APPLICATION FOR A STANDARD PATENT

I/We, SUMITOMO CHEMICAL COMPANY, LIMITED

of 15, KITAHAMA-5-Chome,
HIGASHI-KU,
OSAKA, JAPAN

hereby apply for the grant of a standard patent for an invention entitled "IMPROVED METHOD OF MANUFACTURING THERMOPLASTIC RESIN FILM OR SHEET AND APPARATUS THEREFOR" which is described in the accompanying complete specification.

Details of basic application(s):

Number of basic application Name of Convention country in which basic application was filed Date of basic application

97076/81 JAPAN 22nd June, 1981

My/our address for service is care of CLEMENT HACK & CO., Patent Attorneys, 140 William Street, Melbourne, Victoria, 3000, Australia.

DATED this 15th day of June 1982

SUMITOMO CHEMICAL COMPANY, LIMITED

To: The Commissioner of Patents.

PF/App/3/82
DECLARATION IN SUPPORT OF A CONVENTION OR NON-CONVENTION APPLICATION FOR A PATENT OR PATENT OF ADDITION

In support of the application 84923/82 by SUMITOMO CHEMICAL COMPANY, LIMITED.

for a patent for an invention entitled "IMPROVED METHOD OF MANUFACTURING THERMOPLASTIC RESIN FILM OR SHEET AND APPARATUS THEREFOR",

I, Ken ITO, c/o SUMITOMO CHEMICAL COMPANY, LIMITED, of 15, Kitahama-cho, Nishioishii-ku, Osaka, Japan,

do solemnly and sincerely declare as follows:-

1. I am authorised by the abovementioned applicant to make this declaration on its behalf.

2. The basic application(s) as defined by Section 141 of the Act was/were made in the following country or countries on the following date(s) by the following applicant(s) namely:-

   Country, filing date and name of Applicant(s)

   in Japan on June 22, 1981
   by SUMITOMO CHEMICAL COMPANY, LIMITED

3. The said basic application(s) was/were the first application(s) made in a Convention country in respect of the invention the subject of the application

4. The actual inventor(s) of the said invention are:
   Nobuo FUKUSHIMA, Shuji KITAMURA, Kiyohiko NAKAE, Tadatoshi OGAWA, Kozo KOTANI and Hidekazu HOSONO.
   (Addresses on Reverse)

5. The facts upon which the applicant is entitled to make this application are as follows:-
   The said applicant SUMITOMO CHEMICAL COMPANY, LIMITED is the assignee of the said actual inventors.

DECLARED at Osaka this 30th day of May, 1985.

SIGNED at

REPRESENTATIVE DIRECTOR

This form may be completed and filed after the filing of a patent application but the form must not be signed until after it has been completely filled in as indicated by the marginal notes. The place and date of signing must be filled in. Company stamps or seals should not be used.

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

1 the process
Nobuo FUKUSHIMA, of 4396-14, Sakamotohonmachi, Ootsu-shi, Japan
Shuji KITAMURA, of 7-3, Funakicho, Ibaraki-shi, Japan
Kiyohiko NAKAE, of 4-2-305, Ryoodocho, Nishinomiya-shi, Japan
Tadatoshi OGAWA, of 1-1-730, Chiyodacho, Takatsuki-shi, Japan
Kozo KOTANI, of 6-8, Shiroymacho-1-chome, Toyonaka-shi, Japan
Hidekazu HOSONO, of 10-3-335, Sonehigashinocho-2-chome, Toyonaka-shi, Japan.

The processing speed cannot be raised sufficiently.

As a process wherein almost the same proces-
1. A method of manufacturing a thermoplastic resin film or sheet, characterized by cooling at least one surface of the film or sheet extruded from a die with a mixed cooling medium comprising a cooling liquid in a form of mist having particle diameters of ≤ 1 μm or less and generated by use of an ultrasonic vibrator and a cooling gas.

