

# PATENT SPECIFICATION

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## (54) OLEFIN POLYMERIZATION,

(71) We, NIPPON OIL COMPANY, LIMITED, of No. 3—12 1 - chome, Nishi-Shimbashi, Minato-ku, Tokyo, Japan, a Japanese Company, do hereby declare the invention for which we pray that a patent may be granted to us and the method by which it is to be performed to be particularly described in and by the following statement:—

The invention relates to a process of preparing polyolefins having widely distributed molecular weights, employing Ziegler-type catalysts comprising a transition metal compound supported on a solid carrier and an organometallic compound.

According to the invention, an olefin is polymerized in the presence of a solvent and a Ziegler-type catalyst comprising a transition metal compound supported on a solid carrier and an organometallic compound, the olefin polymerization being effected in a first stage under pressure either in a liquid phase with virtually no gas phase present or with a gas phase containing an inert gas present, the polymerization mixture containing high molecular weight polymer particles dispersed in the solvent being continuously transferred from the first stage to a second stage at a pressure lower than the first stage by the pressure difference, and the olefin polymerization being effected in the second stage in the presence of a gas phase containing olefin and hydrogen for forming polymers having molecular weights lower than the polymers formed in the first stage.

In the first stage, the polymerization can be readily controlled, for instance the heat of reaction can easily be removed as the

reaction takes place even when the concentration of hydrogen is low and the concentration of the monomers also is relatively low. The internal pressure in the first stage may be maintained at a sufficiently high pressure to make it possible conveniently to transfer the reaction mixture to the second stage without using any forced transfer means.

We have also found that the environmental stress cracking resistance and the impact strength of the resulting polymers are remarkably improved when one or more olefin comonomers is supplied to the first stage. It is surprising that these properties are not improved if the comonomers are introduced only into the second stage. The olefin comonomers may be present in the second and any subsequent stages, and if so they decrease the density of the polyolefins produced.

The production ratio between the high molecular weight polymers and the low molecular weight polymers may be accurately controlled within a wide range, and the distribution range of each of the prepared polyolefins may be varied as desired. It is not necessary to use a small polymerization reactor in the first stage so that the reaction mixture may be kept therein for a residence time long enough to form polymers with good reproducibility. The process of the invention can be a continuous process comprising the first stage of forming relatively high molecular weight polymers and a second stage of forming relatively low molecular weight polymers, so the resulting polymer mixture need not contain any gel, and uniform moulded articles can be made therefrom.

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Polyolefins having particularly good workability due to flow characteristics and physical properties can be produced when copolymers of two or more olefins are formed in the first stage wherein the reaction for forming high molecular weight polymers takes place. The invention can be performed in an apparatus as schematically described with reference to the drawings in which:

Figure 1 is a flow diagram of the process having the first stage with virtually no gas phase present; and

Figure 2 is a similar flow diagram in which the first stage is effected in the presence of an inert gas; similar parts being denoted by the same reference numerals as in Figure 1.

In Figures 1 and 2, an upstanding agitating vessel 1 is provided with an agitator 8. When an upstanding agitating vessel is used, the ratio of its height to diameter is generally from 1 to 10, preferably from 1.5 to 5. A pressure vessel having a diameter generally of from 0.5 to 10 m, preferably from 1 to 5 m, may be used. Reactors of other types, such as tubular reactors and recirculating mixer reactors may alternatively be used. A crude olefin in a gaseous or liquid form is fed through a line 3 to the reaction vessel 1. Suitable olefins include those having from 2 to 6 carbon atoms, preferably ethylene, propylene, and butene - 1. A main monomer and an olefin comonomer may be fed through the line 3 in to the reaction vessel 1 in gaseous or liquid form. The olefin comonomer may alternatively be fed separately through another line (not shown) to the vessel.

