

1 A PROCESS FOR PRODUCING ETHYLENE POLYMERS

This invention relates to a process for producing an ethylene polymer or an ethylene-olefin copolymer [briefly "ethylene polymer(s)"] having a broad
5 molecular weight distribution, good melt flowability, and desirable uniformity with very little incompatible or heterogeneous particle content.

Ethylene polymers are required to be of broad molecular weight distribution for the purpose of
10 producing films, pipes, bottles, cables, or the like by extrusion or blow molding, because those having a narrow molecular weight distribution are insufficient in melt flowability, leading to a large power consumption in extrusion, and decreased commercial value of the product
15 owing to the occurrence of melt fracture on the surface, which impairs the appearance of the product.

There are known various methods to broaden the molecular weight distribution. Attempts have heretofore been made to achieve the object by proper
20 selection of the catalyst. However, the degree of broadening of the molecular weight distribution caused by the non-uniform distribution of the active sites on a catalyst is rather small, whereas if it is intended to achieve a large degree of broadening, the catalyst
25 activity frequently tends to become lower, that is, the high activity of a catalyst is sacrificed. When a

1 catalyst of low activity is used, it becomes necessary
to remove the residual catalyst by washing the polymer,
rendering the process uneconomical. Another means to
broaden the molecular weight distribution is to blend
5 an ethylene polymer of high molecular weight with that
of low molecular weight either mechanically or in solutions.
However, the mechanical blending presents a problem of
non-uniformity of the blend, which is intolerably
deleterious to the light gauge products such as film,
10 pipe and bottle, while the solution blending requires an
expensive mixing procedure, rendering the process un-
economical, though the problem of uniformity can be
solved.

Further, there are known several methods of
15 broadening the molecular weight distribution of an
ethylene polymer by carrying out the polymerization in
multiple stages using different hydrogen concentration
in each stage. However, various difficulties are
encountered in practicing the continuous multistage
20 production of an ethylene polymer of broad molecular
weight distribution on an industrial scale and it was
found difficult to produce economically a polymer having
satisfactory properties. The difficult problems encounter-
ed in the continuous multistage polymerization and the
25 means to solve the problems are described below.

In the multistage polymerization (hereinafter
description is limited to the case of two-stage poly-
merization which is typical of the multistage polymeriza-

tion) using different hydrogen concentration in each stage, there are two methods of operation which are different from each other in the sequence of polymerization at low and high hydrogen concentrations. In the one method (method A) the first stage polymerization is conducted at lower hydrogen concentration and the second stage polymerization at higher hydrogen concentration, while in the other (method B) the first stage polymerization is conducted at higher hydrogen concentration and the second stage polymerization at lower hydrogen concentration. In the method B, because of the high hydrogen concentration in the first stage, it is generally necessary to interpose a step for removing the unreacted gas between the first and second reaction zones. For this reason and in view of the nature of slurry, the method A would be preferred. On the other hand, however, a conventional high-activity supported-type Ziegler catalyst tends generally to reduce its activity rather rapidly with the progress of reaction and the rate of polymerization decreases when the hydrogen concentration is increased. Accordingly, in the method A the rate of polymerization is very high in the first stage where the catalyst activity is high and the hydrogen concentration is low, whereas the rate of polymerization becomes very low in the second stage where the catalyst activity has become decreased and the hydrogen concentration is kept high. As a consequence, it becomes necessary to change the residence time of the polymerization mixture

1 in the second stage greatly from that in the first stage.
This means that the capacity of both reactors should
differ markedly from each other, resulting in great
difficulties in the control as well as steadiness of the
5 continuous operation. In addition, because of a high
rate of polymerization in the first stage, the removal
of polymerization heat presents a difficult problem.

This invention is predicated upon the discovery that the above-said difficulties encountered in
10 carrying out the multistage polymerization by the method
A may be overcome by using a supported-type Ziegler
catalyst having a high activity persisting for a long
period of polymerization and setting the average production
of polymer per unit amount of solid catalyst component
15 nent within a specific range.

An object of this invention is to provide a
process for producing an ethylene polymer having a broad
molecular weight distribution and excellent in uniformity
and melt flowability.

20 Other objects and advantages of this invention
will become apparent from the following description.

The accompanying drawings are representation
of the relationships between the polymerization time
and the amount of polymer formation per unit quantity
25 of the solid catalyst component. Figs. 1, 2, 3 and 4
pertain to the results of tests for the persistence of
polymerization activity obtained in Examples 1-(2),
2-(1), 3-(2), and 4-(1), respectively.

According to this invention, there is provided an improved multistage polymerisation process for producing an ethylene polymer having a broad molecular weight distribution by the slurry-type polymerization of ethylene or ethylene and other olefins in two or more reaction zones connected in series and kept full with the liquid phase to substantially exclude the gas phase, using a catalyst system comprising a high-activity supported-type Ziegler catalyst component (briefly "solid catalyst component") and an organometallic compound component and hydrogen as molecular weight regulator, comprising;

(i) using (a) a solid catalyst component whose activity is defined by the formula

$$t_2/t_1 < 2,$$

(where t_1 and t_2 are the time required to produce an ethylene polymer amounting to respectively 30,000 and 40,000 times the weight of Ziegler catalyst component in a polymerization test performed under the same conditions as in the first stage reaction zone of the multistage polymerization) for obtaining the ethylene polymer having a density below 0.945 g/cm^3 , or (b) a solid catalyst component whose activity is defined by the formula

$$t_2/t_1 < 2,$$

(where t_1 and t_2 are the time required to produce an ethylene polymer amounting to respectively 15,000 and

- 1 20,000 times the weight of solid catalyst component in a
polymerization test performed under the same conditions
as in the first stage reaction zone of multistage
polymerization) for obtaining the ethylene polymer
5 having a density of 0.945 g/cm^3 or above;

(ii) feeding the catalyst system continuously to
the first stage reaction zone, allowing the polymeriza-
tion to proceed under application of pressure in the
presence or absence of hydrogen to produce higher
10 molecular-weight polymer particles, withdrawing continu-
ously the resulting polymer slurry, transferring the
slurry to the second stage reaction zone where the
polymerization is further continued under the conditions
of hydrogen-to-ethylene ratio larger than that in the
15 first stage reaction zone to produce a polymer having
a molecular weight lower than that of the polymer formed
in the first stage; if necessary, continuing the poly-
merization in a similar manner in the third and follow-
ing stages;

- 20 (iii) keeping the average amount of polymer produced
in each stage, except for the final stage, (a) below
30,000 times the weight of solid catalyst component
for obtaining a polymer having a density below 0.945 g/cm^3 ,
or (b) at or below 15,000 times the weight of
25 solid catalyst component for obtaining a polymer having
a density 0.945 g/cm^3 or above; and

(iv) selecting the amount of polymer formation in
each stage so as to keep the average amount of polymer

- 1 produced after completion of the multistage polymeriza-
tion at 5,000 times the weight of solid catalyst
component or more.

