

DESCRIPTION"ETHYLENE- α -OLEFIN COPOLYMER COMPOSITION"

1 The present invention relates to an ethylene-
 α -olefin copolymer composition. More particularly, the
 present invention relates to ethylene- α -olefin copolymer
 compositions excellent in processability, impact strength,
5 tensile strength, environmental stress cracking resist-
 ance, low temperature resistance, creep characteristics,
 tear strength, transparency, heat-sealing characteristics
 and chemical characteristics such as chemicals resistance,
 which is obtained by mixing an ethylene- α -olefin copolymer
10 of a relatively higher molecular weight and an ethylene-
 α -olefin copolymer of a relatively lower molecular weight.

 Being excellent in melt rheology characteristics
 as well as in physical and chemical properties, low
 density polyethylenes manufactured by the high pressure
15 method (hereinafter referred to as "high pressure poly-
 ethylene") have been used for various uses such as films,
 sheets, pipes, blow bottles, injection molded products,
 coating materials for steel pipes and foam-molded ma-
 terials. As mentioned above, high pressure polyethylenes
20 are excellent in melt rheology characteristics, and
 therefore, they are excellent in processability.

 When used for extrusion processing or injection molding,
 their production efficiency is high, resulting in rela-
 tively low electricity consumption. In blown film proces-
25 sing, the above polyethylenes give good bubble stability.

- 1 In cast film processing and extrusion lamination processing, there is only slight neck-in. In blow molding, these polyethylenes give good parison stability. However, when they are processed into molded products,
- 5 their mechanical strengths, such as tensile strength and impact strength, are relatively low and accordingly these products can not be used in thin forms.

High pressure polyethylenes have various other problems. They are used in many fields as films. Films

10 of high pressure polyethylenes are required to have the following properties in recent, highly developed automatic packaging systems.

- (1) Good heat-sealing property at low temperatures.
- (2) High sealing strength in a condition where

15 heat-sealed portions are not cooled sufficiently therefore not solidified yet (this strength is called "hot tack" strength). Hot tack strength is required because filling of contents and heat sealing are done almost at the same time.

- (3) Sealing strength in a state where heat-sealing

20 portions are contaminated with oils and the like, in packaging of oils and the like. (This strength is called heat sealing strength in contaminated condition.) However, high pressure polyethylenes are not satisfactory

25 in hot tack and heat sealing strength in contaminated condition. When these polyethylenes are used in blow bottles, pipes and injection molded products, they are inadequate in environmental stress cracking resistance,

1 therefore, cause occasional troubles and are susceptible
to attack by chlorine water. Further, they are not
sufficient in creep characteristics, which makes them
unusable in pipes of high internal pressure. When high
5 pressure polyethylenes are used as coating materials for
steel pipes, their low temperature resistance is not
satisfactory, which makes their use in very cold climatic
areas improper. In their use as coating materials for
electric wires, troubles occur at times due to improper
10 environmental stress cracking resistance and water-tree
resistance.

To improve these defects, some attempts have
been made. However, the quality is still not at
a satisfactory level.

15 For improvement of these defects,
the following polymerisation methods have been
adopted.

(1) Polymerization of ethylene and other polymeriz-
able monomer such as vinyl acetate.

20 (2) Method in which ethylene and acrylic acid (or
methacrylic acid) are polymerized followed by conversion
to a salt with a metal, namely an ionomer.

The former method still has many problems such
as (a) reduction of tear strength, rigidity and heat
25 resistance of films, (b) occurrence of corrosion of
extruder and smell in processing due to liberation of
acetic acid and (c) occurrence of blocking due to sticky
film surface and cold flow. The latter method has

- 1 problems of reduction of thermal stability and weather resistance and of high cost.

Also for improvement of the defects of high pressure polyethylenes, there were made proposals in
5 which a high pressure polyethylene is mixed with another α -olefin polymer such as high density polyethylene, polypropylene, polybutene, or a rubber. However, an improvement in one defect causes another problem and no satisfactory answer has been attained.

- 10 As resins which have low densities about equal to those of high pressure polyethylenes, there are known resins which are prepared by co-polymerizing ethylene and an α -olefin under a medium to low pressure using a transition metal catalyst. Hereinafter, such are abbreviated
15 as "ethylene- α -olefin copolymers"). The copolymers produced with a vanadium catalyst are low in degree of crystallization, and have problems in heat resistance, weather resistance and mechanical strengths. The ethylene- α -olefin copolymers produced under normal poly-
20 merization conditions with a titanium catalyst, having generally narrow molecular weight distributions (narrower than those of high pressure polyethylenes), are relatively excellent in mechanical strengths but poor in melt rheology characteristics and have many problems in
25 processing. In blown film processing, a large quantity of electricity is needed, output is reduced or bubble stability is lost. In high speed processing, "shark skin" appears on film surfaces, thereby decreasing product values.

1 Also in blow molding, parison stability is lost, or
surfaces of molded products turn to "shark skin" and pro-
duct values are lost. In injection molding, processing
temperatures need to be largely raised because of poorer
5 flow property under high pressures as compared with high
pressure polyethylenes, which requires more heat energy
and moreover causes resin deterioration.

Trials have been made in recent years for
solving these problems by improving extruders, screws
10 and dies. These approaches require a large amount of
expenditures and moreover techniques have not been fully
developed. Further, various other problems such as the
following have been encountered.

(1) with respect to mechanical strengths of films
15 produced, balancing of machine direction (MD) and trans-
verse direction (TD) is difficult and the tear strength
of MD is poorer than that of high pressure polyethylenes,
and

(2) film transparency is inferior to that of high
20 pressure polyethylenes, because the ethylene- α -olefin
copolymer of narrow molecular weight distribution has a
faster crystallization speed than high pressure poly-
ethylenes and causes melt fracture more easily.

Low density ethylene- α -olefin copolymers are
25 difficult to obtain under normal polymerization conditions
using a chromium catalyst, because copolymerizability
between ethylene and α -olefin is generally lower with
chromium catalysts than with titanium catalysts. When

1 a chromium-titanium catalyst is used in order to overcome
this problem, ethylene- α -olefin copolymers obtained have
wider molecular weight distributions than copolymers
produced with a titanium catalyst and have slightly im-
5 proved processability. However, their mechanical strengths
largely worsen and their physical properties are not much
different from those of high pressure polyethylenes and
these copolymers provide film sheets and bottles inferior
in transparency.

10 For attempting to improve the transparency of these
copolymers, when the quantity of an α -olefin is largely
increased in polymerisation and the density of the copoly-
mer obtained is reduced, only a sticky copolymer having
much deteriorated mechanical strengths is produced.

15 According to the knowledge of the present in-
ventors, ethylene- α -olefin copolymers polymerized under
a medium to low pressure using a transition metal cata-
lyst, have non-uniform component distributions. Namely
in these copolymers, the number of short chain branching
20 per 1000 carbon atoms (excluding methyl groups at the
ends) (hereinafter referred to as "S.C.B." for brevity)
varies depending upon molecular weight, and generally
lower molecular weight components have larger S.C.B. and
higher molecular weight components have smaller S.C.B.
25 This phenomenon is considered to be due to that α -olefins
tend to act as a chain transfer agent or act even to
active sites of catalyst to which molecular weight
regulators such as hydrogen tend to act. (cf. Reference

1 example 1.)

Because of the above phenomenon, ethylene- α -olefin copolymers polymerized with the α -olefin concentration increased with an aim to reduce to a large extent the density of copolymers produced, only give such products as those having increased S.C.B. in their lower molecular weight components, thereby having increased solubility in solvents and poor mechanical strengths and causing surface stickiness. This tendency is particularly remarkable in those ethylene- α -olefin copolymers which are polymerized with a catalyst giving wider molecular weight distributions. One of the reasons for poor mechanical strengths of ethylene- α -olefin copolymers having wide molecular weight distributions will be explained by the above fact.

As described above, ethylene- α -olefin copolymers having densities about equal to those of high pressure polyethylenes and synthesized under a medium to low pressure with a transition metal catalyst, cannot satisfy all the requirements of processability, mechanical strengths and transparency. For instance, lowering of molecular weight for improvement of processability results in large reduction in mechanical strengths and disappearance of said copolymer characteristics. Broadening of molecular weight distribution leads to large reduction in mechanical strengths as well (cf. Reference example 2.), and moreover transparency worsens and surfaces of molded products get sticky. Thus, both of processability and physical

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1 properties are not met together yet, and any low density ethylene- α -olefin copolymer excellent in processability and mechanical strengths have not yet been provided.

As described above, high pressure polyethylenes
5 are excellent in rheology characteristics and processability but relatively poor in mechanical strengths. On the other hand, ethylene- α -olefin copolymers polymerized under a medium to low pressure with a transition metal catalyst and having densities about equal to those of
10 high pressure polyethylenes, have excellent mechanical strengths due to their narrower molecular weight distributions but are poor in processability. These property differences are considered to originate from molecular structures of polymers.

15 High pressure polyethylenes are obtained from radical polymerization under a pressure of about 1500 to 4000 kg/cm² at a temperature of about 150° to 350°C in an autoclave or a tubular reactor. Their molecular structures are very complicated and, in spite of being
20 homopolymers of ethylene, have short chain branches which are alkyl groups of 1 to 6 carbon atoms. These short chain branches affect crystallinities and therefore densities of polymers. The distribution of short chain branching of high pressure polyethylenes is relatively
25 even, and both lower molecular weight components and higher molecular weight components have almost similar numbers of branches.

Another important feature of high pressure

1 polyethylenes is that the polyethylenes also have long
chain branches in complicated structures. Identification
of these long chain branches is difficult, but these
branches are considered to be alkyl groups of which
5 lengths vary from about lengths of main chains to lengths
having carbon atoms of over several thousands. The pre-
sence of these long chain branches largely affects melt
rheology characteristics of polymers and this is one of the
reasons for the excellent processability of high pressure
10 method polyethylenes.

On the other hand, ethylene- α -olefin copolymers
synthesized under a medium to low pressure with a transi-
tion metal catalyst and having densities about equal to
those of high pressure polyethylenes, are obtained by co-
15 polymerizing ethylene and an α -olefin under a medium to
low pressure of about 5 to 150 kg/cm² and at 0° - 250°C
normally at a relatively low temperature of 30° to 200°C
with a transition metal catalyst in an autoclave or a
tubular reactor. Their molecular structures are relatively
20 simple. These ethylene- α -olefin copolymers seldom possess
long chain branches and have only short chain branches.
These short chain branches are not formed through compli-
cated reaction processes as so in high pressure poly-
ethylenes, but are controlled by the kind of an α -olefin
25 to be used in the copolymerization. As an example, in a
copolymerization between ethylene and butene-1, short
chain branches formed are normally ethyl branches. These
branches could be hexyl branches as a result of dimeriza-

tion of butene-1. Short chain branches formed control crystallinities and densities of polymers.

Distribution of short chain branches is also affected by the nature of a transition metal catalyst used in the copolymerization, the type of polymerization and the temperature of polymerization. Different from the case of high pressure polyethylenes, the distribution is wide. Namely, as a general trend, lower molecular weight components have larger S.C.B. and higher molecular weight components have smaller S.C.B. (cf. Reference example 1.)

Ethylene- α -olefin copolymers obtained by copolymerizing ethylene and an α -olefin under a medium to low pressure with a transition metal catalyst and having densities about equal to those of high pressure polyethylenes, have come to be practically used. Therefore, the conventional classification that polyethylene resins having densities of 0.910 to 0.935 g/cm³ fall in a category of high pressure polyethylenes, is improper and a new classification should be developed, mainly based on whether or not a polymer or resin has long chain branches. As low density polyethylenes substantially not having long chain branches, there are resins which are obtained by polymerization using a transition metal catalyst under a same high pressure and temperature as employed in the manufacture of high pressure method polyethylenes. These resins are also included in "ethylene- α -olefin copolymers" as defined by the present invention.

1 Presence or absence of long chain branches is
clarified to a considerable extent by a theory of solu-
tion. As an example, the presence of long chain branches
in an ethylene polymer can be known by using $[\eta]/[\eta]_g$
5 namely g^*_η . Herein, $[\eta]$ is the intrinsic viscosity of the
ethylene polymer, and $[\eta]_g$ is the intrinsic viscosity of
a reference linear polyethylene (high density poly-
ethylene produced from homopolymerization of ethylene
under a medium to low pressure with a Ziegler catalyst)
10 having the same weight average molecular weight by the
light scattering method. Molecules having more long
chain branches have less spread in a solution, and there-
fore, their g^*_η is small. Normally, g^*_η of high pressure
polyethylenes is 0.6 or less.