A single olefin such as ethylene or propylene may be used as the main olefin monomer, ethylene being most preferred. Examples of olefin comonomers have 2 to 8 carbon atoms, such as ethylene, propylene, butene-1, pentene 1, 4 - methylpentene - 1, hexene - 1, heptene - 1 and octene - 1, and preferably from 3 to 6 carbon atoms. It is preferred to feed the comonomer to the first stage reaction vessel 1 in a ratio of 0.1 to 10 mol% of the main monomer. A single or a plurality of comonomers may be used. In order to improve the properties of the polyolefins prepared, a diolefin such as butadiene, isoprene, piperylene, 1,4 - hexadiene or 5 - ethylidene - norbornene may be added in an amount of 1/10 mol % based on the other olefins. The term "polyolefin" herein includes all such olefin polymers.

A liquid polymerization reaction medium is fed through a line 6. Generally usable liquid reaction media are inert organic liquids for example hydrocarbons having 3 to 20 carbon atoms including aliphatic, aromatic and alicyclic hydrocarbons, representative examples being butane,

pentane, hexane, heptane, benzene, toluene and cyclohexane. A small amount of hydrogen is fed through a line 4, if desired.

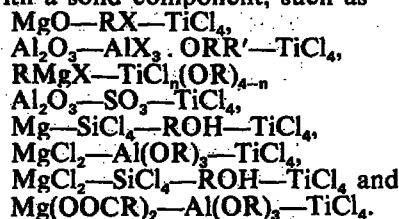
Relatively high molecular weight polymers are formed in the first stage and thus the polymerization in the first stage may be effected without feeding hydrogen thereto. However, a small amount of hydrogen may be fed to the first stage, if required, so as to let the concentration of hydrogen in the first stage be about three quarters or less, for example from one half of one fiftieth, of that in the second stage. The polymerization in first stage reaction vessel 1 is effected generally at from 30 to 100°C, preferably at 40 to 95°C, at a pressure generally of from 2 to 100 kg/cm<sup>2</sup>, preferably from 6 to 70 kg/cm<sup>2</sup>. The pressure in the first stage reaction vessel 1 may be maintained higher than that in the second stage agitating vessel 2 by 10 kg/cm<sup>2</sup> or less, preferably by from 5 to 0.1 kg/cm<sup>2</sup>. The concentration of monomers (in the liquid phase) in the first stage reaction vessel 1 may be from 5 to 200% of that (in the liquid phase) in the second stage agitating vessel 2. It is preferred to keep the concentration of monomers in the first stage within the range of from 20 to 100% of that in the second stage reaction vessel 2, i.e. the monomer concentration in the first stage reaction vessel is preferably kept not higher than that in the second stage reaction vessel.

In the system shown in Figure 2, an inert gas is introduced through a tube 4a. In either Figure 1 or Figure 2, the fed monomers and any hydrogen present are dissolved in the reaction medium. The polymer particles formed are dispersed in the solvent.

In Figure 2, the polymerization reaction proceeds under the condition in which an inert gas monomers and optionally a small amount of hydrogen are present in the gas phase. The concentration of the inert gas in the gas phase may from 20 to 99 mol%, preferably from 40 to 99 mol%, and most preferably from 60 to 99 mol%. If the concentration of the inert gas is too low, the concentration of monomers becomes too high. As the inert gas, there may be used nitrogen, helium, neon, argon and methane; nitrogen being the most preferred.

Catalyst is fed through a line 5. In general, the catalyst may be fed to the reaction vessel mixed with and dispersed in the solvent. The catalyst comprises a solid component and an organometallic compound of a metal of Group I-IV of the Periodic Table, preferably with an organoaluminium or organozinc compound, and has the catalytic activity generally higher than 50, preferably higher than 100 g. polymer/g. catalyst. h: olefin-pressure (kg per cm<sup>2</sup>). The solid component comprises a

solid carrier and a transition metal compound supported on the carrier. Substances which may be used as the solid carrier include metallic magnesium, magnesium hydroxide, magnesium carbonate, magnesium oxide, various alminas, silica, silica-alumina and magnesium chloride; double salts, double oxides, hydrated carbonate and hydrated silicates of magnesium, silicon, aluminium or calcium; and those obtained by treating or reacting the substances stated above with an oxygen-containing compound, a sulphur-containing compound, a hydrocarbon or a halogen-containing compound. As the transition metal compound which is supported on the solid carrier, there may be mentioned halides, alkoxy halides, oxides and halogenated oxides of Ti, V, Zr and Cr. Specific examples of such catalysts are those prepared by combining an organoaluminium or organozinc compound with a solid component, such as



A portion or all of said organometallic compound may be directly fed to the reaction vessel through another feeding line dissolved in a solvent separately rather than combined with the solid component.