In producing an ethylene polymer having a
5 density below 0.945 g/cm^3 , the solid catalyst component
for use in the present invention should show a polymer
producing ability of 40,000-fold or more (in terms of
weight of polymer per unit weight of the solid catalyst
component) and retain sufficient residual activity after
10 the amount of polymer has reached 30,000 times the weight
of solid catalyst component. In case the density of
polymer is 0.945 g/cm^3 or above, the solid catalyst
component should show an ability of 20,000-fold polymer
production or more and retain sufficient residual activity
15 after the 15,000-fold polymer production. To describe
more fully, when tested under the same polymerization
conditions as those in the first reaction zone of
multistage polymerization, the catalyst should satisfy a
relationship represented by the formula

$$\frac{t_2}{t_1} < 2 \quad \text{..... formula (a)}$$

- 20 (where t_1 is the time required for the 30,000-fold
polymer production and t_2 is the time required for 40,000-
fold polymer production) for obtaining the polymer having
a density below 0.945 g/cm^3 , while the catalyst satisfy
a relationship represented by the formula

$$\frac{t_2}{t_1} < 2 \dots\dots \text{formula (a)}$$

1 (where t_1 is the time required for the 15,000-fold
polymer production and t_2 is the time required for the
20,000-fold polymer production) for obtaining the
polymer having a density of 0.945 g/cm^3 or above. The
5 ratio t_2/t_1 in the formulas (a) should be less than
2, preferably less than 1.7. If the multistage polymeri-
zation is carried out by use of a catalyst which shows
the ratio of 2 or more, the rates of polymerization in
the second and succeeding stages become markedly lower
10 than that in the first stage, resulting in disturbance
of the smooth operation and decline in productivity
owing to too much difference in residence time between
the first stage and the succeeding stages, even though
the adjustment of residence time is possible to some
15 extent by the selection of polymerization conditions.
Although the rate of polymerization in the second and
following stages may be increased by an additional
feeding of the solid catalyst component, yet the amount of
such an additional feed is limited to a certain range,
20 because with the increase in the additional feed, there
will arise such difficulties as a decline in uniformity
of the polymer, leading to a defect in molded products
such as fish-eye or unevenness.

Important one of the conditions necessary for
25 the present process is the use of a solid catalyst

- 1 component having a long-lasting activity which meets the
above requirement. If the multistage polymerization
is carried out by use of a solid catalyst component
which does not meet the requirement, it is difficult to
5 obtain a product of good quality with a desirable
economic efficiency.

According to this invention, for obtaining the
ethylene polymer having a density below 0.945 g/cm^3 ,
the average polymer production by weight in each stage,
10 except for the last stage, should be restricted to 30,000
times or less the weight of solid catalyst component,
and the polymer production in each stage is selected so
that the average yield of the final polymer may become
5,000 times or more the weight of solid catalyst compo-
15 nent after completion of the multistage polymerization.
For obtaining the ethylene polymer having a density of
 0.945 g/cm^3 or above, the average polymer production by
weight in each stage, except for the last stage, should
be restricted to 15,000 times or less the weight of solid
20 catalyst component, and the polymer production in each
stage is selected so that the average yield of the final
polymer may become 5,000 times or more the weight of
solid catalyst component after completion of the multi-
stage polymerization. If the average polymer production
25 in any stage excepting the final stage is 30,000-fold or
more in the case of an ethylene polymer having a density
below 0.945 g/cm^3 , or if it is 15,000-fold or more in
the case of an ethylene polymer having a density of

- 1 0.945 g/cm³ or above, the polymerization activity of a catalyst in the succeeding stages will decrease and it becomes difficult to adjust the residence time in each stage so as to keep the productivity favorable.
- 5 Further, if the average yield of polymer after completion of the multistage polymerization is less than 5,000 times the weight of solid catalyst component, a step of catalyst removal will become necessary to decrease the ash content of the polymer, resulting in a decrease in
- 10 economic efficiency of the process.

The effective carriers for the solid catalyst components used in the present process include oxides, hydroxides, chlorides, carbonates of metals and silicon, and mixtures of these compounds such as, for example,

15 magnesium oxide, titanium oxide, silica, alumina, magnesium carbonate, hydroxychlorides of divalent metals, magnesium hydroxide, magnesium chloride, magnesium alkoxides, magnesium haloalkoxides, double oxides of magnesium and aluminum, and double oxides of magnesium

20 and calcium. Of these, magnesium compounds are especially preferred.

Examples of the transition metal compounds being supported on the carriers include titanium compounds, vanadium compounds and zirconium compounds such as

25 titanium tetrachloride, titanium tetrabromide, titanium tetraiodide, titanium trichloride; titanium compounds represented by the general formula $Ti(OR^1)_{4-p}X_p$ (where R^1 represents a hydrocarbon group, X represents a

- 1 halogen atom, and p is a number defined by the formula
 $0 \leq p < 4$) such as alkoxytitanium compounds, aryloxytitanium
compounds, alkoxytitanium halides, and aryloxytitanium
halides; vanadium tetrachloride, vanadium oxytrichloride,
5 zirconium tetrachloride, and zirconium compounds re-
presented by the general formula $Zr(OR^2)_{4-q}X_q$ (where R^2
represents a hydrocarbon group, X represents a halogen
atom, and q is a number defined by the formula $0 \leq q < 4$)
such as alkoxyzirconium compounds, aryloxyzirconium
10 compounds, alkoxyzirconium halides, and aryloxyzirconium
halides. The reaction products of organomagnesium
compounds and transition metal compounds represented by
the general formula $Ti(OR^3)_{4-r}X_r$ (where R^3 represents a
hydrocarbon group, X represents a halogen atom, and r
15 is a number defined by the formula $0 \leq r \leq 4$) such as
titanium tetrahalides, alkoxytitanium compounds, aryloxy-
titanium compounds, alkoxytitanium halides, and aryloxy-
titanium halides are also used as the solid catalyst
component. Examples of suitable solid catalyst components
20 are described in Japanese Patent Publication Nos. 39,037/
79, 40,273/79, 40,274/79, 23,561/80; Japanese Patent
Application "Kokai" (Laid-open) Nos. 126,785/75, 84,884/76,
144,006/80; Japanese Patent Application Nos. 165,341/79,
9,200/80; U.S. Patent 4,223,117.

- 25 The organometallic compounds which form the
catalyst systems in polymerization reaction together with
the above solid catalyst components include trialkyl-
aluminums such as triethylaluminum, tri-n-propylaluminum,

1 triisobutylaluminum, tri-n-butylaluminum, and tri-n-hexylaluminum; dialkylaluminum monohalides such as diethylaluminum monochloride, di-n-propylaluminum monochloride, /diisobutylaluminum monochloride, di-n-butyl-
5 aluminum monochloride, and di-n-hexylaluminum monochloride; alkylaluminum dihalides such as ethylaluminum dichloride, n-propylaluminum dichloride, isobutylaluminum dichloride, n-butylaluminum dichloride, and n-hexylaluminum dichloride; other organoaluminum compounds
10 such as ethylaluminum sesquichloride, n-propylaluminum sesquichloride, isobutylaluminum sesquichloride, n-butylaluminum sesquichloride, and n-hexylaluminum sesquichloride; other organometallic compounds of zinc and others. These organometallic compounds are used each
15 alone or in mixtures.

In the present multistage polymerization process, a desired amount of an ethylene polymer of a desired molecular weight (or of an intrinsic viscosity) is produced in each stage. The molecular weight and
20 the amount of polymer in each stage are determinable by taking into account the processability of the polymer and the physical properties of the molded product.

In the first stage reaction zone, a polymer having an intrinsic viscosity of 2 to 10 dl/g (at 135°C
25 in tetralin) is produced in the absence of hydrogen or under the conditions of a relatively small hydrogen-to-ethylene ratio. If the intrinsic viscosity falls outside the above range, the melt flowability of the final polymer

1 will be unsatisfactory. The amount of polymer formed
in the first stage reaction zone is 5 to 80% by weight of
the total polymer. If the amount of polymer is beyond the
above limits, the melt flowability of the final polymer
5 and the physical properties of the molded product are
both unsatisfactory. In the second stage reaction zone,
a polymer having an intrinsic viscosity of 0.2 to 1.5
dl/g is produced under the conditions of a higher hydrogen-
to-ethylene ratio than that in the first stage reaction
10 zone. If the intrinsic viscosity is higher than 1.5
dl/g, the melt flowability of the final polymer becomes
unsatisfactory, while if it is below 0.2 dl/g, the
polymerization activity is undesirably reduced.

In producing a copolymer of ethylene and other
15 olefins by the present process, the amount of an olefin
in the copolymer in each stage can be determined as
desired by selecting the ratio of ethylene to other
olefins.