15 This method is useful, but practically presence
of long chain branches can be known more easily and
clearly by a correlation between melt index and intrinsic
viscosity of polymer. This correlation was shown in
Reference example 3. In there, the intrinsic viscosity
20 of a high pressure polyethylene is far lower than that
of the ethylene- α -olefin copolymer according to medium
to low pressure method having the same melt index,
because the former polyethylene has long chain branches.

25 Due to the difference of presence or absence of
long chain branches, high pressure polyethylenes and
ethylene- α -olefin copolymers give largely different
properties in melt rheology characteristics, crystallini-
ty, solid mechanical properties and optical properties.

1 The present inventors made strenuous efforts
with an aim to obtain polyethylenes which will solve the
above-mentioned defects of polyethylenes, will have
processability equal to or better than that of high
5 pressure polyethylenes, and will be excellent in tear
strength, impact strength, environmental stress cracking
resistance, low temperature resistance, creep character-
istics, chemicals resistance, transparency and heat-
sealing characteristics. As a result, the present in-
10 ventors have found that, by mixing (a) an ethylene- α -
olefin copolymer having a relatively higher molecular
weight and of which density, intrinsic viscosity, S.C.B.,
kind of α -olefin and (weight average molecular weight)/
(number average molecular weight) are specified and (b)
15 another ethylene- α -olefin copolymer having a relatively
lower molecular weight and of which density, intrinsic
viscosity, S.C.B., kind of α -olefin and (weight average
molecular weight)/(number average molecular weight) are
specified, in such a way that the ratio of S.C.B. of the
20 former copolymer over S.C.B. of the latter copolymer is
in a specified range, ethylene copolymer compositions can be
obtained which have extremely good processability
compared with the conventional polyethylenes, as
well as very excellent physical and chemical properties
25 such as tear strength, impact strength, environmental
stress cracking resistance, low temperature resistance,
creep characteristics, chemicals resistance, transparency,
and heat-sealing characteristics. The present inventors

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have also found that ethylene- α -olefin copolymer compositions substantially not having long chain branches and having a specific distribution of S.C.B. provide extremely good properties such as tensile strength, impact strength,
5 environmental stress cracking resistance, low temperature resistance, creep characteristics, chemicals resistance, transparency and heat-sealing characteristics, compared with the conventional polyethylenes, and therefore, with such ethylene- α -olefin copolymer compositions, improvement of
10 processability by broadening of molecular weight distribution can be attained without deterioration of properties described above. Thus, the present invention has been achieved.

According to the present invention, there is provided an ethylene- α -olefin copolymer composition excellent
15 in transparency and strength and having a density of 0.915 to 0.929 g/cm³, a melt index of 0.02 to 50 g/10 min. and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of an ethylene- α -olefin copolymer A and 90 to 30% by weight of ethylene- α -olefin copolymer B; said copolymer A having a
20 higher molecular weight than copolymer B and being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g, and a short chain branching ("S.C.B.") number per 1000 carbon atoms of 7 to 40 and a
25 (weight average molecular weight)/(number average

molecular weight) value of 2 to 10; said copolymer B being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.949 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g, and S.C.B. of 5 to 35 and a
5 (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said copolymer A and said copolymer B being chosen such that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is 0.6 to 1.7.

The present invention also provides a composition
10 of copolymers of ethylene and an α -olefin of 3 to 18 carbon atoms, having first and second component groups, said first component group having a higher molecular weight than said second component group, having the following properties:

- (1) density of 0.915 to 0.929 g/cm³
- 15 (2) intrinsic viscosity $[\eta]$ of 0.7 to 4.0 dl/g,
- (3) melt index of 0.02 to 50 g/10 min,
- (4) S.C.B. being 5 to 45,
- (5) $[\eta]/[\eta]_L$ namely g_n^* being at least 0.8, where $[\eta]_L$ is an intrinsic viscosity of a linear polyethylene having the
20 same weight average molecular weight measured by a light scattering method, and
- (6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being 0.6 to 0.8, wherein these two component groups are
25 obtained by consolidating fractions obtained by column fractionation in two portions of lower and higher molecular

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weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio of lower and higher molecular weight components obtained in the gas permeation chromatography (GPC) curve,

5 (7) the second components have a density of 0.910 to 0.949 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g and S.C.B of 5 to 35,

(8) the first components have a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g and
10 S.C.B of 7 to 40, and

(9) the second components are 30 to 90% by weight and the first components are 70 to 10% by weight.

The first feature of this invention is to provide an ethylene copolymer composition of which processability is
15 about equal to or better than that of high pressure polyethylenes and of which physical and chemical properties such as tensile strength, impact strength, environmental stress cracking resistance, creep characteristics, tear strength, transparency, heat-sealing characteristics and
20 chemicals resistance are very excellent.

1 The second feature of this invention is that,
because the product of this invention is excellent in
mechanical strengths, has a rigidity higher than those
of high pressure polyethylenes and has a transparency
5 about equal to that of high pressure polyethylenes,
material saving can be expected with the product of this
invention; for instance, when this product is used for
films, the same performance can be obtained with the
thickness 10 to 20% thinner than that of high pressure
10 polyethylenes.

 The third feature of this invention is that,
because the product of this invention has extrusion
processability superior to that of relatively low densi-
ty ethylene- α -olefin copolymers by the conventional
15 technique, conventional extruders being used for high
pressure polyethylenes can be utilized for the present
product without any modification.

 The fourth feature of this invention is that,
because the present product, even if possessing a melt
20 index lower than that of low density ethylene- α -olefin
copolymers by the conventional technique, shows satis-
factory flow properties in actual processing, it gives
excellent bubble stability and mechanical strengths of
machine and transverse directions can be easily balanced,
25 whereby molded products can have a uniform quality.

 The fifth feature of this invention is that,
because a resin composition less sticky than low density
ethylene- α -olefin copolymers by the conventional

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1 technique is obtained even when the density of the composition is lowered, the composition can be applied even for the usages where transparency, flexibility and impact characteristics are required.

5 In the attached drawings, Figs. 1 to ⁵ show curves of molecular weight distributions obtained from gel permeation chromatography. Broken lines in these figures are for dividing lower molecular weight components and higher molecular weight components into two respective
10 territories.

Fig. ⁶ is a typical example showing "distribution of S.C.B. against molecular weight" of an ethylene- α -olefin copolymer of the conventional technique.

Fig. ⁷ shows correlations between melt indices
15 (MI) and tensile impact strengths of ethylene- α -olefin copolymers of the conventional technique, with their melt flow ratios (MFR) used as a parameter.

Fig. ⁸ shows correlations between MI and intrinsic viscosities $[\eta]$ of a high pressure polyethylene
20 and a linear polyethylene of the medium to low pressure method as a method for distinguishing these two polymers. In the figure, a broken line is drawn to separate two territories, the left side territory is for the high pressure polyethylene of the conventional technique and
25 the right side territory is for the linear polyethylene of the medium to low pressure method.

The present invention will be explained in more detail below.

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1 An ethylene- α -olefin copolymer of a relatively
high molecular weight (hereinafter referred to as "co-
polymer A") which is used in the present invention as
one mixing component, is a copolymer of ethylene and an
5 α -olefin of 3 to 18 carbon atoms. This α -olefin is one
represented by the general formula $R-CH=CH_2$ wherein R
is an alkyl group of 1 to 16 carbon atoms. Examples of
the α -olefin include propylene, butene-1, pentene-1,
hexene-1, heptene-1, octene-1, nonene-1, decene-1, 4-
10 methyl-pentene-1, 4-methyl-hexene-1 and 4, 4-dimethyl-
pentene-1. Among these olefins, α -olefins of at least
4 carbon atoms are preferred. Particularly, butene-1,
pentene-1, hexene-1, octene-1 and 4-methyl-pentene-1 are
preferred from the standpoints of monomer availability,
15 copolymerizability and quality of polymer obtained.
These α -olefins can be used alone or in combinations of
two or more. The density of the copolymer A is influenced
by the kind of an α -olefin used, the content of the
olefin and the intrinsic viscosity of the copolymer.
20 For the object of this invention, the density is required
to be 0.895 to 0.935 g/cm³ and more preferably 0.895 to
0.930 g/cm³. At a density smaller than 0.895 g/cm³,
copolymers stick to the reactor walls making polymeri-
zation difficult, or, the density of the relatively
25 lower molecular weight copolymer (namely "copolymer B"
which is described later and used as another mixing
component in the present invention) is required to be
raised, resulting in formation of polymer compositions

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1 of undesirable qualities such as films of poor trans-
parency. In the density higher than 0.935 g/cm^3 , the
content of the α -olefin in the copolymer A becomes very
low, and the copolymer A of such a high density does
5 not give satisfactory mechanical strengths. For instance,
in films, balancing of MD and TD strengths becomes
difficult and heat-sealing characteristics get worse.
S.C.B. in the copolymer A is 7 to 40 and more
preferably 10 to 40. (When R in the above α -olefin
10 formula is a linear alkyl group, the number of methyl
groups at branch ends per 1000 carbon atoms is S.C.B.
When R is an alkyl group with a branch or branches, for
instance, the α -olefin is 4-methyl-pentene-1, the branch
is isobutyl group and the half number of methyl groups
15 at the branch ends is S.C.B.) Short chain branching in
ethylene- α -olefin copolymers occurs due to α -olefins and
it hinders crystallization mainly of ethylene sequences
and lowers densities. These effects vary depending upon
the kind of α -olefin. Short chain branching is con-
20 sidered to also make some contribution to formation of
interlamella molecules, and ultimately affects mechanical
strengths and thermal properties of copolymers obtained.
Therefore, when S.C.B. is below 7, mechanical strengths
and heat-sealing properties of the composition become
25 poor. For instance, in films, balancing of MD and TD
strengths is difficult. When S.C.B. is over 40, there
occur problems in polymerization of the copolymer A.
Also the transparency of polymer compositions obtained

1 from the copolymer becomes poor.

The molecular weight of the copolymer A is 1.2 to 6.0 dl/g as intrinsic viscosity and is preferred to be 1.2 to 4.5 dl/g.

5 When the intrinsic viscosity is below 1.2 dl/g, mechanical strengths of polymer compositions of the present invention are reduced. In over 6.0 dl/g, mixing with the copolymer B becomes difficult, and polymer compositions obtained have fish eyes and further
10 worsened flow properties, as well as reduced transparency. In injection molding, the intrinsic viscosity is preferably 1.2 to 4.0 dl/g and more preferably 1.2 to 3.0 dl/g. If it is less than 1.2 dl/g, mechanical strengths of compositions are lowered. If it is over 4.0 dl/g,
15 mixing with the copolymer B becomes insufficient, and polymer compositions obtained have fish eyes, deteriorated flow properties (tend to cause flow marks) and reduced transparency.

(Weight average molecular weight)/(number
20 average molecular weight) of the copolymer A which is a measure for the molecular weight distribution of the copolymer obtained from gel permeation chromatography (hereinafter abbreviated as "GPC"), is preferably
3 to 8. More generally, if it is less than 2,
25 such a copolymer A is difficult to produce; if it is over 10, polymer compositions have lower mechanical strengths and, when processed into films, cause blocking.

An ethylene- α -olefin copolymer of a relatively

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low molecular weight (hereinafter abbreviated as "copolymer B") which is used in the present invention as another mixing component, is a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms. As

5 α -olefins, there may be selected the α -olefins used in the copolymer A. The density of the copolymer B is 0.910 to 0.949 g/cm³, and preferably it is at least 0.915 g/cm³. When the density is below 0.910 /cm³, the copolymer compositions possess reduced mechanical strengths and cause blocking due
10 to bleeding of lower molecular weight components of low density on film surfaces. In the area of injection molding, the density of the copolymer B is 0.910 to 0.949 g/cm³ and is preferred to be 0.915 to 0.948 g/cm³. When the density is below 0.910 g/cm³ mechanical strengths of compositions are
15 reduced and surface tackiness occurs. S.C.B of the copolymer B is 5 to 35 and is preferred to be 7 to 30. When S.C.B is below 5, the copolymer B has a lower molecular weight as a whole and its crystallization speed is fast, resulting in poor transparency of compositions. In case of over 35,
20 reduction in mechanical strengths as well as blocking in films occurs.