A jacket is provided around the wall of the first stage reaction vessel for passing a cooling medium therethrough. A cooler 10 is mounted in line with a recirculation passage for the polymerization reaction mixture. The heat of reaction may be removed either by flowing a cooling medium through the jacket or by recirculating the reaction mixture through the cooler 10, or both measure may be taken. The first stage reaction vessel 1 as shown is a single reactor, but a plurality of reactors (not shown), which are operated under substantially the same conditions, may be connected in series with one another.

The polymerization reaction mixture from the first stage reaction vessel 1 is continuously transferred through a line 11 to the second stage agitating vessel 2 provided with an agitator 9 by the pressure difference without using any forced transfer means such as a pump. Since no forced transfer means is used, there is almost no danger of fouling or blockage.

The process of the present invention can be operated continuously without virtually separating any portion of the components of the polymerization

mixture. This has an advantage of eliminating a separating operation of handling a pressurized mixture which contains polymers and which tends to cause fouling. Hydrogen and additional monomers are supplied, respectively, through a line 7 and a line 12, to the polymerization reaction mixture delivered to the second stage agitating vessel 2, and the polymerization is thus effected continuously. Hydrogen is fed in an amount such that the concentration of  $\text{H}_2$  in the gas phase is generally in the range of from 30 to 95 mol%, preferably from 40 to 90 mol%.

The concentration of the monomer in the gas phase contained in the second stage agitating vessel 2 may be varied from 5 to 70 mol%, preferably from 10 to 60 mol%, and the concentration of the monomer in the liquid phase is correspondingly determined depending upon the polymerization temperature and pressure and the kind of the monomer used.

Where copolymerization is effected in the first stage agitating vessel, an additional amount of a comonomer may be fed through the line 7 of another line (not shown). The amount of the added comonomer may be varied such that the molar ratio thereof is from 0.1 to 10 mol% per mol of the main monomer contained in the second stage agitating vessel.

An additional catalyst may be fed through a line 13, as required. The second stage vessel 2 may be similar in shape to the one employed as the first stage reactor. The temperature of the second stage agitating vessel is kept generally at from 50 to 100°C, preferably 60 to 95°C. The heat of polymerization reaction is removed by a cooler 14. Cooling may alternatively be effected by removing the gas phase of the second stage agitating vessel, and cooling it to liquefy a portion of the solvent vapor or the monomer which is then recirculated into the vessel (not shown). The polymerization reaction in the second stage may be easily controlled by adjusting the temperature and pressure, and the concentrations of the monomer and hydrogen may be maintained at a high level.

The first stage polymerization continues in the second stage. The ratio between the high molecular weight polymers and the low molecular weight polymers in the formed reaction product may be selected in a wide range. However, it is generally desirable to prepare a composition composed of from 5 to 70% by weight of the high molecular weight polymers and from 30 to 95% by weight of the low molecular weight polymers, preferably from 10 to 60% by weight of the high molecular weight

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polymers and 40 to 90% by weight of the low molecular weight polymers.

The polymerization reaction mixture from the second stage is removed continuously through a line 15, and the polymers are recovered from the solvent. The second stage agitating vessel 2 as shown is a single reactor, but two or more of reactors (not shown), which are operated under the substantially same conditions, may be connected in series with one another.

Polymers may be recovered from the polymerization reaction mixture removed from the second stage agitating vessel by any of the conventional methods for recovering polyolefins. A step of removing inorganic residues which are derived from the catalyst may be eliminated as a Ziegler-type catalyst is employed. Polymers may be recovered from the polymerization reaction mixture by introducing the reaction mixture through the line 15 into a flashing vessel 16 into which steam is fed through a line 17 to distill off the residual hydrogen, unreacted monomers and solvent through a line 18. Polymers are recovered through a line 19 in the form of a water slurry by introducing warm water through a line 20. The hydrogen, monomers and solvent distilled off from the reaction mixture may be refined in a refining step (not shown) and returned to the process for reuse. In the polymer recovery step, two or more flash vessels may be provided in line with one another for recovering the unreacted materials and the solvent.