The multistage polymerization according to this
20 invention permits the production of an ethylene polymer
which is uniform and has a desired molecular weight, broad
molecular weight distribution, and excellent melt flow-
ability.

When it is required to add an additional
25 amount of the solid catalyst component to the second or
subsequent stage reaction zones, it is desirable to employ
a least possible amount in order to keep the polymer free
from the defect such as fish-eye or unevenness. Although

1 the limit of the allowable amount of additional solid
catalyst component varies depending upon the amount of
polymer produced in each stage and the molecular weight,
it is generally desirable to keep the additional amount
5 from exceeding 50% by weight of the amount fed to the
first stage reaction zone.

In the present process, each reaction zone is
kept substantially free from the gas phase by filling
the space entirely with the liquid phase. If the gas
10 phase is present in the reaction zone, a polymer build-up
on the wall will take place and tends to cause fish-eye
or unevenness to appear in the molded product.

For the polymerization, may be used any of the
loop-type, tube-type, and vessel-type reactors. Of these
15 reactors, the loop-type is most suitable for the operation
in each stage of the reaction.

It is also possible to carry out the present
process in such manner that the first stage reactor is
operated under a pressure higher than that in the second
20 stage reactor and the polymer slurry is transferred by
utilizing the pressure difference.

The present process may be carried out by using,
for example, two reactors connected in series. The first
stage polymerization is carried out by feeding continuously
25 to the first reactor prescribed amounts of catalyst,
solvent, ethylene, and, if necessary, other olefins and
hydrogen. The polymer slurry is transferred from the
first reactor continuously to the second reactor, while

1 feeding continuously to the second reactor prescribed
amounts of the solvent, hydrogen, ethylene, and, if
necessary, other olefins to carry out the second stage
polymerization. If the third and succeeding stage poly-
5 merization are to be performed, the operation is similar
to that in the second reactor. In each stage, it is
also possible to employ multiple reactors connected in
series or parallel, which operate under the substantially
the same polymerization conditions.

10 The present process is adaptable to the homo-
polymerization of ethylene as well as to the copolymeri-
zation of ethylene with other olefins. Examples of
olefins used as comonomers are α -olefins such as pro-
pylene, butene-1, pentene-1, hexene-1, octene-1, and
15 4-methylpentene-1. The amount of olefins to be copoly-
merized with ethylene is 15 mole % or less, preferably
10 mole % or less, most preferably 5 mole % or less.

The density of polymer can be easily adjusted
mainly by controlling the amount of olefins to be co-
20 polymerized with ethylene and the molecular weight of
the polymer to be produced.

According to the present process, it is possible
to obtain a polymer having desirable physical properties
and processability on a large scale with favorable
25 economic efficiency by changing the average molecular
weight, molecular weight distribution, and density of
the polymer as desired. Since the ethylene polymer
produced by the process of this invention has broad

molecular weight distribution and excellent melt flowability and can be processed into molded products of sufficient uniformity with little fish-eye or unevenness, it is particularly suitable for the extrusion molding or 5 blow molding of films, pipes, bottles and cables.

The polymerization temperature in the present process generally ranges from room temperature to 120°C, preferably from 50° to 100°C. The polymerization pressure is from atmospheric pressure to 100 kg/cm², preferably from 105 to 50 kg/cm².

The inert solvents used as polymerization solvents include aliphatic hydrocarbons such as propane, butane, pentane, hexane, heptane and octane; alicyclic hydrocarbons such as cyclohexane and cycloheptane; and 15 aromatic hydrocarbons such as benzene, toluene and xylene. Of these hydrocarbons, particularly preferred are aliphatic hydrocarbons. When α -olefins of 3 to 8 carbon atoms such as propylene, butene-1 and pentene-1 are used as the comonomer, it is possible to carry out the liquid- 20 phase bulk copolymerization by utilizing the comonomer itself as the solvent. As compared with the common slurry obtained by using a liquid saturated hydrocarbon of 6 or 7 carbon atoms as solvent, the slurry formed by using a low-boiling saturated hydrocarbon such as propane, 25 butane or pentane has an advantage in that the polymer can be separated by a simple means of flashing. Moreover, in the case of polymerization in such a low-boiling saturated hydrocarbon, the resulting polymer contains

1 smaller amount of polymer soluble in the low-boiling
saturated hydrocarbon and, hence, there are no such
troubles as the viscosity increase in the reactor,
stickiness and adhesion of polymer cake, which troubles
5 are caused by the formation of low-molecular weight
soluble polymer; the nature of polymer particles is better
and the production efficiency per unit volume of the
reactor is higher.

A sufficient concentration of the solid catalyst
10 component in the polymerization system of the first and
second stages is generally 0.001 to 0.1 mmole (in terms
of transition metal atom) per liter of the solvent. The
amount to be used of an organometallic compound component
is not critical, but it is used generally in an amount of
15 0.5 to 500, preferably 2 to 100 mole equivalent per mole
of the transition metal atom in the solid catalyst com-
ponent. The catalyst is fed conveniently by utilizing
an inert solvent as the carrier. The inert solvents
suitable for the purpose include aliphatic hydrocarbons
20 such as propane, butane, pentane, hexane, heptane and
octane.

The invention is further illustrated below in
detail with reference to Examples, but the invention is
not limited unless it departs from the essential feature
25 of the invention. In Examples, the properties of the
polymer were determined in the following way:

The density and the bulk density were determined
in accordance with JIS K 6760 and JIS K 6721, respectively.

31

- 1 The melt flowability was expressed in terms
of "melt flow ratio" (MFR) which, as herein used, is
defined as the ratio of the flow rate under a load of
21.60 kg to the flow rate (i.e. melt index) under a load
5 of 2.160 kg, both flow rates being determined in accordance with ASTM D 1238-57T at 190°C.

$$\text{MFR} = \frac{\text{Flow rate under a load of 21.60 kg}}{\text{Flow rate under a load of 2.160 kg}}$$

Example 1

(1) Preparation of solid catalyst component.

Into a 50-liter autoclave provided with a
10 stirrer, was charged 2.0 kg of magnesium turnings for
Grignard reagent. The autoclave was freed from the air
and moisture by thorough flashing with nitrogen. To
the autoclave were added dropwise at 50°C 8.0 liters of
n-butyl chloride and 25 liters of n-butyl ether over a
15 period of 4 hours. After completion of the dropwise addition,
the reaction was allowed to continue at 60°C for
one hour. The reaction mixture was then cooled to room
temperature and the unreacted magnesium was removed by
filtration. The concentration of n-butyilmagnesium
20 chloride in the n-butyl ether was found to be 2.06 moles/
liter, as determined by hydrolysis with 1 N sulfuric acid
and back titration with 1 N sodium hydroxide solution
with phenolphthalein as indicator. A 50-liter autoclave,
which had been thoroughly flashed with nitrogen to remove

1 the air and moisture, was charged with 30 liters (62 moles)
of the above n-butyl ether solution containing n-butyl-
magnesium chloride. To the autoclave, was added dropwise
at 30°C 7.0 liters (62 moles) of silicon tetrachloride
5 over a period of 2 hours. After completion of the addi-
tion, the reaction was allowed to continue for one hour
at 30°C. The solid product was washed with n-heptane and
allowed to react with 20 liters of titanium tetrachloride
at 100°C for one hour with stirring. After completion
10 of the reaction, the resulting solid was washed repeatedly
with n-heptane until no more titanium tetrachloride had
been detected in the washings, and dried in vacuo to
yield 6.5 kg of a solid catalyst component in which 19 mg
of titanium atom had been supported per g of solid
15 catalyst component.

(2) Persistence test for polymerization activity.

The persistence of polymerization activity was
tested under the conditions similar to those in the first
stage reaction zone of continuous two-stage polymerization
20 described later in paragraph (3).