The molecular weight of the copolymer B is 0.3 to 1.5 dl/g, preferably 0.4 to 1.5 dl/g as intrinsic

1 viscosity. When the intrinsic viscosity is less than
0.3 dl/g, mechanical strengths and transparency of com-
positions are reduced. In case of over 1.5 dl/g,
fluidity of compositions is poor. In the area of injec-
5 tion molding, the molecular weight of the copolymer B
is preferably 0.3 to 1.2 dl/g as intrinsic viscosity
and more preferably 0.4 to 1.2 dl/g. When the intrinsic
viscosity is below 0.3 dl/g, mechanical strengths and
transparency of compositions are reduced. In case of
10 over 1.2 dl/g, fluidity of compositions is poor.

The value of (weight average molecular weight)/
(number average molecular weight), namely, $\bar{M}_w/\bar{M}_n$ of the
copolymer B determined by gel permeation chromatography
(GPC) is 3 to 8. More generally, when
15 $\bar{M}_w/\bar{M}_n$ is below 2, the copolymer B is difficult to
produce; when over 10, mechanical strengths of the
compositions are reduced and surface tackiness of films
occurs.

The copolymer A and the copolymer B as men-
20 tioned above can be obtained by copolymerizing ethylene
and an α -olefin of 3 to 18 carbon atoms under a medium
to low pressure using a transition metal catalyst.
For instance, catalysts such as Ziegler type catalyst
and Phillips type catalyst as well as polymerization
25 methods such as slurry polymerization, gas phase poly-
merization and solution polymerization are used. As
catalysts, a Ziegler type catalyst system using a
carrier-supported Ziegler catalyst component is

1 convenient in this invention from its activity and co-
polymerizability. Specific examples of an effective
carrier of this carrier-supported Ziegler catalyst
component include oxides, hydroxides, chlorides and
5 carbonates of metals and silicon and their mixtures as
well as inorganic complexes. More specifically, they
are magnesium oxides, titanium oxides, silica, alumina,
magnesium carbonates, divalent metal hydroxychlorides,
magnesium hydroxides, magnesium chlorides, magnesium
10 alkoxides, magnesium haloalkoxides, double oxides of
magnesium and aluminum and double oxides of magnesium
and calcium. Among these compounds, magnesium com-
pounds are particularly preferred. The following magne-
sium compounds are particularly preferred. The following
15 magnesium compound carrier is most preferred in the
production of the low density polyethylene type resin
composition of this invention, because it gives a satis-
factory slurry with no abnormal tackiness and there
occurs no sticking of polymers to the reactor wall.
20 (Reference is made to Japanese Patent Publication No.
23561/1980.) Namely, it is the carrier obtained by (a)
reacting in a solvent an aluminum halide represented by
the general formula R_nAlX_{3-n} (R is an alkyl, aryl or
alkenyl group of 1 to 20 carbon atoms and X is a halogen
25 atom and n is an integer of 0 to 3) and/or a silicon
halide represented by the general formula R'_mSiX_{4-m} (R'
is an alkyl, aryl or alkenyl group of 1 to 20 carbon
atoms and X is a halogen atom and m is an integer of 0

- 1 to 4) with an organomagnesium compound represented by the
general formulas $R^{\prime\prime}MgX$ and/or $R_2^{\prime\prime}Mg$ ($R^{\prime\prime}$ is an alkyl,
aryl or alkenyl group of 1 to 20 carbon atoms and X is
a halogen atom), and (b) isolating the solid product
5 formed.

As a transition metal catalyst component supported on carriers, there are, for instance, titanium compounds, vanadium compounds and zirconium compounds. Specific examples include titanium tetrachloride,
10 titanium tetrabromide, titanium tetraiodide, titanium trichloride, titanium alkoxy halides or titanium aryloxy halides represented by the general formula $Ti(OR^1)_{4-p}X_p$ (where R^1 is a hydrocarbon group, X is a halogen atom and p is an integer of $0 < p < 4$), vanadium tetra-
15 chloride, vanadium oxy trichloride, zirconium tetrachloride and zirconium alkoxy halides or zirconium aryloxy halides represented by the general formula $Zr(OR^2)_{4-q}X_q$ (where R^2 is a hydrocarbon group, X is a halogen atom and q is an integer of $0 < q < 4$). Among
20 these compounds, titanium compounds and/or vanadium compounds are particularly preferred in the production of the low density polyethylene type resin composition of this invention, because they give satisfactory slurries with no abnormal tackiness and there occurs almost no
25 sticking of polymers to the reactor wall. (Reference is made to Japanese Patent Publication No.23561/1980.) Titanium compounds are most preferred from the standpoints of weather resistance and heat resistance.

44

1 As a component of carrier-supported Ziegler
catalysts used in this invention, there are also reaction
products between an organomagnesium compound and a
transition metal compound. Here, the transition metal
5 compound is represented by the general formula
 $Ti(OR^3)_{4-r}X_r$ (where R^3 is a hydrocarbon group, X is a
halogen atom and r is an integer of $0 \leq r \leq 4$, and
includes titanium tetrahalides, titanium alkoxides,
titanium aryloxides, titanium alkoxy halides and titanium
10 aryloxy halides.

As an organometal compound component which
forms the catalyst system of this invention together with
the carrier-supported Ziegler catalyst component, there
are organoaluminum compounds such as trialkyl aluminums
15 (triethyl aluminum, tri-n-propyl aluminum, tri-i-butyl
aluminum, tri-n-butyl aluminum, tri-n-hexyl aluminum,
etc.), dialkyl aluminum monohalides (diethyl aluminum
monochloride, di-n-propyl aluminum monochloride, di-i-
butyl aluminum monochloride, di-n-butyl aluminum mono-
20 chloride, di-n-hexyl aluminum monochloride, etc.), alkyl
aluminum dihalides (ethyl aluminum dichloride, n-propyl
aluminum dichloride, i-butyl aluminum dichloride, n-butyl
aluminum dichloride, n-hexyl aluminum dichloride, etc.),
ethyl aluminum sesquichloride, i-propyl aluminum sesqui-
25 chloride, i-butyl aluminum sesquichloride, n-butyl
aluminum sesquichloride and n-hexyl aluminum sesqui-
chloride as well as other organometal compounds such as
organozinc compounds. These organometal compounds may

be used alone or in a combination of two or more.

In compounding the composition of this invention using the ethylene- α -olefin copolymer A of relatively higher molecular weight and the ethylene- α -olefin copolymer B of relatively lower molecular weight both of which are obtained with the above catalyst system under a normal medium to low pressure polymerization method, the following matters must be obeyed.

(1) From the standpoint of transparency, it is necessary that the copolymers A and B are selected in order that (S.C.B. of copolymer A)/S.C.B. of copolymer B) is 0.6 to 1.7. When this ratio is below 0.6, mechanical strengths of the copolymer composition obtained are reduced. In films, for instance, balancing of MD and TD strengths is difficult, heat sealing characteristics worsen and tackiness is seen. From the standpoint of mechanical strengths the ratio will preferably be at least 0.8 more preferably at least 1.0. In the case of over 1.7, transparency of the copolymer composition is reduced.

(2) The density of the copolymer composition is 0.915 to 0.929 g/cm³.

(3) The melt index of the copolymer composition is 0.02 to 50 g/10 min. with preferred ranges being 0.04 to 10 g/10 min., 0.05 to 40 g/10 min. and 0.1 to 30 g/10 min. In addition, the melt flow ratio is preferred to be 35 to 200 and most preferred to be 35 to 150. Furthermore, the product of the melt index and the melt flow ratio is preferred to be at least 4 and more preferred to be at least 7. When the melt index and the melt flow ratio are below the lower limits, extrusion processability worsens. When the melt index is above the upper limit and the melt flow ratio is above 250 bubble stability in blown film processing is lost and mechanical strengths are reduced.

In the field of extrusion processing, the MI of the copolymer compositions is preferred to be 0.02 to 2.0 g/10 min. and more preferred to be 0.05 to 2.0 g/10 min. and most preferred to be 0.10 to 2.0 g/10 min. Further, the MFR is preferred to be 35 to 200 and most preferred to be 35 to 150. Furthermore, the product of MI and MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens. When the MI above the upper limits and the MFR is above 250, mechanical strengths are reduced.

In the field of film processing, the MI of the compositions is preferred to be 0.02 to 5 g/10 min. and more preferred to be 0.05 to 4 g/10 min. and most preferred to be 0.1 to 3 g/10 min. Further, its MFR is preferred to be 35 to

200 and most preferred to be 35 to 150. Furthermore, the product of the MI and the MFR is preferred to be at least 4 and more preferred to be at least 7. When the MI and the MFR are below the lower limits, extrusion processability worsens.

- 5 When MI is above the upper limit and the MFR is above 250 bubble stability in blown film processing is

48

- 1 insufficient and mechanical strengths are reduced.

In the field of injection molding, the MI of the composition is preferred to be 2.0 to 50 g/10 min. and more preferred to be 2.0 to 30 g/10 min. Further, 5 the MFR is preferred to be 35 to 80 and more preferred to be 35 to 70. When the MI is below the lower limit, moldability worsens and flow marks are produced.

When it is above the upper limit, mechanical strengths are reduced.

- 10 In order to provide the composition of this invention excellent in processability and mechanical strengths, it is also important to adequately balance its MI and MFR. A lower MI requires a higher MFR. This requirement is expressed by the product of MI and MFR.

- 15 For instance, a composition having a MI of about 1 g/10 min, even if its MFR is as low as 50 to 60, has processability about equal to that of a high pressure polyethylene having the same MI. On the other hand, a composition having a MI of about 0.05 g/10 min.

- 20 and a MFR of 50 possesses extremely poor processability and, in order to have satisfactory processability, a MFR of at least 80 is required. The product of MI and MFR of a composition is designed appropriately to meet the requirement of its final application. The designed 25 value of the product of MI and MFR can be achieved in the composition by using (a) intrinsic viscosities of the copolymer A of relatively higher molecular weight, and the copolymer B of relatively lower molecular weight,

- 1 (b) values of (weight average molecular weight)/(number
average molecular weight) of these copolymers and (c)
their mixing ratio. If intrinsic viscosities of the
copolymer A and the copolymer B are put as $[\eta]_A$ (dl/g)
5 and $[\eta]_B$ (dl/g), respectively, and their ratios by weight
basis are put as W_A and W_B ($W_A + W_B = 1$), respectively
the intrinsic viscosity of the composition obtained by
mixing the two copolymers namely $[\eta]_T$ (dl/g) is approxi-
mately given by the following formula.

10
$$[\eta]_T = [\eta]_A W_A + [\eta]_B W_B$$

- MI is governed by $[\eta]_T$ unequivocally. Meanwhile, MFR is
generally larger when $[\eta]_A/[\eta]_B$ is larger, and depends
upon W_A and W_B . Therefore, it is difficult to express
MFR unequivocally and, based on preliminary tests, $[\eta]_A$,
15 $[\eta]_B$, W_A and W_B are determined to give an intended MFR.
(4) In order to obtain a composition which satisfies
the above (1) to (3) conditions, the copolymer A and the
copolymer B are mixed in a ratio of 10
to 70% by weight (copolymer A) to 90 to 30% by weight
20 (copolymer B). The ratio of 20 to 65% by weight to 80
to 35% by weight is preferred and the ratio of 30
to 60% by weight to 70 to 40% by weight is most preferred.
The mixing ratio of the two copolymers must be adequately
selected by considering S.C.B., densities, intrinsic
25 viscosities and molecular weight distributions of the
copolymers A and B as well as the density, MI and MFR

1 of an intended composition. When the ratio of the
copolymer A is below its lower limit and the ratio of the
copolymer B is above its upper limit, the ESCR, impact
strength, tear strength and low temperature resistance
5 of the composition obtained are poor, and the high
strength of the composition of this invention which is
obtained when the value of (S.C.B. of copolymer A)/(S.C.B.
of copolymer B) is selected to be at least 0.6 as well
as the good transparency of the composition of this
10 invention which is obtained when the value of (S.C.B. of
copolymer A)/(S.C.B. of copolymer B) is selected to be
0.6 to 1.7, are not achieved. When the ratio of the
copolymer A is above its upper limit and the ratio of
the copolymer B is below its lower limit, the processa-
15 bility of the composition obtained worsens.