The invention is illustrated by the following Examples.

#### Example 1

Using the system shown in Figure 1, polymerization was effected. 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0 g/h of a catalyst comprising TiCl<sub>4</sub> supported on a solid carrier including anhydrous magnesium chloride and 15 kg/h of ethylene were continuously fed to an agitating reactor of 9.0 m<sup>3</sup> internal volume, and the reactor was maintained at 85°C and at a gauge pressure of 17.0 kg/cm<sup>2</sup> with virtually no gas present. The polymerization reaction mixture slurry from the first stage reactor was delivered through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> internal volume by the existing pressure difference and added to ethylene, propylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase in the second stage vessel being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:propylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 28.8:1.2:70. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 4,600 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.33, melt index 0.061, flow parameter

$$\frac{\text{Melt Index at the Loading of 21.6 Kg}}{(\log \frac{\text{Melt Index at the Loading of 21.6 Kg}}{\text{Melt Index at the Loading of 2.16 Kg}})2.30}$$

and density 0.9518 g/cm<sup>3</sup>. The moulding qualities of the polyethylene thus obtained were excellent. A 10μ thick film was moulded therefrom, and it was found that the gels formed in the film were only 18/1000 cm<sup>2</sup>. The properties of the film were satisfactory.

#### Example 2

Using the same system as used in Example 1, 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0 g/h of the Ti-containing solid catalyst the same as in Example 1, 39 kg/h of ethylene and 27 g/h of hydrogen were continuously fed to a 0.9 m<sup>3</sup> first stage reactor which was maintained at 85°C and at a gauge pressure of 16.4 kg/cm<sup>2</sup> with virtually no gas present. The slurry from the first stage reactor was delivered through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> internal volume by the pressure difference and added to ethylene, propylene and hydrogen in the second stage vessel

which was maintained at 85°C and a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase in the second stage vessel being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:propylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 39.5:0.5:60. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 8,400 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.35; melt index 0.31, flow parameter 2.03 and density 0.9570 g/cm<sup>3</sup>. The moulding qualities of the polyethylene thus obtained were excellent, and the properties of a bottle moulded therefrom by blow moulding were also satisfactory.

#### Example 3

Similarly as in Example 1, 1.35 m<sup>3</sup>/h of hexane 1.0 ml/h of triethyl aluminium, 9.0

g/h of the Ti-containing solid catalyst, 35 kg/h of ethylene, 1.2 kg/h of butene-1 and 27 g/h of hydrogen were continuously fed to an agitating reactor of 0.9 m<sup>3</sup> internal volume, and the reactor was maintained at 85°C and at a gauge pressure of 17.0 kg/cm<sup>2</sup> with virtually no gas present. The polymerization reaction mixture slurry from the first stage reactor was transferred through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> internal volume by the pressure difference, and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 35:65. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 9,300 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.34, melt index 0.32, flow parameter 2.05, and density 0.9544 g/cm<sup>3</sup>. The stiffness of the polymer obtained measured by ASTM D747-63 was 13.7×10<sup>4</sup> psi, the environmental stress cracking resistance (ESCR) measured by ASTM D-1693-60T was 120 h, and the critical shear rate measured using an Instron (Trade Mark) rheometer was 1650 sec<sup>-1</sup>. These figures show that the properties of this polymer were well balanced.

#### Example 4

1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0/h of the Ti-containing solid catalyst as in Example 1, 17 kg/h of ethylene and 0.5 kg/h of propylene were continuously fed to a first stage reactor of 0.9 m<sup>3</sup> internal volume which was maintained at 85°C and at a gauge pressure of 17.0 kg/cm<sup>2</sup> with virtually no gas present. The polymerization reaction mixture slurry from the first stage reactor was delivered through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> in volume by the pressure difference and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 30:70. This two stage polymerization was operated very stably for 100 h. The reaction mixture was removed, and the polymers were recovered and dried to obtain a mixture of widely distributed molecular weight polyethylenes of bulk density 0.31, melt index 0.063, flow parameter 2.33 and density 0.9514 g/cm<sup>3</sup>. The moulding qualities of the

polyethylene thus obtained were excellent. A 10μ thick film was moulded therefrom, and the gels formed in the film were only 13/1000 cm<sup>2</sup>. The Dart impact strength measured by ASTM D1709-62T was 173 g, and other properties of the film were also satisfactory.