(2) - (a)

Into a 50-liter stainless steel autoclave, which
had been thoroughly flashed with nitrogen, were charged
12.5 kg of butane and 17 mmols of triethylaluminum.
25 To the mixture, which had been heated to 80°C, was added
ethylene until the total pressure had reached 16 kg/cm²,
followed by hydrogen until the ethylene-to-hydrogen molar
ratio had become 1/0.009. The polymerization was initiated

1 by adding 296 mg of the solid catalyst component prepared
in (1) above. The polymerization was allowed to continue
for one hour at 80°C, while continuously feeding
ethylene to keep the total pressure constant. The poly-
5 merization was then terminated with isopropyl alcohol.
After releasing the butane and unreacted monomer, the
polymer was dried in vacuo at 60°C. The yield of polymer
was 2.34 kg corresponding to 7,910 g per g of the solid
catalyst component.

10 (2)-(b) to (e)

Polymerization was carried out under the same
conditions as described in (2)-(a), except that the
polymerization time was varied. The results obtained
were as shown in Table 1. In the polymerization tests
15 of (2)-(a) to (e), the ethylene-to-hydrogen ratio in the
liquid phase was maintained at 1 : 0.009. By plotting the
results of Table 1, a curve representing the relationship
between the polymerization time and the yield of
polymer per unit weight of the solid catalyst component
20 was obtained as shown in Fig. 1. From the curve, it is
seen that the time t_1 required for the 15,000-fold
polymer production based on the weight of solid catalyst
component was 2.4 hours and the time t_2 required for
the 20,000-fold polymer production was 3.8 hours. There-
25 fore, the ratio t_2/t_1 was about 1.6.

(3) Continuous two-stage polymerization.

The continuous polymerization was carried out
by using two loop-type reactors connected in series. Both

1 reactors were always filled with the liquid phase so as
to exclude substantially the gas phase. To the 250-liter
first reactor, were continuously fed 53 kg/hour of
butane, 74 mmole/hour of triethylaluminum, 1.2 g/hour
5 of the solid catalyst component prepared above in (1),
and 17 kg/hour of ethylene. Hydrogen was continuously
fed so as to maintain the ethylene-to-hydrogen molar ratio
in the liquid phase at 1 : 0.009. The temperature was
80°C and the total pressure was 38 kg/cm².G. The
10 polymer slurry was continuously transferred by the
pressure difference from the first reactor to the second
500-liter reactor while feeding continuously to the second
reactor 6.3 kg/hour of butane, 8.8 mmole/hour of tri-
ethylaluminum, and 22 kg/hour of ethylene. Hydrogen was
15 continuously fed so as to keep the ethylene-to-hydrogen
ratio (by mole) in the liquid phase at 1 : 0.12. The
temperature was maintained at 80°C and the total pressure
at 35 kg/cm².G. The polymer slurry was continuously
removed from the second reactor and the polymer was
20 recovered and dried. The continuous polymerization was
operated for 100 hours with satisfactory operational
control. (The polymer yield was 35 kg/hour which cor-
responded to an average polymer production of 29,200 g
per g of solid catalyst component. The polymer production
25 ratio of the first stage to the second stage was 40 : 60
by weight, as calculated from the material balance. The
average polymer production per g of solid catalyst
component in the first and second stage reaction zones

1 was 11,700 g and 17,500 g, respectively. Properties of polymer: density, 0.961 g/cm³; melt index, 0.29 g/10 min.; MFR, 104; bulk density, 0.45 g/cm³.

The resulting polymer was extruded to form a tubular film of 10 μ thickness by the inflation process. The extrusion pressure was relatively low and the stability of the bubble was also excellent. The number of fish-eyes in the film was as low as 7 in 1,000 cm². The tensile strength, impact resistance and tear strength were satisfactory. The color shade and the appearance were both good.

Table 1

Example No.	Polymerization time (hour)	Solid catalyst component (mg)	Yield of polymer (kg)	Polymer production (g polymer per g solid catalyst component)
1-(2)-(a)	1	296	2.34	7910
1-(2)-(b)	2	249	3.21	12900
1-(2)-(c)	3	225	3.89	17300
1-(2)-(d)	4	212	4.34	20500
1-(2)-(e)	5	179	4.21	23500

Example 2

(1) Persistence test for polymerization activity.

Using the solid catalyst component prepared

1 in Example 1-(1), the persistence of polymerization
activity was tested under the conditions similar to
those in the first stage reaction zone of continuous
two-stage polymerization described below in paragraph (2).

5 (1)-(a)

Into a 50-liter stainless steel autoclave, which
had been thoroughly flashed with nitrogen, were charged
12.5 kg of butane, 290 g of butene-1 and 17 mmoles of
triethylaluminum. To the mixture, which had been heated
10 to 70°C, was added ethylene until the total pressure had
reached 12.5 kg/cm².G, followed by hydrogen until the
ethylene-to-hydrogen ratio in the liquid phase had
become 1:0.002 (molar ratio). The polymerization was
initiated by adding 293 mg of the solid catalyst component
15 prepared in Example 1-(1). The polymerization was
allowed to continue for one hour at 70°C, while feeding
ethylene continuously to keep the total pressure constant.
The polymerization was then terminated with isopropyl
alcohol. After releasing the butane and unreacted
20 monomer, the polymer was dried in vacuo at 60°C. The
yield of polymer was 2.22 kg, corresponding to 7,580 g
per g of the solid catalyst component.

(1)-(b) to (e)

Polymerization was carried out under the same
25 conditions as described above in (1)-(a). The results
obtained were as shown in Table 2. In the polymerization
tests of (1)-(a) to (e), the molar ratio of ethylene:
butene-1:hydrogen in the liquid phase was maintained at

1 1 : 0.4 : 0.002. By plotting the results of Table 2,
a curve representing the relationship between the
polymerization time and the yield of polymer per unit
weight of the solid catalyst component was obtained
5 as shown in Fig. 2. From the curve, it is seen that
the time t_1 required for the 15,000-fold polymer produc-
tion based on the weight of solid catalyst component was
2.6 hours and the time t_2 required for the 20,000-fold
polymer production was 3.9 hours. Therefore, the ratio
10 t_2/t_1 was about 1.5.

(2) Continuous two-stage polymerization.

The continuous two-stage polymerization was
carried out by using two loop-type reactors connected in
series. Both reactors were kept full with the liquid
15 phase so as to exclude substantially the gas phase. To
the 250-liter first reactor, were continuously fed 51
kg/hour of butane, 73 mmoles/hour of triethylaluminum,
1.5 g/hour of the solid catalyst component prepared in
Example 1-(1), and 19 kg/hour of ethylene. Butene-1
20 and hydrogen were continuously fed so as to maintain the
molar ratio of ethylene : butene-1 : hydrogen at 1 : 0.4 :
0.002. The temperature was maintained at 70°C and the
total pressure at 38 kg/cm².G. The polymer slurry was
continuously transferred by the pressure difference to
25 the second 500-liter reactor while feeding continuously
to the second reactor 8.5 kg/hour of butane, 11 mmoles/
hour of triethylaluminum and 20 kg/hour of ethylene.
Butene-1 and hydrogen were continuously fed so as to keep

- 1 the molar ratio of ethylene : butene-1 : hydrogen in the liquid phase at 1 : 0.2 : 0.2. The temperature was maintained at 70°C and the total pressure at 35 kg/cm²·G. The polymer slurry was continuously removed from the
- 5 second reactor and the polymer was recovered and dried. The continuous polymerization was operated for 100 hours with satisfactory operation control. The polymer yield was 35 kg/hour which corresponds to an average polymer production of 23,400 g per g of solid catalyst component.
- 10 The polymer production ratio of the first stage to the second stage was 50 : 50 by weight, as calculated from the material balance. The average polymer production per g of solid catalyst component in the first and second stage reaction zones was 11,700 g and 11,700 g,
- 15 respectively. Properties of polymer : density, 0.949 g/cm³; melt index, 0.070 g/10 min.; MFR, 150; bulk density, 0.45 g/cm³.