As long as the scope of this invention is
obeyed, mixing of the ethylene- α -olefin copolymer A of
relatively higher molecular weight and the ethylene- α -
olefin copolymer B of relatively lower molecular weight
20 is not necessarily limited to mixing one of each kind.
The mixing may be also done by using two or more
kinds of each of the copolymer A and the copolymer B

There is no particular limitation to mixing
methods of the copolymers A and B, and known methods can
25 be used in mixing of these two polymers. Commonly used
are a batch type melt kneading method which employs a
twin roll or a Banbury mixer after separate production
of the copolymers A and B, a continuous melt kneading

1 method employing a twin rotor mixer such as CIM (manu-
factured by the Japan Steel Works) or FCM (manufactured
by Kobe Steel) or a single screw extruder and a solution
mixing method in which a mixture is obtained by dissolv-
5 ing the copolymers A and B in a solvent separately or
together, blending and finally removing the solvent.
When the copolymers A and B are produced by a high
temperature solution polymerization method, it is ad-
vantageous from the process standpoint that their
10 composition is obtained by mixing A and B in a solution
state at high temperatures and removing the solvent.

Mixing by a two- or multi-stage polymerization
method is also possible. In this method, in the first
stage, the copolymer A is polymerized for a certain
15 length of time and, successively in the second stage,
the copolymer B is polymerized using the same catalyst
but changing other polymerization conditions until the
composition containing the copolymers A and B at an
intended ratio is obtained. In this case, the order of
20 polymerization of A and B is not restricted.

The above two- or multi-stage polymerization
method is an ideal mixing method, because the copolymers
A and B undergo molecular dispersion.

The most effective mixing method can be se-
25 lected from above various mixing methods, in order to
obtain a uniform composition, which meets intended
requirements.

The intrinsic viscosity $[\eta]$ of the ethylene- α -

- 1 olefin copolymer composition of this invention is preferred to be 0.7 to 4 dl/g and more preferred to be 0.8 to 3.5 dl/g and most preferred to be 0.9 to 3 dl/g. When the intrinsic viscosity is below the lower limit,
- 5 mechanical strengths are reduced and, in blown film processing, bubble stability is insufficient. In case of above the upper limit, extrusion processability worsens.

S.C.B. of the composition is preferred

10 to be 5 to 45 and more preferred to be 7 to 40 and most preferred to be 10 to 40. When S.C.B. is below its lower limit, transparency worsens. When S.C.B. is above its upper limit, mechanical strengths are reduced and molded products have tackiness.

- 15 Next, the "index of long chain branching" of the copolymer composition of this invention is described. When the intrinsic viscosity of a copolymer composition of this invention is put as $[\eta]$ and the intrinsic viscosity of a linear polyethylene having the same $\bar{M}_w$ measured by
- 20 light scattering method (a high density polyethylene obtained by homopolymerization of ethylene under a medium to low pressure using a Ziegler catalyst) is put as $[\eta]_2$, $[\eta]/[\eta]_2$ namely g_n^* is called the "index of long chain branching" of the composition and indicates the extent
- 25 of presence of long chain branching in the composition. Now, intrinsic viscosities of two polymers are compared. One polymer X is a polyethylene having long chain branches of which index of branching is unknown (for

1 instance, a high pressure polyethylene) and the other
polymer is a linear polyethylene containing no long
chain branches but having the same $\bar{M}_w$ measured by light
scattering method. When these two polymers are made into
5 respective very dilute solutions with one same solvent,
the polymer X gives a less-viscous solution because the
spread of its molecular chain is smaller than that of the
linear polyethylene. Accordingly, by measuring the
intrinsic viscosities of the two polymers and calculating
10 their ratio namely g_{η}^* , the index of long chain branching
can be known. When a polymer has no long chain branches,
its g_{η}^* is almost 1 within the range of experimental
errors. When the polymer has long chain branches, g_{η}^* is
smaller than 1. In most cases, high pressure polyethylenes
15 show g_{η}^* of below 0.6 and have considerable quantities of
long chain branches.

The ethylene- α -olefin copolymer composition of
this invention is preferred to have g_{η}^* of at least 0.8
and more preferably at least 0.9 and practically has no
20 long chain branches. When g_{η}^* is below 0.8 and contain
a large quantity of long chain branches, the copolymer
is poor in tensile strength, impact strength, environ-
mental stress cracking resistance, low temperature
resistance and chemicals resistance.

25 (S.C.B. of higher molecular weight components)/
(S.C.B. of lower molecular weight components) of the
copolymer composition of this invention is %
at least 0.6 and more preferred to be at least 0.8

5K

1 and most preferred to be at least 1.0. In applications
where transparency is required, 0.6 to 0.8 is preferred.
Here, these S.C.B. are obtained by dividing the compo-
5 sition of this invention into two groups of lower mole-
cular weight components and higher molecular weight
components using molecular weight fractionation and then
measuring S.C.B. of each group. When the ratio is below
0.6, mechanical strengths of the composition are poor,
and when the composition is subjected to extrusion proces-
10 sing and injection molding, balancing of MD and TD
strengths is difficult and molded products have sticky
surfaces, and in films, heat-sealing characteristics
worsen. When the ratio is over 0.8, transparency worsens.
The above molecular weight fractionation of the ethylene-
15 α -olefin copolymer into two groups of lower and higher
molecular weight components refers to the following
method.

(1) A curve of molecular weight distribution is
obtained by gel permeation chromatography.

20 In this case, the abscissa is the logarithm of
chain length (unit $\text{\AA}$) calibrated with a standard poly-
styrene sample, and the ordinate is relative weight
fraction. The standard measurement method is described
later.

25 (2) An example of cases where curves of molecular
weight distributions have one peak was shown in Fig. 1.
This pattern is seen most typically in ethylene- α -olefin

- 1 copolymers. In this case, a lower molecular weight components side and a higher molecular weight components side are divided by a line drawn between the peak of the curve and the midpoint of a line drawn between the end of lower molecular weight components in the curve and the end of higher molecular weight components; and the ratio of areas of these two sides is the weight ratio of lower and higher molecular weight components. Separately, fractions of the same sample are prepared by column fractionation. These fractions are consolidated into two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions become closest to the weight ratio obtained above.
- 15 (3) An example of cases where curves of molecular weight distributions have two peaks was shown in Fig. 2. Also, an example having one peak but showing a shoulder at higher molecular weight components side was shown in Fig. 3. Examples having three or more peaks are handled as modifications of two peaks and are treated similarly to two peaks. In the case of two or more peaks including shoulders, a tangent line is drawn between main two peaks of the higher molecular weight components side or between one peak and a shoulder of the same side, and then a perpendicular is drawn from a point where the distance between the GPC curve and the tangent line becomes largest. This perpendicular splits the lower molecular weight components side and the higher molecular weight components

1 side, and the ratio of areas of these two sides becomes
the weight ratio of these two components portions. When
peaks are continuous and can not be detected (case of
somewhat square curve), the technique of one peak
5 distribution is applied. Separately, fraction of the
same sample are prepared by column fractionation. These
fractions are consolidated into two portions of lower
and higher molecular weight components, in order that
the weight ratio of these two portions becomes closest
10 to the weight ratio thus obtained.

Molecular weight fractionation is conducted by
the known column fractionation method. Its detailed
explanation is made in "Polymer Fractionation" (compiled
by M.J.R. Cantow, Academic Press, published in 1967),
15 and therefore, only the outline of the method is described
below.

About 5 g of a sample is adsorbed on a carrier,
Celite 745, in xylene and the carrier is charged into a
column. The column is heated to 130°C and a mixed solvent
20 of butyl cellosolve and xylene is passed through the
column with their mixing ratio being gradually changed
(namely with the solvency of the mixed solvent being
gradually changed). The lower molecular weight fractions
to higher molecular weight fractions are successively
25 fractionated. To each eluate is added methanol to cause
precipitation. After recovery of each polymer, they are
dried under reduced pressure to be used as each fraction.
To prevent the decomposition of polymers during

1 fractionation, 100 ppm of Irganox[®] 1076 is added to
the original sample as a stabilizer, and also nitrogen
is passed through the column to shut off oxygen. The
polymer fractions obtained are divided into two groups
5 of lower and higher molecular weight components so that
the weight ratio of these two groups become the above-
mentioned weight ratio. Each group is made into a press
sheet of about 100 to 300 μ thickness and these sheets
are subjected to Fourier-transform infra-red absorption
10 spectroscopy.

Further, it is preferable that the character-
istic values of the sample obtained by dividing the
ethylene- α -olefin copolymer of this invention into two
fractions such as a higher molecular weight component
15 and a lower molecular weight component are same to the
characteristic values of copolymer A and copolymer B,
respectively, as previously defined.

When compared with low density ethylene- α -
olefin copolymers obtained from the conventional medium
20 to low pressure method (normally called "linear low
density polyethylene or LLDPE"), the polyethylene type
resin composition of this invention has the following
advantages.

In the field of extrusion processing, the com-
25 position of this invention is largely excellent in
processability (about equal even to high pressure poly-
ethylenes) and moreover has excellent mechanical
strengths (ESCR, tensile strength, impact strength and

1 tear strength) as well as excellent low temperature
resistance. Therefore, reduction in thicknesses of
molded products becomes possible. The composition of
this invention has wide applications and can be used
5 even in the application where transparency is required.

In case of films, the present composition is
far superior in processability (about equal even to high
pressure polyethylenes). Further, the composition has
excellent mechanical strengths such as tensile strength,
10 impact strength and tear strength, by which reduction
in thicknesses of films becomes possible. Moreover, the
present composition has excellent transparency and heat-
sealing characteristics, by which it is used as a high
quality film in wide applications including high speed
15 bag manufacturing.

In the field of injection molding, the present
composition is largely excellent in processability (about
equal even to high pressure polyethylenes). Moreover,
there occurs no flow marks, there is no warpage with
20 molded products, and transparency, low temperature
resistance and mechanical strengths such as environmental
stress cracking resistance, tensile strength and impact
strength are excellent. Thereby, reduction in thicknesses
of molded products is possible and the present composition
25 has wide applications including the case where transparency
is required.

To the composition of this invention, can be
added if necessary various additives being commonly used

1 in the industries such as oxidation inhibitors, lubricants,
anti-blocking agents, anti-static agents, photostabilizers,
and coloring pigments. Also, other polymers can be added
in small quantities as long as the scope of this invention
5 is kept.

Next, the definitions of physical and chemical
properties used in this invention are explained below.

(1) Intrinsic viscosity

This implies $[\eta]$ in tetralin of 135°C.

10
$$[\eta] = 11.65 \times \log R$$

$$R = t/t_0$$

t : Seconds of dropping in a concentration of
0.2 dl/g

t_0 : Seconds of dropping of tetralin itself

15 (2) Density

According to the specification in JIS-K-6760.

With respect to the copolymer B of lower mole-
cular weight, when it has a large S.C.B., it is regarded
as a low density product, and according to the specifi-
20 cation, it must be subjected to annealing of 100°C and
1 hour. However, the copolymer B was conformed in all
cases to the specification for high density products and
was not subjected to the above annealing.

(3) S.C.B.

25 Using the C_{14} labelled product described in
the following literature, the subject property was calcu-
lated by employing the FT-IR spectrum subtraction method.

1 "Characterization and Properties of Polymers"

Published by KAGAKU DOJIN

Compiled by Mitsuru Nagasawa et al.

Issued on July 10, 1970

5 Pages 131 to 146

Determination formulas for various branches are given
below.

Branch	Determination formula
Methyl	Branches/1000 C = 0.49 · K 7.25 μ
Ethyl	" = 0.70 · K 7.25 μ
n-Butyl	" = 0.80 · K 7.25 μ
n-Decyl	" = 0.78 · K 7.25 μ
Other linear chains	" = 0.80 · K 7.25 μ
i-Butyl	" = 0.45 · K 7.23 μ

(62)

- 1 $K_{7.25\mu}$ (absorptivity) was obtained by using as
a reference a linear ethylene homopolymer having the
almost same molecular weight and molecular weight distri-
bution and the same $[\eta]$ as those of a given sample and
5 employing the spectrum subtraction method. Therefore,
effects of methyl groups at the ends were cleared.

When R of an α -olefin $R-CH=CH_2$ is a linear
alkyl, (the number of methyl groups at the branch ends)/
1000C is S.C.B. When R is a branched alkyl group, for
10 instance, an α -olefin is 4-methyl-pentene-1, the branch
is the i-butyl group and half number of methyl groups
at the branch ends per 1000 carbon atoms is S.C.B.

(4) Weight average molecular weight by light
scattering method

- 15 This item was measured at 125°C by the normal
method, with α -chloronaphthalin used as a solvent and
employing a photoelectric type light scattering photo-
meter (manufactured by SHIMAZU SEISAKUSHO).

(5) Melt index (MI)

- 20 According to the condition E of ASTM D 1238.