#### Example 5

Using the system shown in Figure 2, polymerization was effected. 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethylaluminium, 9.0 g/h of the Ti-containing solid catalyst the same as in Example 1 and 15 kg/h of ethylene were continuously fed to an agitating reactor of 0.9 m<sup>3</sup> internal volume which was maintained at 85°C. The upper portion of the reactor was then purged with pressurized nitrogen gas to form an inert gas phase, and the reactor was maintained at a gauge pressure of 17.0 kg/cm<sup>2</sup>. The polymerization reaction mixture slurry from the first stage reactor was delivered from the bottom of the reactor through a conduit, to a 2.0 m<sup>3</sup> second stage agitating vessel by the action of the differential pressure, and added to ethylene, propylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:propylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 29.0:1.0:70. This two stage polymerization was operated very stably for 100 h. The reaction mixture was removed, and the polymers were recovered and dried to obtain 4,850 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.31, melt index 0.059, flow parameter 2.32 and density 0.9523 g/cm<sup>3</sup>. The moulding qualities of the polyethylene thus obtained were excellent. A 10μ thick film was moulded therefrom, and the gels formed in the film were only 15/1000 cm<sup>2</sup>. The other properties of the film were also satisfactory.

#### Example 6

Using the system shown in Figure 2, 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0 g of the Ti-containing solid catalyst used in Example 1, 39 kg/h of ethylene and 27 g/h of hydrogen were continuously fed to a 0.9 m<sup>3</sup> first stage reactor which was maintained at 85°C. The upper portion of the reactor was then purged with nitrogen gas to form an inert gas phase, and the reactor was maintained at a gauge pressure of 16.2 kg/cm<sup>2</sup>. The slurry from the first stage reactor was delivered through a conduit to a 2.0 m<sup>3</sup> second stage agitating vessel by the pressure difference and added to ethylene, propylene, and hydrogen in the second

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stage vessel which was maintained at 85°C and at a total gauge pressure of 15.8 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:propylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 39.1:1.2:59.7. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 9,150 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.33, melt index 0.36, flow parameter 2.01 and density 0.9550 g/cm<sup>3</sup>. The moulding qualities of the polyethylene thus obtained were excellent, and the properties of a bottle moulded therefrom by blow moulding were also satisfactory.

#### Example 7

Using the system shown in Figure 2, polymerization was effected. 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0 g of the Ti-containing solid catalyst which was the same as used in Example 1, 37 kg/h of ethylene 1.3 kg/h of butene - 1 and 25 g/h of hydrogen were continuously fed to an agitating reactor of 0.9 m<sup>3</sup> internal volume, and the reactor was maintained at 85°C. The upper portion of the reactor was then purged with nitrogen gas to form an inert gas phase, and the reactor was maintained at a gauge pressure of 17.0 kg/cm<sup>2</sup>. The polymerization reaction mixture slurry from the first stage reactor was delivered from the bottom of the reactor through a conduit to a 2.0 m<sup>3</sup> second stage agitating vessel by pressure difference, and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 35:65. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 9,630 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.33, melt index 0.32, flow parameter 2.05 and density 0.9548 g/cm<sup>3</sup>. The stiffness of the polymer thus obtained measured by ASTM D747-63 was 13.1×10<sup>4</sup> psi, the environmental stress cracking resistance (ESCR) measured by ASTM D-1693-60T was 128 h, and the critical shear rate measured using an Instron rheometer was 1710 sec<sup>-1</sup>. These figures show that the properties of this polymer were well balanced.