The polymer was extruded to form a tubular film of 10 μ in thickness by the inflation process. The

20 extrusion pressure was relatively low and the stability of the bubble was also excellent. The number of fish-eyes in the film was as low as 8 in 1,000 cm². The film properties such as tensile strength, impact resistance and tear strength were excellent. The color shade

25 and the appearance were both good.

Table 2

Example No.	Polymerization time (hour)	Solid catalyst component (mg)	Yield of polymer (kg)	Polymer production (g polymer per g solid catalyst component)
2-(1)-(a)	1	293	2.22	7580
2-(1)-(b)	2	241	2.96	12300
2-(1)-(c)	3	245	4.06	16600
2-(1)-(d)	4	230	4.67	20300
2-(1)-(e)	5	188	4.42	23500

1 Comparative Example 1

Continuous two-stage polymerization was carried out under the same conditions as in Example 2-(2), except that the average polymer production per unit weight

5 of the solid catalyst component was increased in the first stage reaction zone by increasing the concentrations of ethylene, butene-1 and hydrogen.

The continuous polymerization was carried out by using two loop-type reactors connected in series.

10 Each reactor was kept full with the liquid phase so as to exclude substantially the gas phase. To the 250-liter first reactor, were continuously fed 50 kg/hour of butane, 67 mmole/hour of triethylaluminum, 1.0 g/hour of the solid catalyst component prepared in Example 1-(1),
15 and 19 kg/hour of ethylene. Butene-1 and hydrogen were

1 continuously fed so as to maintain the molar ratio of
ethylene : butene-1 : hydrogen in the liquid phase at
1 : 0.4 : 0.002. The temperature was maintained at 70°C
and the total pressure at 38 kg/cm²·G. The concentrations
5 of ethylene, butene-1 and hydrogen in the liquid phase
were set at a level of 1.5 times that in the first reac-
tion zone of Example 2-(2). The polymer slurry was
continuously transferred by the pressure difference to
the second 500-liter reactor while feeding continuously
10 to the second reactor 7.7 kg/hour of butane, 10 mmoles/
hour of triethylaluminum and 22 kg/hour of ethylene.
At the same time, 0.55 g/hour of the solid catalyst
component prepared in Example 1-(1) was continuously fed
in order to establish the same polymer production ratio
15 (50 : 50) of the first stage to the second stage as that
in Example 2-(2). Butene-1 and hydrogen were also fed
continuously so as to maintain the molar ratio of
ethylene: butene-1 : hydrogen in the liquid phase at
1 : 0.2 : 0.2. The temperature was maintained at 70°C
20 and the total pressure at 35 kg/cm²·G. The concentrations
of ethylene, butene-1 and hydrogen in the liquid phase
were the same as those in the second stage reaction zone
of Example 2-(2). The polymer slurry was continuously
withdrawn from the second reactor and the polymer was
25 recovered and dried. The polymer yield was 35 kg/hour
which corresponds to an average polymer production of
22,600 g per g of solid catalyst component. The polymer
production ratio of the first stage to the second stage

1 was 50 : 50 by weight, as calculated from the material
balance. The average polymer production per g of solid
catalyst component in the first stage reaction zone was
17,500 g. Properties of polymer : density, 0.950 g/cm^3 ;
5 melt index, 0.073 g/10 min. ; MFR, 147; bulk density:
 0.41 g/cm^3 .

The polymer was extruded to form a tubular
film of 10μ in thickness by the inflation process.
Although the extrusion pressure was relatively low, yet
10 the stability of bubble was insufficient and the film
revealed unevenness and a great many fish-eyes, making
the film practically valueless.

From the results of the present Comparative
Example, it is seen that if the average polymer produc-
15 tion in the first stage exceeds 15,000 times the weight
of solid catalyst component, it becomes necessary to
supply to the second stage reaction zone an additional
amount of the solid catalyst component to compensate the
declined rate of polymerization and the resulting polymer
20 becomes inferior in uniformity, leading to defective
molded products.

Comparative Example 2

(1) Preparation of solid catalyst component.

Commercial anhydrous magnesium chloride was
25 ground in a ball mill and heated at 300°C for 7 hours
under reduced pressure. To 250 g of the magnesium
chloride thus treated and placed in a 5-liter flask,

1 was added 3 liters of n-heptane to form a suspension.
To the suspension, were added dropwise at room tempera-
ture 426 ml of tetrahydrofuran and 750 ml of ethyl
benzoate over a period of one hour. The mixture was heat-
5 ed to 50°C and stirred for 2 hours. The supernatant of
the suspension was removed by filtration and the residue
was thoroughly washed with n-heptane. After addition of
3 liters of titanium tetrachloride, the mixture was
stirred at 100°C for one hour to allow the reaction to
10 proceed. After completion of the reaction, the solid
product was washed repeatedly with n-heptane until no
more titanium tetrachloride had been detected in the
washings, and then dried under reduced pressure to obtain
a solid catalyst component which was found to have
15 supported 58 mg of titanium atom per g of the solid
catalyst component.

(2) Persistence test for polymerization activity.

The persistence of polymerization activity
was tested under the same conditions as in Example
20 2-(1)-(a) to (e), except that the solid catalyst component
prepared above in (1) was used. The time t_1 required
for the 15,000-fold polymer production based on the
weight of solid catalyst component was 6.6 hours, while
the time t_2 required for the 20,000-fold polymer production
25 was 16.5 hours. Therefore, the ratio t_2/t_1 was 2.5.

(3) Continuous two-stage polymerization.

Using two loop-type reactors connected in
series, continuous two-stage polymerization was carried

1 out under the same conditions as in Example 2-(2), except
that the solid catalyst component prepared above in (1)
was used. Both reactors were kept full with the liquid
phase to exclude substantially the gas phase. To the
5 first 250-liter reactor, were continuously fed 53 kg/hour
of butane, 71 mmole/hour of triethylaluminum, 3.6 g/hour
of the solid catalyst component prepared above in (1),
and 17 kg/hour of ethylene. Butene-1 and hydrogen were
continuously fed so as to maintain the molar ratio of
10 ethylene : butene-1 : hydrogen in the liquid phase at
1 : 0.4 : 0.002. The temperature was maintained at 70°C
and the total pressure at 38 kg/cm².G. The polymer
slurry was continuously transferred by pressure dif-
ference from the first reactor to the second 500-liter
15 reactor while feeding continuously to the second reactor
9.6 kg/hour of butane, 13 mmoles/hour of triethylaluminum,
and 17 kg/hour of ethylene. At the same time, 2.0 g/hour
of the solid catalyst component prepared above in (1)
was continuously fed in order to establish the same
20 polymer production ratio (50 : 50 by weight) of the first
stage to the second stage as that in Example 2-(2).
Butene-1 and hydrogen were also fed continuously so as
to maintain the molar ratio of ethylene : butene-1 :
hydrogen in the liquid phase at 1 : 0.2 : 0.2. The tempera-
25 ture was maintained at 70°C and the total pressure at
35 kg/cm².G. The polymer slurry was continuously with-
drawn from the second reactor and the polymer was re-
covered and dried. The polymer yield was 30 kg/hour which

- 1 corresponds to an average polymer production of 5,360 g per g of solid catalyst component. The polymer production ratio of the first stage to the second stage was 50 : 50 by weight, as calculated from the material
- 5 balance. The average polymer production per g of solid catalyst component in the first stage reaction zone was 4,170 g. Properties of polymer: density, 0.951 g/cm^3 ; melt index, 0.080 g/10 min.; MFR, 143; bulk density, 0.30 g/cm^3 .
- 10 The polymer was extruded to form a tubular film of 10μ in thickness by the inflation process. Although the extrusion pressure was relatively low, yet the stability of bubble was insufficient and the film revealed unevenness and a great many fish-eyes making the film
- 15 practically valueless.

