is applied.

(3) Melt flow ratio (MFR):

10 The $MI_{21.6}$ (indicated by grams per 10 minutes at 190°C and under 21.6 kg load) is first determined according to ASTM-D1238 condition F.

$$\text{Melt flow ratio} = MI_{21.6}/MI$$

(4) Haze:

The method specified in ASTM-D1003 is applied.

15 This invention will be illustrated in more detail referring to Examples, but it is not limited to these Examples so long as its scope is obeyed.

Examples 1 - 4

20 By use of the apparatus shown in Fig. 1 and under the following conditions, a low density ethylene-butene-1 copolymer obtained by medium to low pressure polymerization using a Ziegler type catalyst was subjected to inflation processing to give films as shown in Table 1.

Ethylene-butene-1 copolymer: density = 0.920,

25

MI = 0.8, MFR = 30

- 1 Thickness of film : 40 μ
 Layflat width of film: 170 mm
 B. U. R. (Blow up ratio) : 2.2
 Take-off speed : 8 m/min.
- 5 Take-off unit 5 : refer to Fig. 1
 Die : 50 ϕ mm diameter spiral die

The ethylene-butene-1 copolymer was extruded by use of a 30 mm ϕ extruder under the following conditions: die, 50 mm ϕ spiral die; lip gap, 2.5 mm; processing temperature, 210°C; extrusion rate, 5.6 kg/hour.

The clearance of the outlet slit 5a of the cooling apparatus 5 was 10 mm, and the horizontal distance to the bubble 2 was 20 mm. The bubble 2 was cooled under conditions of the angle of blowing out of the gas from the slit of 60° upwards to the horizontal plane and the velocity of the cooling gas at the slit outlet of 25 - 35 m/second, while varying the content of the mist in the air by varying the generated amount of the mist of the cooling liquid.

20 The position at which the molten resin is crystallized and solidified by cooling (frost line distance : F.L.D.), the transparency of the film and the stability of the bubble were evaluated. The result was as shown in Table 1.

1 Comparative Examples 1 and 2

The inflation processing was conducted under the same conditions as those in Examples 1 - 4 except that the amount of mist generated was different

5 (causing naturally the change in F.L.D.). The result was as shown in Table 1.

Table 1

No.	Velocity of cooling air (m/sec.)	Amount of mist generated (l/Hr)	Position of frost line of bubble (F.L.D.) (mm)	Bubble stability	Appearance of film (gloss and smoothness)	Transparency of film (Haze value shown in parenthesis)
Comparative Example 1	25	0	180	o	o	x (15)
Example 1	25	1	170	o	o	o (9)
Example 2	25	3	150	o	⊙	⊙ (5)
Comparative Example 2	25	5	150	o	some unevenness	⊙ (6)
Example 3	35	3	150	o	o	o (8)
Example 4	35	5	150	o	⊙	⊙ (5)

Note. x : poor; o : good; ⊙ : excellent

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1 Example 5

The inflation processing was conducted under the same conditions as those in Examples 1 - 4 except that Sumitomo Noblen[®] FY4012 (MI = 4, propylene homo-
5 polymer) was employed as the sample resin to obtain a film. The result was as shown in Table 2.

Example 6

The inflation processing was conducted under the same conditions as those in Examples 1 - 4 except
10 that Sumitomo Noblen[®] FA6411 (MI = 6, propylene - ethylene random copolymer, ethylene content 4.5% by weight) was used as the sample resin and the processing temperature was 200°C to obtain a film. The result was as shown in Table 2.

15 Comparative Example 3

The inflation processing was conducted under the same conditions as those in Example 5 except that the amount of mist generated was different (causing naturally the change in F.L.D.). The result was as
20 shown in Table 2.

Comparative Example 4

The inflation processing was conducted under the same conditions as those in Example 6 except that the amount of mist generated was different (causing
25 naturally the change in F.L.D.). The result was as shown in Table 2.

Table 2

No.	Velocity of cooling air (m/sec.)	Amount of mist generated (l/Hr)	Position of frost line of bubble (F.L.D.) (mm)	Bubble stability	Appearance of film (gloss and smoothness)	Transparency of film (Haze value shown in parenthesis)
Example 5	25	3	150	o	o	⊙ (5)
Comparative Example 3	25	0	180	o	o	x (20)
Example 6	25	3	150	o	o	⊙ (4)
Comparative Example 4	25	0	180	o	o	x (15)

Note. x : poor; o : good; ⊙ : excellent

1 From the results shown in Tables 1 and 2,
it can be seen that the cooling effect was improved
when the cooling mist was jointly used properly with
the cooling gas, as compared with that obtained with
5 no joint use. As the result, the transparency and
gloss of the obtained film were also markedly improved.

The mist of the cooling liquid generated with
the ultrasonic vibrator was composed of fine particles
having diameters of about 1 μ . Upon observation of
10 the film obtained, it showed good gloss and trans-
parency and no speckled pattern due to uneven cool-
ing.

Comparative Example 5

Under the same conditions as those in the
15 inflation processing in Comparative Example 1, a water
mist having a particle diameter of about 100 μ was
sprayed by use of a commercially available spray nozzle.
Though the amount of sprayed water was very small, speckled
patterns due to uneven cooling were observed on the film
20 surface and the transparency of the film was poor.



C L A I M S

1. A method of manufacturing a thermoplastic resin film or sheet, which comprises cooling at least one surface of the film or sheet extruded from a die
5. with a mixed cooling medium comprising a cooling liquid in the form of a mist having particle diameters of 10 μ or less and generated by means of an ultrasonic vibrator, and a cooling gas.
2. A method according to claim 1, wherein the
- 10 thermoplastic resin is an ethylene- α -olefin copolymer type resin.
3. A method according to claim 2, wherein the ethylene- α -olefin copolymer type resin is an ethylene-butene-1 copolymer.
- 15 4. A method according to claim 2, wherein the ethylene- α -olefin copolymer type resin is an ethylene-4-methylpentene-1 copolymer.
5. A method according to claim 2, wherein the ethylene- α -olefin copolymer type resin is an ethylene-
- 20 hexene-1 copolymer.
6. A method according to Claim 2, wherein the ethylene- α -olefin copolymer type resin is an ethylene-octene-1 copolymer.
7. A method according to any one of claims 2 to 6,
- 25 wherein the ethylene- α -olefin copolymer type resin has a density of 0.915 to 0.935 g/cm³ and a melt index of 0.3 - 4 g/10 minutes.
8. A method according to claim 1, wherein the

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thermoplastic resin is a polypropylene type resin.

9. A method according to claim 8, wherein the polypropylene type resin is a propylene homopolymer.

10. A method according to claim 8, wherein the polypropylene type resin is a propylene-ethylene random copolymer.

11. A method according to claim 9, 10 or 11 wherein the propylene type resin has a melt index of 0.3 - 20 g/10 minutes.

12. A method according to claim 1 substantially as described in any one of the Examples.

13. A method according to claim 1 substantially as hereinbefore described with reference to either one of the Figures of the accompanying Drawings.

14. An apparatus for cooling a thermoplastic resin film or sheet comprising means for straightening flow of a cooling gas, an ultrasonic vibrator for generating mist from a cooling liquid arranged upstream or downstream of the straightening means, and a chamber with a slit outlet for mixing uniformly the cooling liquid generated in a mist form with the cooling gas and blowing the resulting mixed cooling medium uniformly against a film or sheet of molten thermoplastic resin.

15. An apparatus according to claim 14 substantially as hereinbefore described with reference to either one of the Figures of the accompanying Drawings.