#### Example 8

1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl

aluminium, 9.0 g/h of the Ti-containing solid catalyst as in Example 1, 15 kg/h of ethylene and 0.7 kg/h of propylene were continuously fed to a 0.9 m<sup>3</sup> first stage reactor which was maintained at 85°C. The upper portion of the reactor was then purged with nitrogen gas to form an inert gas phase and the reactor was maintained at a gauge pressure of 17.0 kg/cm<sup>2</sup>. The polymerization reaction mixture slurry from the first stage reactor was delivered from the bottom of the reactor through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> internal volume by pressure difference, and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase in the vessel being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 30:70. This two-stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 5,580 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.29, melt index 0.061, flow parameter 2.33 and density 0.9511 g/cm<sup>3</sup>. The moulding qualities of the polymer thus obtained were excellent. A 10μ film was moulded therefrom, and the gels formed in the film were only 9/1000 cm<sup>2</sup>. The Dart impact strength measured in accordance with ASTM D1709-62T was 168 g. The other properties of the film were also satisfactory.

#### WHAT WE CLAIM IS:—

1. A process of preparing a polyolefin wherein an olefin is polymerized in the presence of a solvent and a Ziegler-type catalyst comprising a transition metal compound supported on a solid carrier and an organometallic compound, the olefin polymerization being effected in a first stage under pressure in a liquid phase with virtually no gas phase present, the polymerization reaction mixture containing high molecular weight polymer particles dispersed in the solvent being continuously transferred from the first stage to a second stage at a pressure lower than the first stage by pressure difference, and the olefin polymerization being effected in the second stage in the presence of a gas phase containing olefin and hydrogen for forming polymers having molecular weights lower than those of polymers formed in the first stage.

2. A process as claimed in claim 1, wherein a single olefin monomer is polymerized in the first stage and said single olefin monomer is further polymerized in the second stage.

stage vessel which was maintained at 85°C and at a total gauge pressure of 15.8 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene: propylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 39.1:1.2:59.7. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 9,150 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.33, melt index 0.36, flow parameter 2.01 and density 0.9550 g/cm<sup>3</sup>. The moulding qualities of the polyethylene thus obtained were excellent, and the properties of a bottle moulded therefrom by blow moulding were also satisfactory.

#### Example 7

Using the system shown in Figure 2, polymerization was effected. 1.35 m<sup>3</sup>/h of hexane, 1.0 mol/h of triethyl aluminium, 9.0 g of the Ti-containing solid catalyst which was the same as used in Example 1, 37 kg/h of ethylene 1.3 kg/h of butene - 1 and 25 g/h of hydrogen were continuously fed to an agitating reactor of 0.9 m<sup>3</sup> internal volume, and the reactor was maintained at 85°C. The upper portion of the reactor was then purged with nitrogen gas to form an inert gas phase, and the reactor was maintained at a gauge pressure of 17.0 kg/cm<sup>2</sup>. The polymerization reaction mixture slurry from the first stage reactor was delivered from the bottom of the reactor through a conduit to a 2.0 m<sup>3</sup> second stage agitating vessel by pressure difference, and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 35:65. This two stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 9,630 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.33, melt index 0.32, flow parameter 2.05 and density 0.9548 g/cm<sup>3</sup>. The stiffness of the polymer thus obtained measured by ASTM D747-63 was 13.1×10<sup>4</sup> psi, the environmental stress cracking resistance (ESCR) measured by ASTM D-1693-60T was 128 h, and the critical shear rate measured using an Instron rheometer was 1710 sec<sup>-1</sup>. These figures show that the properties of this polymer were well balanced.

#### Example 8

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aluminium, 9.0 g/h of the Ti-containing solid catalyst as in Example 1, 15 kg/h of ethylene and 0.7 kg/h of propylene were continuously fed to a 0.9 m<sup>3</sup> first stage reactor which was maintained at 85°C. The upper portion of the reactor was then purged with nitrogen gas to form an inert gas phase and the reactor was maintained at a gauge pressure of 17.0 kg/cm<sup>2</sup>. The polymerization reaction mixture slurry from the first stage reactor was delivered from the bottom of the reactor through a conduit to a second stage agitating vessel of 2.0 m<sup>3</sup> internal volume by pressure difference, and added to ethylene and hydrogen in the second stage vessel which was maintained at 85°C and at a total gauge pressure of 16 kg/cm<sup>2</sup>, the volume of the liquid phase in the vessel being kept at 1.5 m<sup>3</sup>. The molar ratio of ethylene:hydrogen in the gas phase contained in the second stage vessel was maintained at 30:70. This two-stage polymerization was operated very stably for 100 h. The reaction mixture was continuously removed, and the polymers were recovered and dried to obtain 5,580 kg of a mixture of widely distributed molecular weight polyethylenes of bulk density 0.29, melt index 0.061, flow parameter 2.33 and density 0.9511 g/cm<sup>3</sup>. The moulding qualities of the polymer thus obtained were excellent. A 10μ film was moulded therefrom, and the gels formed in the film were only 9/1000 cm<sup>2</sup>. The Dart impact strength measured in accordance with ASTM D1709-62T was 168 g. The other properties of the film were also satisfactory.