1. The cooling liquid 6 is supplied via the feed pipe 8, and excess liquid is discharged via the drain pipe 9.
The following statement is a full description of this invention, including the best method of performing it known to me:

1. Cooling a blowing opening 5a to the outside of the apparatus to be blown against the outer surface of the running bubble.
This invention relates to a method of manufacturing a thermoplastic resin film or sheet and an apparatus therefor, and more particularly relates, in the manufacture of a thermoplastic resin film by 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 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 optical properties of the film.

Linear low density or medium density polyethylene obtained by medium to low pressure polymerization has attracted attention in recent years as a resin which, by virtue of its excellent mechanical 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 inflation film process by air cooling which is being
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 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 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 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 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 on the film surface must be removed and dried effectively after water cooling in order to increase the processing speed, the process is inevitably subjected
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
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 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 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 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 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 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
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 or downstream side of said straightening mechanism, and a slit part 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 thermoplastic 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 used widely in a conventional air cooling process, without 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 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 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 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, 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 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 detail below.

The cooling liquid in a form of mist mentioned in the present invention is preferably as fine as possible in size, and preferably in sizes of 10 μ or less, more preferably 5 μ or less, in terms of a 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
of generating the mist, of fine particles of sizes of 1 \( \mu \) 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 diameters are not uniform and in a larger size range of from several tens to several hundreds \( \mu \), 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 is high.

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

As the cooling liquid to be contained in the mixed cooling medium, water is usually used satisfactorily. 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.

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
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 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 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.

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, polyamide and polyester.

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 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.
The polypropylene type resins which can be used include various resins such as propylene homopolymer, propylene-ethylene random copolymer and propylene-ethylene block copolymer. Among these, 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.

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 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 polymerization 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 metal catalyst. The α-olefins which are a component to be copolymerized with ethylene are compounds represented by the general formula R-CH=CH₂ (wherein R denotes an alkyl group having 1 to 16 carbon atoms) and...
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 a-olefins, those having 4 or more 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 these a-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. 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 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. A melt index of less than 0.1 g/10 minutes is unfavorable because a rough pattern appears distinctly on the surface of the film when the molten resin comes out of the die so that no film having good
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.

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.

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 density polyethylene, it need not be limited to a pure ethylene-a-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.

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 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 numericals in the figure indicating the following apparatus respectively:

1 ... circular die, 2 ... bubble, 3 ... guide plate,
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 numericals 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.

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 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
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 fire mist of the cooling liquid generated with the ultrasonic vibrators and having a particle diameter of about 1 micron 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 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 specifically, but is generally in the range of 45 to 60° upwards. There may be provided a mechanism which makes 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 vibrator is controlled, or the generated mist is controlled with a damper or the like before being mixed with the cooling gas. But the mechanism is not limited to these examples.

The cooling gas such as air supplied 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 generated with ultrasonic vibrators and is exhausted from

- 14 -
The following statement is a full description of this invention, including the best method of performing it known to me:

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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 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 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 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 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 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
Cooling a thermoplastic resin film and the apparatus thereof 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 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 apparatus thereof of the present invention, a thermoplastic 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 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 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 in the present invention are shown below.

(1) Density: The method specified in JIS-K-6760 is applied.
to the restriction imposed by the drying step and

1  (2) Melt index (MI):
   For polyethylene type resin, the method
   specified in ASTM-D1238 condition E is
   applied.
   For polypropylene type resin, the method
   specified in ASTM-D1238 condition L is applied.

5  (3) Melt flow ratio (MFR):
   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.
   Melt flow ratio = \frac{\text{MI}_{21.6}}{\text{MI}}

10 (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

By use of the apparatus shown in Fig. 1 and
20 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
The ethylene-butene-1 copolymer was extruded by use of a 30 mmø extruder under the following conditions: die, 50 mmø 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.