From the results of the present Comparative Example, it is seen that if a solid catalyst component which does not meet the requirements as herein specified is used, it becomes necessary to supply to the second stage

20 reaction zone an additional amount of the said catalyst component to compensate the declined rate of polymerization and the resulting polymer becomes inferior in uniformity, leading to defective molded products.

Example 3

- 25 (1) Preparation of solid catalyst component.

A solid catalyst component was prepared in a manner similar to that in Example 1-(1). It was found that

- 1 21 mg of titanium atom were supported per g of this solid catalyst component.

(2) Persistence test for polymerization activity.

- 5 The persistence of polymerization activity was tested under the conditions similar to those in the first stage reaction zone of continuous two-stage polymerization described below in (3).

(2)-(a)

- 10 Into a 50-liter stainless steel autoclave, which had been thoroughly flashed with nitrogen, were charged 10.0 kg of butane, 2.5 kg of butene-1, and 17 mmoles of triethylaluminum. To the mixture, which had been heated to 60°C, was added ethylene to a total pressure of 11.0 kg/cm².G, followed by hydrogen until the ethylene-to-
15 hydrogen molar ratio in the liquid phase had become 1 : 0.006. The ethylene-to-butene-1 molar ratio in the liquid phase was 1 : 4.3. The polymerization was initiated by adding 136 mg of the solid catalyst component prepared above in (1). The polymerization was allowed to continue
20 for one hour at 60°C, while feeding ethylene continuously to keep the total pressure constant. The polymerization was then terminated with isopropyl alcohol. After releasing the butane and the unreacted monomers, the polymer was dried under reduced pressure at 60°C.
25 The yield of polymer was 2.78 kg, corresponding to 20,400 g per g of the solid catalyst component.

(2)-(b) to (f)

Polymerization was carried out under the same

1 conditions as described above in (2)-(a), except that
the polymerization time was varied. The results obtained
were as shown in Table 3. In the polymerization tests
of (2)-(a) to (f), the molar ratio of ethylene:butene-1:
5 hydrogen in the liquid phase was maintained at 1:4.3:
0.006. By plotting the results of Table 3, a curve re-
presenting the relationship between the polymerization
time and the yield of polymer per unit weight of the
solid catalyst component was obtained as shown in
10 Fig. 3. From the curve it is seen that the time t_1
required for the production of 30,000-fold polymer based
on the weight of solid catalyst component was 1.7 hours,
while the time t_2 required for the production of 40,000-
fold polymer was 2.7 hours. Therefore, the ratio
15 t_2/t_1 was about 1.6.

(3) Continuous two-stage polymerization.

The continuous two-stage polymerization was
carried out by using two loop-type reactors connected in
series. Both reactors were kept full with the liquid
20 phase so as to exclude substantially the gas phase. To
the first 250-liter reactor, were continuously fed 58
kg/hour of butane, 99 mmoles/hour of triethylaluminum,
900 mg/hour of the solid catalyst component prepared
above in (1), and 21 kg/hour of ethylene. Butene-1 and
25 hydrogen were continuously fed so as to maintain the
molar ratio of ethylene:butene-1:hydrogen in the liquid
phase at 1:4.3:0.006. The temperature was maintained
at 60°C and the total pressure at 36 kg/cm².G. The

- 1 polymer slurry was continuously transferred by the pressure difference from the first reactor to the second 500-liter reactor while feeding continuously to the second reactor 14.5 kg/hour of butane, 26 mmol/hour of triethylaluminum, and 32 kg/hour of ethylene. Butene-1 and hydrogen were also fed continuously so as to maintain the molar ratio of ethylene : butene-1 : hydrogen in the liquid phase at 1 : 1.2 : 0.08. The temperature was maintained at 60°C and the total pressure at 33 kg/cm².G.
- 10 The polymer slurry was continuously withdrawn from the second reactor and the polymer was recovered and dried. The above polymerization operation was continued for 100 hours with satisfactory operational control. The polymer yield was 51 kg/hour corresponding to an average polymer production of 56,700 g per g of solid catalyst component.
- 15 The polymer production ratio of the first stage to the second stage was 45 : 55 by weight, as calculated from the material balance. The average polymer production per g of solid catalyst component was 25,500 g in the first stage
- 20 reaction zone and 31,200 g in the second stage reaction zone. Properties of polymer : density, 0.920 g/cm³; melt index, 1.0 g/10 min.; MFR, 75; bulk density, 0.43 g/cm³.

Physical properties of the press-molded sheet were very good as shown below.

- 1 Tensile impact strength: 295 kg-cm/cm² (ASTM D 1822)

Press conditions: ASTM D 1898 Method C

Test piece: S-type dumbbell; 1 mm thick.

Annealing: 1 hour in boiling water.

Test temperature: 20°C

Olsen stiffness: 2,600 kg/cm² (ASTM D 747)

Resistance to environmental stress-cracking:

F₅₀ > 1,000 hours (ASTM D 1693)

- 5 The polymer was molded by extrusion into pipe, 30 mm in diameter and 3 mm in wall thickness. The extrusion pressure was low. The molded product was desirable in appearance and excellent in physical properties such as impact resistance, environmental stress-cracking resistance, and the like.

Table 3

Example No.	Polymerization time (hour)	Solid catalyst component (mg)	Yield of polymer (kg)	Polymer production (g polymer per g solid catalyst component)
3-(2)-(a)	1	136	2.78	20400
3-(2)-(b)	1.5	115	3.12	27100
3-(2)-(c)	2	101	3.31	32800
3-(2)-(d)	2.5	112	4.27	38100
3-(2)-(e)	3	106	4.59	43300
3-(2)-(f)	3.5	89	4.28	48100

1 Comparative Example 3

Continuous two-stage polymerization was carried out in a manner similar to that in Example 3-(3), except that in the first stage reaction zone, the polymer production per unit weight of solid catalyst component was increased by increasing the concentrations of ethylene, butene-1 and hydrogen.

The continuous polymerization was carried out by using two loop-type reactors connected in series.

10 Both reactors were kept full with the liquid phase so as to exclude substantially the gas phase. To the first 250-liter reactor, were continuously fed 51 kg/hour of butane, 97 mmoles/hour of triethylaluminum, 680 mg/hour

1 of the solid catalyst component prepared in Example 3-(1),
and 22 kg/hour of ethylene. Butene-1 and hydrogen
were continuously fed so as to maintain the molar ratio
of ethylene : butene-1 : hydrogen in the liquid phase at
5 1 : 4.3 : 0.006. The temperature was maintained at 60°C
and the total pressure at 36 kg/cm².G. The concentrations
of ethylene, butene-1 and hydrogen in the liquid phase
were set at about 1.4 times those in the first reaction
zone of Example 3-(3). The polymer slurry was continuously
10 transferred by the pressure difference from the first
reactor to the second 500-liter reactor, while feeding
continuously to the second reactor 21 kg/hour of butane,
27 mmoles/hour of triethylaluminum, and 34 kg/hour of
ethylene. At the same time, 370 mg/hour of the solid
15 catalyst component prepared in Example 3-(1) was con-
tinuously fed in order to establish the same polymer
production ratio (45 : 55 by weight) of the first stage to
the second stage as that in Example 3-(3). Butene-1 and
hydrogen were also fed continuously so as to maintain the
20 molar ratio of ethylene : butene-1 : hydrogen in the liquid
phase at 1 : 1.2 : 0.08. The temperature was maintained at
60°C and the total pressure at 33 kg/cm².G. The concentra-
tions of ethylene, butene-1 and hydrogen in the liquid
phase were the same as those in the second reaction zone
25 of Example 3-(3). The polymer slurry was continuously
removed from the second reactor and the polymer was re-
covered and dried. The polymer yield was 50 kg/hour cor-
responding to an average polymer production of 47,600 g

1 per g of solid catalyst component. The polymer production
ratio of the first stage to the second stage was 45 : 55
by weight, as calculated from the material balance.
The average polymer production per g of solid catalyst
5 component in the first stage reaction zone was 33,100 g.
Properties of polymer: density, 0.921 g/cm^3 ; melt index,
1.0 g/10 minutes; MFR, 72; bulk density, 0.35 g/cm^3 .