#### WHAT WE CLAIM IS:—

1. A process of preparing a polyolefin wherein an olefin is polymerized in the presence of a solvent and a Ziegler-type catalyst comprising a transition metal compound supported on a solid carrier and an organometallic compound, the olefin polymerization being effected in a first stage under pressure in a liquid phase with virtually no gas phase present, the polymerization reaction mixture containing high molecular weight polymer particles dispersed in the solvent being continuously transferred from the first stage to a second stage at a pressure lower than the first stage by pressure difference, and the olefin polymerization being effected in the second stage in the presence of a gas phase containing olefin and hydrogen for forming polymers having molecular weights lower than those of polymers formed in the first stage.

2. A process as claimed in claim 1, wherein a single olefin monomer is polymerized in the first stage and said single olefin monomer is further polymerized in the second stage.



3. A process as claimed in claim 2, wherein the single olefin monomer is ethylene, propylene or butene - 1.
- 5 4. A process as claimed in any preceding claim, wherein there is a concentration of hydrogen in the first stage three quarters or less of that in the second stage.
- 10 5. A process as claimed in any preceding claim, wherein the monomer concentration in the liquid phase in the first stage is from 5 to 200% of that in the liquid phase in the second stage.
- 15 6. A process as claimed in any preceding claim wherein polymerization in the first stage is effected at from 30° to 100°C and from 2 to 100 kg/cm<sup>2</sup>.
- 20 7. A process as claimed in any preceding claim, wherein hydrogen is supplied to the second stage such that the hydrogen concentration in gas phase is from 30 to 95 mol%.
- 25 8. A process as claimed in any preceding claim, wherein the polymerization temperature in the second stage is from 50° to 100°C.
- 30 9. A process as claimed in any preceding claim modified in that a gas phase containing an inert gas is present in the first stage.
- 35 10. A process as claimed in any of claims 1 to 8 wherein a main olefin monomer is copolymerized with one or more other olefin comonomers in the first stage, and said main olefin monomer is further polymerized in the second stage.
- 40 11. A process as claimed in claim 10, wherein an additional olefin comonomer is supplied to the second stage.
12. A process as claimed in claim 10 or claim 11 wherein the olefin comonomer is supplied to the first stage reactor in a ratio of 0.1 to 10 mol% based on the main olefin monomer.
13. A process as claimed in any of claims 10 to 12 wherein the main olefin monomer is ethylene, and the olefin comonomer is one or more of propylene, butene - 1, pentene - 1, 4 - methylpentene - 1, hexene - 1, heptene - 1 or octene - 1.
14. A process as claimed in claim 9, wherein a main olefin monomer is copolymerized with one or more other olefin comonomers in the first stage, and said main olefin monomer is further polymerized in the second stage.
15. A process as claimed in claim 9, wherein an additional olefin comonomer is supplied to the second stage.
16. A process as claimed in claim 9, wherein the olefin comonomer is supplied to the first stage reactor in a ratio of 0.1 to 10 mol% based on the main olefin monomer.
17. A process as claimed in claim 9, wherein the main olefin monomer is ethylene, and the olefin comonomer is one or more of propylene, butene - 1, pentene - 1, 4 - methylpentene - 1, hexene - 1, heptene - 1 or octene - 1.
18. A process of preparing a polyolefin as herein described in any of Examples 1 to 4.
19. A process of preparing a polyolefin as herein described in any of Examples 5 to 8.
20. A polyolefin prepared by a process as claimed in any preceding claim.

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