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.
Comparative Examples 1 and 4

The inflation processing was conducted under the same conditions as those in Examples 1 - 4 except that the amount of mist generated was different (causing naturally the change in F.L.D.). The result was as shown in Table 1.
<table>
<thead>
<tr>
<th>No.</th>
<th>Velocity of cooling air (m/sec.)</th>
<th>Amount of mist generated (l/Hr)</th>
<th>Position of frost line of bubble (F.L.D.) (mm)</th>
<th>Bubble stability</th>
<th>Appearance of film (gloss and smoothness)</th>
<th>Transparency of film (Haze value shown in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Comparative Example 1</td>
<td>25</td>
<td>0</td>
<td>180</td>
<td>o</td>
<td>o</td>
<td>× (15)</td>
</tr>
<tr>
<td>Example 1</td>
<td>25</td>
<td>1</td>
<td>170</td>
<td>o</td>
<td>o</td>
<td>o (9)</td>
</tr>
<tr>
<td>Example 2</td>
<td>25</td>
<td>3</td>
<td>150</td>
<td>o</td>
<td>○</td>
<td>○ (5)</td>
</tr>
<tr>
<td>Comparative Example 2</td>
<td>25</td>
<td>5</td>
<td>150</td>
<td>o</td>
<td>some unevenness</td>
<td>○ (6)</td>
</tr>
<tr>
<td>Example 3</td>
<td>35</td>
<td>3</td>
<td>150</td>
<td>o</td>
<td>o</td>
<td>o (8)</td>
</tr>
<tr>
<td>Example 4</td>
<td>35</td>
<td>5</td>
<td>150</td>
<td>o</td>
<td>○</td>
<td>○ (5)</td>
</tr>
</tbody>
</table>

Note. ×: poor; ○: good; ○: excellent
appear on the film surface. The mist generated by the use of an ultrasonic vibrator consists, from the principle nonionic,

Table 1

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

Note. x: poor; ○: good; ◎: excellent
<table>
<thead>
<tr>
<th>Appearance of film (gloss and smoothness)</th>
<th>Transparency of film (Haze value shown in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>o</td>
<td>× (15)</td>
</tr>
<tr>
<td>o</td>
<td>o (9)</td>
</tr>
<tr>
<td>o</td>
<td>o (5)</td>
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<tr>
<td>some uneveness</td>
<td>o (6)</td>
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<tr>
<td>o</td>
<td>o (8)</td>
</tr>
<tr>
<td>o</td>
<td>o (5)</td>
</tr>
</tbody>
</table>
applied to the processing apparatus by air cooling inflation conventionally used widely in inflation processing of polyethylene and the like.

1 Example 5

The inflation processing was conducted under the same conditions as those in Examples 1 - 4 except that Sumitomo Nobel® FY4012 (MI = 4, propylene homo-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 that Sumitomo Nobel® 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.

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 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 naturally the change in F.L.D.). The result was as shown in Table 2.
Table 2

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

Note. x: poor; o: good; ☝: excellent
is unfavorable because a rough pattern appears distinctly on the surface of the film when the molten resin comes out of the die so that no film having good

Table 2

<table>
<thead>
<tr>
<th>No.</th>
<th>Velocity of cooling air (m/sec.)</th>
<th>Amount of mist generated (l/Hr)</th>
<th>Position of frost line of bubble (P.L.D.) (mm)</th>
<th>Bubble stability</th>
<th>Appearance of film (gloss and smoothness)</th>
<th>Transparency of film (Haze value shown in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Example 5</td>
<td>25</td>
<td>3</td>
<td>150</td>
<td>○</td>
<td>○</td>
<td>☀ (5)</td>
</tr>
<tr>
<td>Comparative Example 3</td>
<td>25</td>
<td>0</td>
<td>160</td>
<td>○</td>
<td>○</td>
<td>× (20)</td>
</tr>
<tr>
<td>Example 6</td>
<td>25</td>
<td>3</td>
<td>150</td>
<td>○</td>
<td>○</td>
<td>☀ (4)</td>
</tr>
<tr>
<td>Comparative Example 4</td>
<td>25</td>
<td>0</td>
<td>180</td>
<td>○</td>
<td>○</td>
<td>× (15)</td>
</tr>
</tbody>
</table>

Note. × : poor; ○ : good; ☀ : excellent
but it is not limited thereto so long as the scope of the invention is obeyed.