(6) Melt flow ratio (MFR)

- Firstly, $MI_{21.6}$ (grams per 10 min. under a load
of 21.6 kg at 190°C) is measured according to ASTM D 1238
condition F. Then, MFR is calculated using the following
25 formula.

$$MFR = MI_{21.6}/MI$$

- (7) Rigidity (expressed by Olsen's flexural modulus)
According to ASTM D 747.

1

Press condition: ASTM D 1898 method C

Test piece: 25 x 70 x 1 mm thickness

Span: 25 mm

Measurement temperature: 20°C

5 (8)

Tensile impact strength: According to ASTM D 1822

Press condition: ASTM D 1898 method C

Test piece: S type dumbbell, 1 mm thickness

Annealing: 1 hour in boiling water

Measurement temperature: 20°C

10 (9)

Molecular weight distribution ($\bar{M}_w/\bar{M}_n$)

GPC method (gel permeation chromatography
method)

HLC-811 (manufactured by TOYO SODA)

Column: TSK-GEL (GMSP + G₇₀₀₀H₄ + GMHx2)

15

Solvent: 1,2,4-trichlorobenzene (TCB)

Temperature: 145°C

Detector: Differential refractometer

Flow quantity: 1 ml/min.

Concentration: 15 mg/10 ml TCB

20

Measurement data on standard polystyrenes are
shown below.

Polystyrene	Nominal value			Measured value		
	$\bar{M}_w$	$\bar{M}_n$	$\bar{M}_w/\bar{M}_n$	$\bar{A}_w$	$\bar{A}_n$	$\bar{A}_w/\bar{A}_n$
#41955 (Waters')	9.82×10^4	9.62×10^4	1.02	2083	1744	1.19
A 5000 (TOYO SODA'S)	6.2×10^3	5.96×10^3	1.04	140	112	1.25

- 1 (10) Environmental stress cracking resistance (ESCR)
According to ASTM D 1693.
Expressed in F_{50} (hr).
The following exceptions were adopted.
- 5 Concentration of AntaroX-CO630: 10% by weight
Sample: 3 mm thickness, 0.5 mm notch
- (11) Tensile strength
According to ASTM D 638.
- (12) Resistance to chlorine water
- 10 Test solution: 0.2% chlorine water
Solution quantity: A quantity which gives
1.2 ml/cm² against a pressed
sample. The solution is
replaced daily.
- 15 Temperature: 40°C
Evaluation: 10 stage evaluation on a sample
after 72 hours.
1: Excellent,
10: Overall surface like "foam"
- 20 (13) Transparency (haze value)
Press condition: 180°C x 10 min, rapid cooling
in ice water
Sample: 100μ thickness
Haze measurement: Internal haze
- 25 (14) Brabender torque
Brabender plastograph [®] was used.
Jacket: W 50 model, 45 g filled
Temperature: 190°C

1 Rotor revolution: 60 rpm
A torque after 30 min. is expressed in kg-m.

(15) Spiral flow length

Injection molding machine: 5 ounce injection
5 molding machine manufactured by the
Japan Steel Works, Ltd.

Mold: Spiral mold (7.5 mm ϕ semicircle, 2000 mm
length)

Molding condition: Resin temperature 250°C
10 Mold temperature 40°C

Injection pressure 840 kg/cm²

Injection molding is carried out with this mold-
ing condition and spiral flow length is measured.

15 The present invention is explained below in more
detail by the following examples, but it is not restricted
by these examples.

Example 1

(1) Synthesis of Organomagnesium Compound

20 In a 500 ml four-necked flask equipped with a
stirrer, a reflux condenser, and a dropping funnel was
placed 16.0 g of flake-shaped magnesium to be used for
the production of Grignard reagents. The air and mois-
ture inside the flask were completely replaced by
25 nitrogen. Into the dropping funnel were charged 68 ml
(0.65 mol) of n-butyl chloride and 30 ml of n-butyl
ether. About 30 ml of this solution was dropped into

1 the flask to initiate a reaction, and thereafter the rest
of the solution was dropped in 4 hours at 50°C. After
the completion of dropping, the reaction was continued
for further 1.5 hours at 60°C. Then, the reaction system
5 was cooled to room temperature and the unreacted magnesium
was filtered off by the use of a glass filter.

n-Butyl magnesium chloride in the n-butyl ether
was measured for its concentration by hydrolyzing with 1 N
sulfuric acid and back-titrating with 1 N sodium hydroxide
10 using phenolphthalein as an indicator. The concentration
was 1.96 mol/l.

(2) Synthesis of Solid Catalyst Component

The air and moisture inside a 500 ml four-
necked flask equipped with a stirrer, a dropping funnel
15 and a thermometer was completely replaced by nitrogen.
In the flask was placed 130 ml of the n-butyl ether
solution containing 0.26 mol of n-butyl magnesium chloride
synthesized in the above step (1). From the dropping
funnel was dropped 30 ml (0.26 mol) of silicon tetra-
20 chloride over 2 hours at 50°C. The reaction was con-
tinued further for 1 hour at 60°C. The formed white
solid was separated, washed with n-heptane and dried
under reduced pressure to obtain 31.5 g of a white solid.
Ten grams of this white solid was placed in a 100 ml
25 four-necked flask and 50 ml of titanium tetrachloride
was added. They were allowed to react with stirring for
1 hour at 100°C. After the completion of the reaction,
n-heptane washing was applied until the washing became

1 free from titanium tetrachloride. After drying under reduced pressure, 7.9 g of a solid catalyst component was obtained. Each 1 g of this solid catalyst component supported 14 mg of titanium.

5 Example 2

Ethylene- α -olefin copolymers A were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α -olefins and other polymerization conditions as shown in Table 1.

10 Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these polymers obtained were also shown in Table 1.

These copolymers are used in the following examples as mixing components.

15 Example 3

Ethylene- α -olefin copolymers B were polymerized, using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing various α -olefins and other polymerization conditions as shown in Table 2.

20 Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene- α -olefin copolymers were also shown in Table 2.

These copolymers are used in following examples
25 as mixing components.

Table 1

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
Al-1	Slurry	65	134	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.84
Al-2	Solution	1	25.3	DEAC 2.5	C ₇ 0.25	4-MP-1 0.110	0.1
Al-3	Slurry	65	130	TEA 50	C ₄ 6.0	C ₄ ' 6.14	0.25
Al-4	"	65	310	TEA 100	"	"	0.86
Al-5	"	65	102	TEA 50	"	"	0.059
Al-6	Solution	1	26.0	DEAC 2.5	C ₇ 0.30	C ₆ ' 0.060	0.1
Al-7	"	1	327	TEA 100	"	"	1.8
Al-8	"	1	24.5	DEAC 2.5	"	4-MP-1 0.050	0.15
Al-9	Slurry	65	330	TEA 100	C ₄ 6.0	C ₄ ' 6.14	1.1
Al-10	"	65	309	TEA 100	"	"	1.2
Al-11	"	65	121	TEA 50	"	"	0.98
Al-12	"	65	320	TEA 100	"	"	3.0
Al-13	Solution	1	25.0	DEAC 2.5	C ₇ 0.25	C ₈ ' 0.140	0.1

- Cont'd -

Table 1 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
5.6	50	0.900	2.2	38	5.9
20	140	0.904	2.5	23	3.6
6.0	50	0.905	3.2	30	5.8
9.5	50	0.915	2.5	19	5.5
4.5	50	0.908	4.4	25	6.0
20	140	0.903	2.5	25	3.7
12.0	140	0.922	2.2	13	5.3
20	140	0.920	2.5	10	3.7
12.0	50	0.921	2.5	13	5.5
8.0	50	0.911	2.2	25	5.7
6.5	50	0.907	2.2	30	5.7
20	50	0.928	2.2	8	5.3
20	140	0.903	2.5	24	3.9

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1: 4-Methylpentene-1

C₂' = EthyleneC₄ = n-ButaneC₄' = Butene-1C₆' = Hexene-1C₈' = Octene-1C₇ = n-Heptane

Table 2

No.	Polymeri- zation method	Polymeri- zation vessel capacity (ℓ)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
B1-1	Slurry	65	345	TEA 100	C ₄ 15.2	C ₄ ' 1.2	11.5
B1-2	Solution	1	25.5	DEAC 2.5	C ₇ 0.28	4-MP-1 0.030	3.0
B1-3	Slurry	65	415	TEA 50	C ₄ 15.2	C ₄ ' 1.6	11.0
B1-4	"	65	425	"	"	C ₄ ' 2.0	10.5
B1-5	"	65	286	"	C ₄ 6.0	C ₄ ' 6.14	9.4
B1-6	"	65	410	TEA 100	C ₄ 12.0	C ₄ ' 3.0	11.0
B1-7	Solution	1	25.7	DEAC 2.5	C ₇ 0.25	4-MP-1 0.050	2.5
B1-8	Slurry	65	250	TEA 100	C ₄ 15.2	C ₄ ' 0.4	13.5
B1-9	"	65	407	"	"	C ₄ ' 0.5	13.0
B1-10	"	65	422	TEA 50	"	C ₄ ' 1.8	11.0
B1-11	"	65	405	"	"	C ₄ ' 1.4	11.0
B1-12	Solution	1	26	DEAC 2.5	C ₇ 0.25	C ₈ ' 0.040	3.0

- Cont'd -

Table 2 (Cont'd)

C ₂ '- pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
5.0	70	0.943	0.63	15	5.5
10	140	0.938	0.50	13	3.5
5.0	70	0.936	0.62	20	5.6
5.0	70	0.929	0.65	25	5.7
8.5	50	0.927	1.1	25	5.8
3.0	50	0.910	0.60	35	5.9
10	140	0.912	0.52	22	3.6
1.5	50	0.930	0.28	25	5.7
5.0	70	0.954	0.62	8	5.2
5.0	70	0.934	0.61	22	5.6
5.0	70	0.939	0.62	18	5.5
10	140	0.937	0.49	14	3.6

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1

C₂' = Ethylene

C₄ = n-Butane

C₄' = Butene-1

C₆' = Hexane-1

C₈' = Octene-1

C₇ = n-Heptane

72 70

1 Example 4

Ethylene- α -olefin copolymers A were polymerized, using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing various
5 α -olefins and other polymerization conditions shown in Table 3. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/ α -olefin copolymers were also shown in Table 3.

10 These copolymers are used in the following examples as mixing components.

Example 5

Ethylene- α -olefin copolymers B were polymerized, using the catalyst produced in Example 1 and organoalumi-
15 num compounds (co-catalyst) and employing various α -olefins and other polymerization conditions as shown in Table 4. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these ethylene/ α -olefin copolymers were also
20 shown in Table 4.

These copolymers are used in the following examples as mixing components.

70

Table 3

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
A2-1	Slurry	65	145	TEA 100	C ₄ 6.0	C ₄ ' 6.14	1.38
A2-2	Solution	1	25.5	DEAC 2.5	C ₇ 0.25	4-MP-1 0.11	0.5
A2-3	Slurry	65	141	TEA 50	C ₄ 6.0	C ₄ ' 6.14	0.59
A2-4	"	65	307	TEA 100	"	"	2.3
A2-5	"	65	311	"	"	"	1.84
A2-6	"	65	321	"	"	"	3.2
A2-7	Solution	1	26.5	DEAC 2.5	C ₇ 0.3	4-MP-1 0.05	0.9
A2-8	Slurry	65	315	TEA 100	C ₄ 6.0	C ₄ ' 6.14	2.6
A2-9	"	65	118	"	"	"	4.6
A2-10	Solution	1	24.5	DEAC 2.5	C ₇ 0.3	C ₆ ' 0.025	0.9

- Cont'd -

Table 3 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
6.0	50	0.902	1.8	38	5.9
20	140	0.908	1.8	23	3.8
6.5	50	0.907	2.5	30	5.8
11	50	0.918	1.8	17	5.4
8.4	50	0.914	1.8	25	5.7
14	50	0.925	1.8	13	5.3
20	140	0.923	1.8	10	3.6
8.5	50	0.914	1.6	25	5.5
17	50	0.929	1.6	10	5.3
20	140	0.918	1.8	13	3.8

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1

C₂' = Ethylene

C₄ = n-Butane

C₄' = Butene-1

C₆' = Hexene-1

C₇ = n-Heptane

Table 4

No.	Polymeri- zation method	Polymeri- zation vessel capacity (ℓ)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α-olefin (kg)	H ₂ partial pressure (kg/cm ²)
B2-1	Slurry	65	348	TEA 100	C ₄ 15.2	C ₄ ' 1.0	12
B2-2	Solution	1	26.5	DEAC 2.5	C ₇ 0.28	4-MP-1 0.03	3.0
B2-3	Slurry	65	405	TEA 50	C ₄ 15.2	C ₄ ' 1.6	8.8
B2-4	"	65	421	"	"	"	12
B2-5	"	65	407	TEA 100	C ₄ 12.0	C ₄ ' 2.5	12
B2-6	Solution	1	25.7	DEAC 2.5	C ₇ 0.25	4-MP-1 0.05	2.5
B2-7	Slurry	65	245	"	C ₄ 15.2	C ₄ ' 0.3	12
B2-8	"	65	420	TEA 50	"	C ₄ ' 1.2	12
B2-9	Solution	1	23.9	DEAC 2.5	C ₇ 0.30	C ₆ ' 0.017	3.0

- Cont'd -

Table 4 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
3.0	70	0.943	0.51	15	5.9
10	140	0.938	0.50	13	3.5
5.0	70	0.935	0.73	20	5.9
3.0	70	0.929	0.54	25	5.9
3.0	50	0.910	0.51	35	6.0
10	140	0.912	0.52	22	3.6
1.0	50	0.931	0.25	25	5.9
3.0	70	0.938	0.50	18	5.4
10	140	0.937	0.52	18	3.4

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-methylpentene-1

C₂' = Ethylene

C₄ = n-Butane

C₄' = Butene-1

C₆' = Hexene-1

C₇ = n-Heptane

The below-described are mixing methods of an ethylene- α -olefin copolymer A having a relatively higher molecular weight and an ethylene- α -olefin copolymer B having a relatively lower molecular weight.