The press-molded sheet of the polymer was
inferior in physical properties such as tensile-impact
10 strength and resistance to environmental stress-cracking
as shown below.

Tensile-impact strength: 123 kg-cm/cm^2

Olsen stiffness: 2640 kg/cm^2

Resistance to environmental stress-cracking:

530 hours (F₅₀)

The testing methods for these physical properties were
the same as in Example 3-(3).

The resulting polymer was molded by extrusion
15 into pipe, 30 mm in diameter and 3 mm in wall thickness.
Although the processability was good, the molded product
showed a great many fish-eyes and inferior appearance.
The physical properties were also inferior in impact
resistance and the like.

20 From the results of the present Comparative
Example, it is seen that if the average polymer production
per unit weight of the solid catalyst component in the
first stage exceeds 30,000-fold, it becomes necessary to

- 1 supply an additional amount of the solid catalyst compo-
nent to the second stage reaction zone to compensate
the declined rate of polymerization and the uniformity
of the polymer becomes inferior, leading to inferior
5 molded products.

Comparative Example 4

(1) Persistence test for polymerization activity.

The persistence test for polymerization activity
10 was performed in the same manner as in Example 3-(1)-(a)
to (f), except that the solid catalyst component prepared
in Comparative Example 2-(1) was used. The time t_1
required for the production of 30,000-fold polymer based
on the weight of solid catalyst component was 3.8 hours,
15 while the time t_2 required for the production of 40,000-
fold polymer was 9.1 hours. Therefore, the ratio t_2/t_1
was about 2.4.

(2) Continuous two-stage polymerization.

Using two loop-type reactors connected in series
20 and the solid catalyst component prepared above in Compara-
tive Example 2-(1), a continuous two-stage polymerization was
carried out under the same condition as similar to that of
Example 3-(3). Both reactors were kept full with the
liquid phase so as to exclude substantially the gas
25 phase. To the first 250-liter reactor, were continuously
charged 60 kg/hour of butane, 101 mmoles/hour of tri-
ethylaluminum, 1.3 g/hour of the solid catalyst component
prepared above in (1), and 19 kg/hour of ethylene.

1 Butene-1 and hydrogen were continuously fed so as to
maintain the molar ratio of ethylene : butene-1 : hydrogen
in the liquid phase at 1 : 4.3 : 0.006. The temperature and
the total pressure were maintained at 60°C and 36 kg/cm².G,
5 respectively. The polymer slurry was continuously trans-
ferred by the pressure difference from the first reactor
to the second 500-liter reactor while feeding continuously
to the second reactor 16 kg/hour of butane, 27 mmoles/hour
of triethylaluminum, and 29 kg/hour of ethylene. At the
10 same time, 0.79 g/hour of the solid catalyst component
prepared above in Comparative Example 2-(1) was con-
tinuously fed in order to establish the same polymer
production ratio (45 : 55 by weight) of the first stage to
the second stage as that in Example 3-(3). Butene-1 and
15 hydrogen were also fed so as to maintain the molar ratio of
ethylene : butene-1 : hydrogen in the liquid phase at
1 : 1.2 : 0.08. The temperature and the total pressure
were maintained at 60°C and 33 kg/cm².G. The polymer
slurry was continuously removed from the second reactor
20 and the polymer was recovered and dried. The polymer yield
was 44 kg/hour corresponding to an average polymer
production of 21,100 g per g of solid catalyst component.
The polymer production ratio of the first stage to the
second stage was 45 : 55 by weight, as calculated from the
25 material balance. The average polymer production per g
of solid catalyst component in the first stage reaction
zone was 15,200 g. Properties of polymer: density, 0.921
g/cm³, melt index, 1.2 g/10 min.; MFR, 71; bulk density,

1 0.32 g/cm³.

The press-molded sheet of the polymer was inferior in physical properties such as tensile-impact strength and resistance to environmental stress-cracking
5 as shown below.

Tensile-impact strength: 105 kg-cm/cm²

Olsen stiffness : 2,650 kg/cm²

Resistance to environmental stress-cracking:
340 hours (F₅₀)

The testing methods for these physical properties were the same as in Example 3-(3).

The polymer was molded by extrusion into pipe, 30 mm in diameter and 3 mm in wall thickness. Although
10 the processability was good, the molded product showed a great many fish-eyes and inferior appearance. The physical properties were also inferior in impact resistance and the like.

From the results of the present Comparative
15 Example, it is seen that if a solid catalyst component which does not meet the requirements for the persistence of polymerization activity was used, it becomes necessary to supply an additional amount of the solid catalyst component to the second stage reaction zone to compensate
20 the declined rate of polymerization and the uniformity of the polymer becomes inferior, leading to inferior molded products.

1 Example 4

(1) Persistence test for polymerization activity.

Using the solid catalyst component prepared in Example 3-(1), the persistence test for polymerization activity was performed under the conditions similar to those in the first stage reaction zone of the continuous two-stage polymerization described below in (2).

(1)-(a)

Into a 50-liter stainless steel autoclave, which had been thoroughly flashed with nitrogen, were charged 11.8 kg of butane, 0.70 kg of butene-1, and 17 mmoles of triethylaluminum. To the mixture, which had been heated to 60°C, was added ethylene to the total pressure of 10.5 kg/cm².G, followed by hydrogen until the ethylene-to-hydrogen molar ratio in the liquid phase had become 1 : 0.007. The ethylene-to-butene-1 molar ratio in the liquid phase was 1 : 1.2. The polymerization was initiated by adding 152 mg of the solid catalyst component prepared in Example 3-(1). The polymerization was allowed to continue for one hour at 60°C, while feeding ethylene continuously to keep the total pressure constant. The polymerization was then terminated with isopropyl alcohol. After releasing the butane and unreacted monomers, the polymer was dried in vacuo at 60°C. The yield of polymer was 2.84 kg, corresponding to 18,700 g per g of the solid catalyst component.

(1)-(b) to (g)

Polymerization was carried out under the same

1 conditions as described above in (1)-(a). The results
obtained were as shown in Table 4. In the polymerization
tests of (1)-(a) to (g), the molar ratio of ethylene :
butene-1 : hydrogen in the liquid phase was maintained at
5 1 : 1.2 : 0.007. By plotting the results of Table 4, a
curve representing the relationship between the polymeri-
zation time and the yield of polymer per unit weight of
the solid catalyst component was obtained as shown in
Fig. 4. From the curve, it is seen that the time t_1
10 required for the 30,000-fold polymer production based on
the weight of solid catalyst component was 2.0 hours and
the time t_2 required for the 40,000-fold polymer produc-
tion was 3.2 hours. Therefore, the ratio t_2/t_1 was about
1.6.

15 (2) Continuous two-stage polymerization.