In the attached drawings, Fig. 1 is a

<table>
<thead>
<tr>
<th>Reference (and mass)</th>
<th>Transparency of film (Haze value shown in parenthesis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>@</td>
<td>(5)</td>
</tr>
<tr>
<td>x</td>
<td>(20)</td>
</tr>
<tr>
<td>©</td>
<td>(4)</td>
</tr>
<tr>
<td>x</td>
<td>(15)</td>
</tr>
</tbody>
</table>
tank to be filled with a cooling liquid 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

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 no joint use. As the result, the transparency and gloss of the obtained film were also markedly improved.

The mist of the coding liquid generated with the ultrasonic vibrator was composed of fine particles having a sizes of about 10 μm. Upon observation of the film, it showed good gloss and transparency and no speckled pattern due to uneven cooling.

Comparative Example 5

Under the same conditions as those in the inflation processing in Comparative Example 1, a water mist having a particle diameter of about 100 μm 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 surface and the transparency of the film was poor.
ed with ultrasonic vibrators and is exhausted from

- 14 -

THE CLAIMS

1. A resin film on one surface with a mixed in a form of less and get a cooling gas.
2. The thermoplastic type resin.
3. The ethylene-1-ol butene-1 copo.
4. The ethylene-1-ol methylpentene.
5. The ethylene-1-ol hexene-1 copo.
6. The the ethylene-ethylene-oct.
7. The the ethylene-density of 0.3 - 4 g/100
8. The
THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A method of manufacturing a thermoplastic resin film or sheet, characterized by cooling at least one surface of the film or sheet extruded from a die with a mixed cooling medium comprising a cooling liquid in a form of mist having particle diameters of 10 or less and generated by use of an ultrasonic vibrator and a cooling gas.

2. The method according to Claim 1, wherein the thermoplastic resin is an ethylene-a-olefin copolymer type resin.

3. The method according to Claim 2, wherein the ethylene-a-olefin copolymer type resin is an ethylene-butene-1 copolymer.

4. The method according to Claim 2, wherein the ethylene-a-olefin copolymer type resin is an ethylene-4-methylpentene-1 copolymer.

5. The method according to Claim 2, wherein the ethylene-a-olefin copolymer type resin is an ethylene-hexene-1 copolymer.

6. The method according to Claim 2, wherein the ethylene-a-olefin copolymer type resin is an ethylene-octene-1 copolymer.

7. The method according to Claim 2, wherein the ethylene-a-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. The method according to Claim 1, wherein the
thermoplastic resin is a polypropylene type resin.

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

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

11. The method according to Claim 9, wherein the propylene homopolymer has a melt index of 0.3 - 20g/10 minutes.

12. The method according to Claim 10, wherein the propylene-ethylene random copolymer has a melt index of 0.3 - 20g/10 minutes.

13. In an apparatus for cooling molten thermoplastic resin film or sheet comprising a mechanism for straightening the flow of the cooling gas, a built-in device for generating mist from a cooling liquid arranged at the upstream or downstream side of said straightening mechanism, and a slit part for mixing uniformly the cooling liquid generated in a mist form with a cooling gas and blowing the mixed cooling medium effectively and uniformly against the film or sheet of molten thermoplastic resin, the improvement wherein the cooling liquid is generated in a mist form by an ultrasonic vibrator.

DATED this 2nd DAY of August 1985

SUMITOMO CHEMICAL COMPANY, LIMITED
By Its Patent Attorneys

CLEMMENT HACK & CO.