- 5 (a) Mixing with a Banbury mixer (hereinafter referred to as Banbury mixing).

A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 1.0 kg. The mixture is kneaded in a Banbury mixer for 5 min.
10 with a rotor revolution of 150 to 230 rpm. At that time, nitrogen replacement should be made sufficiently and the polymer temperature must not exceed 250°C.

- (b) Mixing in a solution state (hereinafter referred to as solution mixing)

15 A copolymer A and a copolymer B are mixed in a fixed ratio and in order to give a total quantity of 100 g. This mixture is charged into a 3 liter autoclave. Two liters of xylene is added as a solvent. With stirring, the mixture is heated up to 200°C and is subjected to
20 1 hour of solution mixing. Then, it is cooled below the boiling point, and is added into 10 liters of methanol to cause precipitation. The precipitate is dried for 48 hours in a vacuum drier of 80°C to obtain an intended

1 polymer composition.

Example 7

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization.

5 The first stage polymerization was carried out for 100 min. by using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing other polymerization conditions as shown in Table 5. Successively, the second stage polymerization was conducted for
10 150 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 5. In both polymerization stages, the liquid phase molar ratio of ethylene/butene-1/hydrogen was maintained at respective fixed levels. The polymerized quantities
15 in each stage were examined from the quantities of fed ethylene. The result indicated that the total polymer consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. The sample polymer of the
20 former stage was taken out immediately before the completion of the polymerization and was measured for its density, intrinsic viscosity, S.C.B. and (weight average molecular weight / number average molecular weight). Similar measurements were made also for the whole polymer
25 obtained after the two stage polymerization. Using the values of the former stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. for the polymer formed

- 1 in the latter stage alone were calculated. These calculated values are also shown in Table 5. The whole polymer gave: density 0.923 g/cm^3 , melt index 6 g/10 min., melt flow ratio 55, intrinsic viscosity 1.10 dl/g, S.C.B.
- 5 25. The whole polymer was subjected to injection molding and the molded composition was measured for its physical properties. Results are shown in Table 9.

Table 5

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α -olefin (g)	H ₂ partial pressure (kg/cm ²)
1st stage	Slurry	5	25	5	C ₄ 1000	C ₄ ' 120	0.45
2nd stage	Slurry						16

Note C₄ = n-Butane

C₄' = Butene-1

C₂' = Ethylene

TEA = Triethyl aluminum

Values in parenthesis are calculated values.

-- Cont'd --

Table 5 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Polymeri- zation time (min)	Properties			
			Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
20	50	100	0.910	1.75	30	5.8
4.0		150	-	(0.5)	(20)	-

Table 6

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Comparative Example 1	-	-	-	-	-	0.922	0.3	65	-
Comparative Example 2	-	-	-	-	-	0.920	1.0	30	-

- Cont'd -

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 6 (Cont'd)

Physical properties of composition					
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F50 (hr)	Tensile strength (kg/cm ²)	Brabender torque (kg.m)	Chlorine water resistance
200	2200	30	180	2.2	5
230	3200	1000	250	2.9	2

Examples 11, 12 and 14.

Ethylene- α -olefin copolymers A obtained in Example 2 and ethylene- α -olefin copolymers B obtained in Example 3 were mixed in various ratios and the compositions 5 having densities, MIs and MFRs shown in Table 8 are obtained. Their physical properties are also shown in Table 8.

For the purpose of comparison, in Table 8 were also shown Comparative Examples 5, 6 and 7 as examples of 10 low density ethylene- α -olefin copolymers of the conventional technique of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

15 As is obvious from Table 8, in the compositions of this invention, S.C.B. in higher molecular weight components is more than or about equal to that in lower molecular weight components as seen in distribution index of S.C.B. (compare Example 14 with Comparative Examples 5 and 6). Therefore, 20 the compositions of this invention have much higher tensile impact strengths and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative Example 2 in Table 6 with Comparative Example 5 in Table 8, it is seen that widening of molecular weight 25 distribution in the manufacture of a low density ethylene- α -olefin copolymer of the conventional technique maintaining density and MI (larger MFR gives wider distribution)

- 1 results in large reduction in tensile impact strength and tensile strength.

Table 7

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Comparative Example 3	-	-	-	-	-	0.920	6	35	-
Comparative Example 4	-	-	-	-	-	0.924	5	30	-

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

- Cont'd -

Table 8 (Cont'd)

Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F ₅₀ (hr)	Tensile strength (kg/cm ²)	Spinal blow length (mm)
120	2100	2	150	120
110	3500	30	180	80

Table 8

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 11	Banbury	A1-3	50	B1-3	50	0.920	0.25	80	1.5
Example 12	"	A1-4	50	B1-4	50	0.920	0.8	50	0.7
Example 14	Solution	A1-13	60	B1-12	40	0.919	0.5	70	1.7
Comparative Example 5	Banbury	A1-7	50	B1-6	50	0.920	1.1	65	0.37
Comparative Example 6	Solution	A1-8	60	B1-7	40	0.919	0.5	70	0.50
Comparative Example 7	Banbury	A1-12	50	B1-10	50	0.930	1.2	70	0.36

- Cont'd -

(S.C.B. of copolymer A)

* Distribution index =
of S.C.B.

(S.C.B. of copolymer B)

90

Table 8 (Cont'd)

Physical properties of composition			
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Tackiness
480	2700	320	o
300	2900	260	o
500	2500	310	o
110	3200	180	x
200	3100	200	x
70	4500	200	o

Examples 16 and 17

Ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 were mixed in various ratios and the compositions having densities, melt indices and melt flow ratios shown in Table 9 were obtained. Their physical properties are also shown in Table 9.

In Table 9 is also shown a similar composition obtained from two stage polymerization (Example 7). For the purpose of comparison, in Table 9 were also shown Comparative examples 8, 9 and 10 as examples of low density ethylene- α -olefin copolymers of the conventional technique of which molecular weight distributions are made wider, and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

As is obvious from Table 9, in the compositions of this invention, the higher molecular weight components have larger S.C.B. than the lower molecular weight components do, as seen in distribution index of S.C.B.

(compare Examples 7 and 16 with Comparative examples 8 and 9, and Example 17 with Comparative example 10).

Therefore, the compositions of this invention have much higher tensile impact strengths ESCRs and tensile strengths than the comparative compositions of the conventional technique do. By comparison of Comparative example 4 in Table 7 with Comparative example 9 in Table 9, it is seen that widening of molecular weight

- 1 distribution in the manufacture of a low density ethylene-
α-olefin copolymer of the conventional technique maintain-
ing density and MI (larger MFR gives wider distribution)
results in large reduction in tensile impact strength,
5 ESCR and tensile strength.

Examples 18 to 20

Ethylene-α-olefin copolymers A obtained in
Example 2 and ethylene-α-olefin copolymers B obtained in
Exmample 3 were mixed in various ratios and the composi-
10 tions having densities, MIs and MFRs shown in Table 10
are obtained. Their physical properties were also
shown in Table 10.

For the purpose of comparison, in Table 10
is also shown an example (Comparative example 1) of
15 high pressure polyethylenes of the conventional techni-
que; an example (Comparative example 11) of low density
ethylene-α-olefin copolymers of the conventional techni-
que of which molecular weight distributions are made
wider, and of which lower molecular weight components
20 have larger S.C.B. and of which higher molecular weight
components have smaller S.C.B.; and an example (Compara-
tive example 12, to be compared with Example 19) of
ethylene-α-olefin copolymers compositions of which
distribution indices of S.C.B. meet the object of this
25 invention but of which lower molecular weight components
have a too low intrinsic viscosity.

It is clearly seen from Table 10 that proper

- 1 selection of distribution index of S.C.B. gives good transparency about equal to that of high pressure polyethylenes as well as a much more excellent tensile impact strength and tensile strength than those of high pressure
- 5 polyethylenes.

It is learned from comparison of Example 19 with Comparative example 12 that a too low intrinsic viscosity of lower molecular weight components badly affects the tensile impact strength and transparency of

10 the copolymer composition.

Table 9

	Mixing method	Copolymer A		Copolymer B		Properties of composition				
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*	
Example 7		- Two stage polymerization -				0.923	6	55	(1.5)	
Example 16	Solution	A2-3	30	B2-3	70	0.924	3	60	1.5	
Example 17	Banbury	A2-8	45	B2-8	55	0.929	10	45	1.4	
Comparative Example 8	Solution	A2-7	50	B2-6	50	0.922	5	50	0.45	
Comparative Example 9	Banbury	A2-4	50	B2-5	50	0.920	5	50	0.49	
Comparative Example 10	"	A2-9	45	B2-4	55	0.930	10	45	0.40	

- Cont'd -

$$\text{* Distribution index of S.C.B.} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

Table 9 (Cont'd)

Physical properties of composition					
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F ₅₀ (hr)	Tensile strength (kg/cm ²)	Tackiness	
170	3000	50	220	o	
190	3000	30	230	o	
120	4000	5	200	o	
100	3600	15	150	x	
80	3200	13	130	x	
40	4500	1	110	o	

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Table 10

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Example 18	Solution	A1-5	30	B1-5	70	0.920	0.15	100	1.0
Example 19	"	A1-6	50	B1-11	50	0.920	0.8	50	1.0
Example 20	Banbury	A1-1	50	B1-4	50	0.916	1.1	65	1.6
Comparative Example 1	-	-	-	-	-	0.922	0.3	65	-
Comparative Example 11	Banbury	A1-9	50	B1-6	50	0.920	0.8	50	0.4
Comparative Example 12	"	A1-10	65	B1-8	35	0.920	0.8	50	1.0

- Cont'd -

*Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 10 (Cont'd)

Physical properties of composition					
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Tackiness	Haze (%)	
480	2800	320	o	5	
400	2800	250	o	5	
420	2100	250	o	5	
200	2200	180	o	5	
150	3300	200	x	12	
130	2800	220	o	15	

1 Examples 21, 22, 23

Ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 were mixed at various ratios, and the compositions having densities, MIs and MFRs shown in Table 11 are obtained. Their physical properties were also shown in Table 11. For the purpose of comparison, in Table 11 are also shown Comparative example 3 using a high pressure polyethylene of the conventional technique; Comparative example 13 using a composition of low density ethylene- α -olefin copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have more S.C.B. and of which higher molecular weight components have less S.C.B.; and Comparative example 14 (to be compared with Example 22) using a composition of ethylene- α -olefin copolymers of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosity. It is obvious from Table 11 that proper selection of distribution index of S.C.B. gives good transparency about equal to that of high pressure polyethylenes and much more excellent tensile impact strength, tensile strength and ESCR than those of high pressure polyethylenes. From comparison of Example 22 with Comparative example 14, it is learned that a too low intrinsic viscosity of lower molecular weight components badly affects tensile impact strength and transparency.