The continuous two-stage polymerization was
carried out by using two loop-type reactors connected in
series. Both reactors were kept full with the liquid
phase so as to exclude substantially the gas phase. To
20 the first 250-liter reactor, were continuously fed 63
kg/hour of butane, 82 mmoles/hour of triethylaluminum,
1.0 g/hour of the solid catalyst component prepared in
Example 3-(1), and 26 kg/hour of ethylene. Butene-1 and
hydrogen were continuously fed so as to keep the molar
25 ratio of ethylene : butene-1 : hydrogen in the liquid
phase at 1 : 1.2 : 0.007. The temperature and the total
pressure were maintained at 60°C and 41 kg/cm².G, respec-
tively. The polymer slurry was continuously transferred

1 by the pressure difference from the first reactor to
the second 500-liter reactor, while feeding continuously
to the second reactor 10 kg/hour of butane, 13 mmole/
hour of triethylaluminum, and 34 kg/hour of ethylene.
5 Butene-1 and hydrogen were also continuously fed so as to
keep the molar ratio of ethylene : butene-1 : hydrogen
in the liquid phase at 1 : 0.35 : 0.12. The temperature
and the total pressure were maintained at 60°C and 41
kg/cm².G, respectively. The polymer slurry was continu-
10 ously withdrawn from the second reactor and the polymer
was recovered and dried. The continuous polymerization
was allowed to continue for 100 hours with satisfactory
operation control. The polymer yield was 44 kg/hour
corresponding to an average polymer production of 44,000
15 g per g of solid catalyst component. The polymer produc-
tion ratio of the first stage to the second stage was
50 : 50 by weight, as calculated from the material balance.
The average polymer production per g of solid catalyst
component {in the first and second stage was both 22,000 g.
0
20 Properties } of polymer: density, 0.938 g/cm³; melt index,
0.20 g/10 min.; MFR, 90; bulk density, 0.47 g/cm³.

By using a crosshead circular die, the polymer
obtained above was coated on a steel pipe, 12 inches in
outer diameter, to a thickness of 3 mm. The coating
25 operation was very smooth and the coating layer was excel-
lent in low-temperature resistance, impact resistance,
and resistance to environmental stress-cracking.

Table 4

Example No.	Polymerization time (hour)	Solid catalyst component (mg)	Yield of polymer (kg)	Polymer productivity (g polymer per g solid catalyst component)
4-(1)-(a)	1	152	2.84	18700
4-(1)-(b)	1.5	133	3.27	24600
4-(1)-(c)	2	115	3.43	29800
4-(1)-(d)	2.5	120	4.11	34300
4-(1)-(e)	3	110	4.23	38500
4-(1)-(f)	3.5	94	4.03	42900
4-(1)-(g)	4	93	4.34	46700



CLAIMS:

1. A multistage polymerization process for producing an ethylene polymer by the slurry-type polymerization of ethylene or ethylene and another olefin using a catalyst system comprising a high-activity supported Ziegler catalyst component and an organometallic compound component and hydrogen as molecular weight regulator in two or more reaction zones connected in series and kept full with the liquid phase substantially to exclude the gas phase, in

10 which:

(i) either (a) a Ziegler catalyst component whose activity is defined by the formula

$$t_2/t_1 < 2$$

(where t_1 and t_2 are the time required to produce an ethylene polymer amounting, respectively, to 30,000 and 40,000 times the weight of Ziegler catalyst component in a polymerization test performed under the same conditions as in the first stage reaction zone of the multistage polymerization) is used to obtain an ethylene polymer having a density below 0.945 g/cm^3 , or (b) a Ziegler catalyst component whose activity is defined by the formula

$$t_2/t_1 < 2$$

(where t_1 and t_2 are the time required to produce an ethylene polymer amounting, respectively, to 15,000 and 20,000 times the weight of Ziegler catalyst component in a polymerization test performed under the same conditions as in



the first stage reaction zone of the multistage polymerization) is used to obtain an ethylene polymer having a density of 0.945 g/cm^3 or above;

(ii) the catalyst system is fed continuously to the first stage reaction zone, the polymerization proceeds under the application of pressure in the presence or absence of hydrogen to produce higher molecular-weight polymer particles, the resulting polymer slurry is withdrawn continuously and transferred to the second stage reaction zone where the polymerization is further continued with a hydrogen-to-ethylene ratio larger than that in the first stage reaction zone to produce a polymer having a molecular weight lower than that of the polymer formed in the first stage: if desired, the polymerization is continued in a similar manner in a third and optionally following stages;

(iii) the average amount of polymer produced in each stage, except for the final stage, is kept either (a) below 30,000 times the weight of Ziegler catalyst component, to obtain a polymer having a density below 0.945 g/cm^3 , or (b) at or below 15,000 times the weight of Ziegler catalyst component, to obtain a polymer having a density of 0.945 g/cm^3 or above, the intrinsic viscosity of the polymer produced being from 2 to 10 d l/g in the first stage and 0.2 to 1.5 d l/g in the second stage;

(iv) the amount of polymer formed in each stage is selected so as to keep the average amount of polymer produced after completion of the multistage polymerization at 5,000 or more times the weight of Ziegler catalyst



component, the amount formed in the first stage being from 5 to 80% by weight of the total polymer; and

(v) the amount of said other olefin copolymerized in the copolymer is 15 mole % or less.

5 2. A process according to claim 1, wherein the first stage reactor is a loop reactor.

3. A process according to claim 1 or claim 2, wherein the second stage reactor is a loop reactor.

4. A process according to any one of the preceding 10 claims, wherein the Ziegler catalyst component satisfies the formula $t_2/t_1 < 1.7$, where t_1 and t_2 are as defined in claim 1.

5. A process according to any one of the preceding claims, wherein said other olefin is propylene, butene-1, pentene-1, 15 hexene-1, octene-1 or 4-methylpentene-1.

6. A process according to any one of the preceding claims, wherein the polymerization temperature is from ambient temperature to 120°C.

7. A process according to any one of the preceding claims, 20 wherein the polymerization pressure is from 1 to 100 kg/cm².

8. A process according to any one of the preceding claims,

62



wherein the concentration of Ziegler catalyst component in both the first and second stage reaction zones is from 0.001 to 0.1 millimoles in terms of transition metal atom per litre of the solvent.

5 9. A process according to any one of the preceding claims, wherein the amount of the organometallic compound component is from 0.5 to 500 mole equivalent of the transition metal atom contained in the Ziegler catalyst component.

10 10. A process according to any one of the preceding claims, wherein the carrier for the Ziegler catalyst component is magnesium oxide, titanium oxide, silica, alumina, magnesium carbonate, a hydroxychloride of a divalent metal, magnesium hydroxide, magnesium chloride,
15 a magnesium alkoxide, a magnesium haloalkoxide, a double oxide of magnesium and aluminium, or a double oxide of magnesium and calcium.

11. A process according to claim 10, wherein the carrier is a magnesium compound.

20 12. A process according to any one of the preceding claims, wherein the transition metal compound supported on the carrier of the Ziegler catalyst component is titanium tetrachloride, titanium tetrabromide, titanium



63

tetraiodide, titanium trichloride, a compound of formula $Ti(OR^1)_{(4-p)}X_p$ (wherein R^1 represents a hydrocarbon group, X represents a halogen atom, and p is a number such that $0 \leq p < 4$), vanadium tetrachloride, 5 vanadium oxytrichloride, zirconium tetrachloride, a compound of formula $Zr(OR^2)_{(4-q)}X_q$ (where R^2 represents a hydrocarbon group, X represents a halogen atom, and q is a number such that $0 \leq q < 4$).

13. A process according to any one of the preceding 10 claims, wherein the Ziegler catalyst component is a reaction product of an organomagnesium compound and a transition metal compound of formula $Ti(OR^3)_{(4-r)}X_r$, wherein R^3 represents a hydrocarbon group, X represents a halogen atom, and r is a number such that $0 \leq r \leq 4$.

15 14. A process according to any one of the preceding claims, wherein said organometallic compound is one or more of triethylaluminium, tripropylaluminium, triisobutylaluminium, tributylaluminium, trihexylaluminium diethylaluminium monochloride, dipropylaluminium monochloride, 20 diisobutylaluminium monochloride, dibutylaluminium monochloride, dihexylaluminium monochloride, ethylaluminium dichloride, propylaluminium dichloride, isobutylaluminium dichloride, utylaluminium dichloride, hexylaluminium dichloride, ethylaluminium sesquichloride, propylaluminium 25 sesquichloride, isobutylaluminium sesquichloride, butylaluminium sesquichloride, hexylaluminium sesquichloride, and organozinc compounds.