Table 11

	Mixing method	Copolymer A		Copolymer B		Properties of composition				
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*	
Example 21	Solution	A2-10	50	B2-9	50	0.923	5	50	0.72	
Example 22	Banbury	A2-5	50	B2-4	50	0.922	5	50	1.0	
Example 23	"	A2-1	50	B2-4	50	0.920	5	50	1.6	
Comparative Example 13	"	A2-6	50	B2-5	50	0.923	5	50	0.37	
Comparative Example 14	"	A2-8	65	B2-7	35	0.922	5	50	1.0	
Comparative Example 3	-	-	-	-	-	0.920	6	35	-	

- Cont'd -

* Distribution index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

Table 11 (Cont'd)

Physical properties of composition						
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F50 (hr)	Tensile strength (kg/cm ²)	Tackiness	Haze (%)	
200	3100	20	250	o	7	
170	2900	30	220	o	7	
260	2500	200	230	o	7	
50	3600	10	130	x	12	
80	3200	30	190	o	12	
120	2100	2	150	o	7	

1 Comparative Example 1

A commercial high pressure polyethylene (Sumikathene® F101-1 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and
5 subjected to blow molding.

Results are shown in Table 6 and 10.

Comparative Example 2

An ethylene- α -olefin copolymer of the conventional technique was synthesized employing polymerization
10 conditions as shown in Table 12 in which the catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.920 g/cm^3 , MI 1.0 g/10 min. , MFR 30. Its physical properties are shown in Table 6.

Table 12

Poly-meri-zation method	Poly-meri-zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Sol-vent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)	C ₂ ' partial pressure (kg/cm ²)	Polymeri-zation temperature (°C)	Polymeri-zation time (min)
Slurry	65	197	100	C ₄ 7.0	C ₄ ' 7.16	4.2	10	50	100

Note TEA = Triethyl aluminum

C₄ = n-Butane

C₂' = Ethylene

C₄' = Butene-1

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1 Comparative Example 3

A commercial high pressure polyethylene (Sumikathene® G701 manufactured by Sumitomo Chemical Co., Ltd.) was measured for its physical properties and sub-
5 jected to injection molding.

Results are shown in Table 7 and 11.

Comparative Example 4

A low density ethylene- α -olefin copolymer of the conventional technique was synthesized employing polymerization conditions shown in Table 13 in which the
10 catalyst prepared in Example 1 and triethyl aluminum (co-catalyst) were used. The copolymer gave: density 0.924 g/cm³, melt index 5 g/10 min., melt flow ratio 30. Its physical properties are shown in Table 7.

Table 13

Poly- meri- zation method	Poly- meri- zation vessel capacity (L)	Catalyst quantity (mg)	Co- catalyst TEA (mmol)	Sol- vent (kg)	α - olefin (kg)	H ₂ partial pressure (kg/cm ²)	C ₂ ' partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Polymeri- zation time (min)
Slurry	65	199	25	C ₄ 6.0	C ₄ ' 6.14	10.2	11.3	50	90

Note: TEA = Triethyl aluminum C₂' = Ethylene

C₄ = n-Butane C₄' = Butene-1

1 Comparative Examples 5, 6, 7 and 11

Compositions of ethylene- α -olefin copolymers of the conventional technique were prepared by blending ethylene- α -olefin copolymers A obtained in Example 2 and
5 ethylene- α -olefin copolymers B obtained in Example 3 at ratios shown in Table 8 or 10. However in these copolymer compositions, molecular weight distributions are made wider and lower molecular weight components have larger S.C.B. and higher molecular weight components have
10 smaller S.C.B. Densities, MIs, MFRs and physical properties of these compositions are shown in Table 8 or 10.

Comparative Example 12

By blending an ethylene- α -olefin copolymer A obtained in Example 2 and an ethylene- α -olefin copolymer
15 B obtained in Example 3 at a mixing ratio shown in Table 10, a composition of ethylene- α -olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of the present invention but of which lower molecular weight components have a too low intrinsic viscosi-
20 ty. Its density, MI, MFR and physical properties are shown in Table 10.

Comparative Examples 8, 9, 10 and 13

Compositions of ethylene- α -olefin copolymers of the conventional technique were prepared by blending
25 ethylene- α -olefin copolymers A obtained in Example 4 and ethylene- α -olefin copolymers B obtained in Example 5 at

1 mixing ratios shown in Table 9 or 11. However in these
compositions, molecular weight distributions are made
wider and lower molecular weight components have larger
S.C.B. and higher molecular weight components have smaller
5 S.C.B. Densities, MIs, MFRs and physical properties of
these compositions are shown in Table 9 or 11.

Comparative Example 14

By blending an ethylene- α -olefin copolymer A
obtained in Example 4 and an ethylene- α -olefin copolymer
B obtained in Example 5 at a mixing ratio shown in Table
10 11, a composition of ethylene- α -olefin copolymers was
prepared of which distribution index of S.C.B. meets the
scope of this invention but of which lower molecular
weight components have too low an intrinsic viscosity.
Its density, MI, MFR and physical properties are shown
15 in Table 11.

Example 24

Ethylene- α -olefin copolymers A were polymerized
using the catalyst produced in Example 1 and organoalumi-
num compounds (co-catalyst) and employing α -olefins and
other polymerization conditions as shown in Table 14.
20 Their densities, intrinsic viscosities, S.C.B. and (weight
average molecular weight/number average molecular weight)
are shown in Table 14.

These polymers are used in the following examples
as mixing components.

Table 14

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
A3-1	Slurry	65	131	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.45
A3-2	Solution	1	25.1	DEAC 2.5	C ₇ 0.22	4-MP-1 0.130	0.10
A3-3	"	1	24.8	"	C ₇ 0.30	C ₆ ' 0.055	0.10
A3-4	Slurry	65	307	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.9
A3-5	"	65	130	TEA 50	"	"	0.22
A3-6	"	65	125	"	"	"	1.8
A3-7	"	65	301	TEA 100	"	"	1.2
A3-8	"	65	318	"	"	"	2.0
A3-9	"	65	308	"	"	"	1.4

Note TEA = triethyl aluminum DEAC = Diethyl aluminum chloride - Cont'd -

4-MP-1 = 4-Methylpentene-1

C₂' = Ethylene C₄ = n-Butane

C₄' = Butene-1

C₆' = Hexene-1 C₇ = n-Heptane

Table 14 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
5.0	50	0.899	2.6	38	5.9
20	140	0.899	2.6	27	3.5
20	140	0.902	2.6	24	3.7
9.0	50	0.914	2.4	22	6.0
5.5	50	0.906	3.2	28	5.8
18	50	0.923	2.6	9	5.5
12	50	0.919	2.4	16	5.8
20	50	0.928	2.4	8	5.4
9.0	50	0.914	2.2	22	5.7

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1 Example 25

Ethylene- α -olefin copolymers B were polymerized using the catalyst produced in Example 1 and organocaluminum compounds (co-catalyst) and employing α -olefins and
5 other polymerization conditions shown in Table 15. Their densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) are shown in Table 15.

These copolymers are used in the following
10 examples as mixing components.

Table 15

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
B3-1	Slurry	65	405	TEA 50	C ₄ 12.0	C ₄ ' 2.0	10.8
B3-2	Solution	1	25.5	DEAC 2.5	C ₇ 0.30	4-MP-1 0.025	2.4
B3-3	"	1	24.2	"	C ₇ 0.32	C ₆ ' 0.013	2.4
B3-4	Slurry	65	330	TEA 100	C ₄ 15.2	C ₄ ' 0.7	7.5
B3-5	"	65	391	"	"	C ₄ ' 1.8	7.2
B3-6	"	65	408	"	C ₄ 12.0	C ₄ ' 4.0	5.2
B3-7	"	65	350	"	C ₄ 15.2	C ₄ ' 1.3	7.5
B3-8	"	65	405	TEA 50	"	C ₄ ' 1.6	8.8
B3-9	"	65	390	TEA 100	"	C ₄ ' 0.20	15.0

- Cont'd -

Note TEA = triethyl aluminum DEAC = Diethyl aluminum chloride
 4-MP-1 = 4-Methylpentene-1 C₂' = Ethylene C₄ = n-Butane
 C₄' = Butene-1 C₆' = Hexene-1 C₇ = n-Heptane

Table 15 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
8.3	70	0.942	0.83	15	5.5
10	140	0.943	0.81	10	3.7
10	140	0.940	0.82	12	3.8
5.0	70	0.949	0.75	11	5.3
8.0	70	0.941	0.92	14	5.4
4.0	50	0.910	0.82	35	5.9
5.0	70	0.942	0.75	16	5.8
5.0	70	0.935	0.74	20	5.9
1.5	70	0.949	0.27	11	5.6

Table 16

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min)	MFR	Distribution index of S.C.B.*
Comparative Example 15	-	-	-	-	-	0.923	1.4	50	-
Comparative Example 16	-	-	-	-	-	0.922	0.3	65	-
Comparative Example 17	-	-	-	-	-	0.920	0.5	30	-

$$\text{* Distribution index of S.C.B.} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

- Cont'd -

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Table 16 (Cont'd)

Physical properties of composition				
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F ₅₀ (hr)	Tensile strength (kg/cm ²)	Brabender torque (kg·m)
130	2400	0.3	160	1.9
200	2200	30	180	2.2
280	3200	>1000	260	3.5

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Example 32

The low density ethylene- α -olefin copolymer of the conventional technique used in Comparative Example 17 was subjected to film processing under the following conditions.

5

Processing conditions

Extruder: Tanabe 30 mm ϕ extruder

Screw: Full flight L/D = 28, C.R. = 2.5

Die: Diameter 50 mm, die gap 2.0 mm

10

Temperature control: C₁ 170°, C₂ 220°, C₃ 220°,
HD 220°C

Screw revolution: 35 rpm

Output: 3.2 kg/hr

Blow up ratio: 2.5

15

Frost line height: 180 mm

15

Take-off speed: 5 m/min

Film thickness: 35 μ

Also, the commercial high pressure polyethylenes used in Comparative examples 15 and 16 were subjected to film processing under the following conditions.

20

Die gap: 1.0 mm

Temperature control: C₁ 140°, C₂ 160°, C₃ 160°,
HD 160°C

(Other conditions were same as those applied above.)

25

In the case of the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 17, a satisfactory film was not obtained with too much load put on the motor and with

shark skin formed on the film surface.

In the cases of the commercial high pressure polyethylenes used in Comparative Examples 15 and 16, satisfactory films were obtained with no excessive motor
5 loads. The physical properties of these films were shown in Table 17.

In the films of Comparative Examples 15 and 16, heat sealing strength in contaminated condition were slightly lower than heat-sealing strength.

10 The measurement methods of the physical properties shown in Table 17 are described below.

Dart impact strength: In accordance with ASTM D 1709A.

Elmendorf tear strength: In accordance with JIS Z 1702.

Tensile strength: In accordance with JIS K 6732-62

15 Heat-sealing characteristics: Heat-sealing strength of a film heat-sealed with a heat sealer of bar type. The maximum heat-sealing strength was obtained when pulled under conditions

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1 of film thickness of 35 μ , width of 15 mm
and pulling speed of 200 mm/min. after heat-
sealing under sealing pressure of 1 kg/cm²,
0.5 sec. and each incremental 5°C.

5 Hot tack property: A test sample (25 mm wide and
400 mm long) was folded into two, and the one
end was fixed to the upper clamp and a stripping
weight was placed on the other end.

10 The area near the crease was inserted between
heating bars and heat-sealed under a sealing
pressure of 1 kg/cm² for 0.5 sec., and then
the length of the stripped surface was measured.

Heat Sealing strength in contaminated condition:

15 This is a test method for evaluating the heat-
sealing characteristics in the condition that
the heat-sealed surface is soiled with contents
such as mayonaise, edible oils and flours.

20 Specifically, a test film sample was folded in
such a way that the surface soiled with an
edible oil came inside, and was heat-sealed
under the same conditions as used in heat-
sealing characteristics. Then, its heat-
sealing strength was measured.

Comparative Example 15

25 A commercial high pressure polyethylene
(Sumikathene[®] F208-1 manufactured by Sumitomo Chemical
Co., Ltd.) was subjected to measurements of physical

properties and film processing. Results are shown in Tables 16 and 17.

Comparative Example 16

5 A commercial high pressure polyethylene (Sumikathene^R F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurements of physical properties and film processing. Results are shown in Tables 16 and 17.

Comparative Example 17

10 A low density ethylene- α -olefin copolymer of the conventional technique was synthesized, using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and employing the other polymerization conditions shown in Table 18. The copolymer gave: density
15 0.920 g/cm³, MI 0.5 g/10 min., MFR 30. The physical properties of this polymer are shown in Table 16.

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Table 17

	Dart impact strength (kg·cm/mm)	Elmendorf tear strength MD/TD (kg/cm)	Tensile strength MD/TD (kg/cm ²)	Heat- sealing strength (kg/15mm width)	Hot tack property (mm)	Heat sealing strength in contaminated condition.
Comparative Example 15	270	80/50	250/210	0.7	4.0	Δ
Comparative Example 16	250	70/70	280/250	0.7	3.0	Δ

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Table 18

Poly-meri-zation method	Poly-meri-zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Sol-vent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)	C ₂ ' partial pressure (kg/cm ²)	Polymeri-zation temperature (°C)	Polymeri-zation time (min)
Slurry	65	202	100	C ₄ 7.0	C ₄ ' 7.16	3.0	10	50	90

Note TEA = Triethyl aluminum

C₄ = n-Butane

C₄' = Butene-1

C₂' = Ethylene

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1 Example 33

Ethylene- α -olefin copolymers A were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins
5 and other polymerization conditions as shown in Table 19. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 19 .

These copolymers are used in the following
10 examples as mixing components.

Example 34

Ethylene- α -olefin copolymers B were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins
15 and other polymerization conditions as shown in Table 20. Densities, intrinsic viscosities, S.C.B. and (weight average molecular weight/number average molecular weight) of these copolymers are shown in Table 20.

These copolymers are used in the following
20 examples as mixing components.

Table 19

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
A4-1	Slurry	65	310	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.70
A4-2	Solution	1	24.3	DEAC 2.5	C ₇ 0.27	4-MP-1 0.090	0.15
A4-3	Slurry	65	83	TEA 50	C ₄ 6.0	C ₄ ' 6.14	0.09
A4-4	"	65	309	TEA 100	"	"	1.2
A4-5	"	65	145	TEA 50	"	"	0.59
A4-6	Solution	1	25.2	DEAC 2.5	C ₇ 0.30	C ₆ ' 0.035	0.2
A4-7	Slurry	65	303	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.36
A4-8	"	65	125	"	"	"	1.8
A4-9	Solution	1	24.5	DEAC 2.5	C ₇ 0.40	4-MP-1 0.040	0.25
A4-10	Slurry	65	121	TEA 100	C ₄ 6.0	C ₄ ' 3.7	1.2
A4-11	"	65	302	"	"	C ₄ ' 6.14	1.4

- Cont'd -

Table 19 (Cont'd)

C2'- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[n] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
7.8	50	0.912	2.6	24	5.6
20	140	0.912	2.5	17	3.4
7.0	50	0.912	4.4	20	5.8
3.0	50	0.911	2.2	25	5.7
6.7	50	0.906	2.6	29	5.8
20	140	0.909	2.2	18	3.4
9.0	50	0.917	3.3	16	5.6
18	50	0.923	2.6	9	5.5
20	140	0.923	2.5	8	3.3
20	50	0.925	3.3	6	5.5
8.5	50	0.913	2.1	23	5.4

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1

C₄ = n-ButaneC₄' = Butene-1C₆' = Hexene-1C₇ = n-Heptane

Table 20

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
B4-1	Slurry	65	402	TEA 50	C ₄ 12.0	C ₄ ' 3.2	7.8
B4-2	Solution	1	24.2	DEAC 2.5	C ₇ 0.80	4-MP-1 0.045	2.2
B4-3	Slurry	65	405	TEA 50	C ₄ 12.0	C ₄ ' 3.2	7.0
B4-4	"	65	425	"	C ₄ 15.2	C ₄ ' 2.0	10.5
B4-5	"	65	411	"	"	C ₄ ' 1.6	6.5
B4-6	Solution	1	25.1	DEAC 2.5	C ₇ 0.82	C ₆ ' 0.017	2.7
B4-7	Slurry	65	346	TEA 100	C ₄ 15.2	C ₄ ' 1.1	12
B4-8	"	65	408	"	C ₄ 12.0	C ₄ ' 4.0	5.2
B4-9	Solution	1	24.9	DEAC 2.5	C ₇ 0.28	4-MP-1 0.055	2.0
B4-10	Slurry	65	250	TEA 100	C ₄ 15.2	C ₄ ' 0.4	13.5
B4-11	"	65	410	TEA 50	"	C ₄ ' 1.4	12
B4-12	"	65	290	"	C ₄ 6.0	C ₄ ' 6.14	8.1

- Cont'd -

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Table 20 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties			
		Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
6	70	0.929	0.85	24	5.8
10	140	0.929	0.81	17	3.6
6	70	0.928	0.90	24	5.7
5	70	0.929	0.65	25	5.7
5	70	0.935	0.83	20	5.5
10	140	0.926	0.63	18	3.5
3	70	0.941	0.52	16	5.4
4	50	0.910	0.82	35	5.9
10	140	0.912	0.85	22	3.7
1.5	50	0.930	0.28	25	5.7
3	70	0.934	0.53	22	5.8
9	50	0.927	1.2	23	5.7

Note

TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpenten-1

C₄ = n-Butane

C₄' = Butene-1

C₆' = Hexene-1

C₇ = n-Heptane

1 Example 35

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using
5 the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 21. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial
10 pressure as shown in Table 21. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymers consisted of about 50%
15 by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity, S.C.B.
20 and (weight average molecular weight/number average molecular weight). The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and S.C.B. of the polymer formed in the second stage alone were calculated.
25 These values were shown in Table 21. The whole polymer gave: density 0.921 g/cm³, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24. Flow

1 characteristics and solid physical properties of the whole
polymer were shown in Table 23.

Example 36

By mixing the ethylene- α -olefin copolymer A4-1
5 obtained in Example 33 and the ethylene- α -olefin copolymer
B4-1 obtained in Example 34 at a 50/50 weight ratio and
kneading the mixture in a Banbury mixer, a composition
of ethylene- α -olefin copolymers having the density, MI
and MFR shown in Table 22 was prepared. Physical pro-
10 perties of this composition were also shown in Table 22.
For comparison, in Table 22 were also shown Comparative
examples 15 and 16 using high pressure polyethylenes of
the conventional technique (commercial product
Sumikathene[®] F 208-1, F 101-1 manufactured by Sumitomo
15 Chemical Co., Ltd.) as well as Comparative example 17
using a low density ethylene- α -olefin copolymer of the
conventional technique.

As is obvious from Table 22, the polymer com-
position of the present invention, when compared with high
20 pressure polyethylenes, has about an equal Brabender
torque (satisfactory in processability), and is much
superior in tensile impact strength, rigidity, ESCR and
tensile strength, and further is about equally satis-
factory in transparency.

25 Compared with the low density ethylene- α -olefin
copolymer of the conventional technique, this polymer
composition has a much lower Brabender torque (farmore

1 excellent in processability) and a higher tensile impact strength and tensile strength.

Example 37 - see Tables 22 and 24.

Examples 38, 39, 40, 41, 42, 43

By mixing the ethylene- α -olefin copolymers A
5 obtained in Example 33 and the ethylene- α -olefin copolymers B obtained in Example 34 at ratios as shown in Table 23, compositions having densities, MIs and MFRs shown in Table 23 were obtained. Physical properties of these compositions are also shown in Table 23.

10 In Table 23 is also shown a similar composition prepared by two stage polymerization (Example 35) and, for the purpose of comparison, compositions of low density ethylene- α -olefin copolymers of the conventional technique (Comparative examples 22, 23, 25) of which
15 molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. In Table 23 is also shown a composition of ethylene- α -olefin copolymers (Comparative example 24,
20 to be compared with Examples 40 and 42) of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have a too low intrinsic viscosity.

As seen in Table 23, in the compositions of this
25 invention, S.C.B. of higher molecular weight components are more than or about equal to those of lower molecular weight components. (Compare Examples 35, 38 and 41 with

- 1 Comparative examples 22 and 23, and Example 43 with Com-
parative example 25.) Therefore, compared with the
compositions of the conventional technique, the composi-
tions of this invention are far excellent in tensile
5 impact strength and tensile strength, and are superior in
transparency.

From the comparison between Comparative example
17 of Table 22 and Comparative example 22 of Table 23,
it is learned that widening of molecular weight distri-
10 bution (higher MFR gives wider distribution) in the
manufacture of a low density ethylene- α -olefin copolymer
of the conventional technique with its density and MI
kept constant results in large reduction in tensile
impact strength and tensile strength.

- 15 From the comparison of Examples 40 and 42 with
Comparative example 24, it is learned that a too low
intrinsic viscosity of lower molecular weight components
badly affects its tensile impact strength, tensile
strength and transparency.

Table 21

No.	Polymeri- zation method	Polymeri- zation vessel capacity (ℓ)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α -olefin (g)	H ₂ partial pressure (kg/cm ²)
1st stage	Slurry	5	24.3	5	C ₄ 1000	C ₄ ' 250	0.6
2nd stage	Slurry						10

- Cont'd -

Note C₄ = n-Butane TEA = Triethyl aluminumC₄' = Butene-1 () = Calculated valuesC₂' = Ethylene

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Table 21 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Polymeri- zation time (min)	Properties			
			Density (g/cm ³)	[η] (dl/g)	S.C.B.	$\bar{M}_w/\bar{M}_n$
4	50	70	0.912	2.6	24	5.7
5		180	-	(0.8)	(23)	-

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Table 22

	Mixing method	Copolymer A		Copolymer B		Properties of composition			
		Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min.)	MFR	Distribution index of S.C.B.*
Example 36	Banbury	A4-1	50	B4-1	50	0.920	0.5	70	1.0
Example 37	"	A4-11	50	B4-12	50	0.921	0.7	40	1.0
Comparative Example 15	High pressure polyethylene	(Sumikathene ^(R) F208-1)				0.923	1.4	50	-
Comparative Example 16	"	(Sumikathene ^(R) F101-1)				0.922	0.3	65	-
Comparative Example 17	Low density ethylene/ α -olefin copolymer of the conventional technique					0.920	0.5	30	-

- Cont'd -

$$\text{* Distribution index of S.C.B.} = \frac{(\text{S.C.B. of copolymer A})}{(\text{S.C.B. of copolymer B})}$$

Table 22 (Cont'd)

Physical properties of composition						
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	ESCR F ₅₀ (hr)	Tensile strength (kg/cm ²)	Haze (%)	Brabender torque (kg.m)	
350	2800	>1000	280	5	2.0	
370	3000	>1000	290	5	2.6	
130	2400	0.3	160	4	1.9	
200	2200	30	180	6	2.2	
280	3200	>1000	260	5	3.5	

Table 23

Mixing method	Copolymer A		Copolymer B		Properties of composition			
	Designation	% by weight	Designation	% by weight	Density (g/cm ³)	MI (g/10 min.)	MFR	Distribution index of S.C.B.*
Example 35	- Two stage polymerization -				0.921	0.5	70	(1.0)
Example 38	Solution	50	B4-2	50	0.920	0.6	70	1.0
Example 39	"	30	B4-3	70	0.921	0.3	90	0.8
Example 40	Banbury	50	B4-4	50	0.920	1.1	65	1.0
Example 41	"	50	B4-5	50	0.920	0.5	70	1.5
Example 42	Solution	50	B4-6	50	0.920	1.1	65	1.0
Example 43	Banbury	50	B4-7	50	0.929	0.2	100	1.0
Comparative. Example 22	"	50	B4-8	50	0.920	0.5	70	0.26
Comparative Example 23	Solution	50	B4-9	50	0.920	0.6	65	0.36
Comparative Example 24	Banbury	65	B4-10	35	0.920	0.8	50	1.0
Comparative Example 25	"	50	B4-11	50	0.930	0.2	100	0.27

- Cont'd -

* Distribution Index of S.C.B. = (S.C.B. of copolymer A)/(S.C.B. of copolymer B)

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Table 23 (Cont'd)

Physical properties of composition				
Tensile impact strength (kg-cm/cm ²)	Olsen's flexural modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Haze (%)	Tackiness
340	2800	280	6	o
430	2800	320	5	o
370	2800	300	7	o
290	2800	250	6	o
400	2700	300	8	o
360	2800	310	5	o
370	4200	300	8	o
150	3300	210	12	x
180	3200	220	12	Δ
130	2800	220	15	o
170	4800	230	20	o

1 Example 44

The compositions prepared in Examples 36 and 37 as well as the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 5 17 were subjected to film processing in the same conditions as used in Example 32.

The commercial high pressure polyethylenes used in Comparative examples 15 and 16 were also subjected to film processing in the same conditions. A satisfactory 10 film was not obtained from the low density ethylene- α -olefin copolymer of the conventional technique used in Comparative example 17, with too much load put on the motor and with shark skin formed on the film surface.

Satisfactory films having good transparency 15 were obtained from the compositions prepared in Examples 36 and 37 and the commercial high pressure polyethylenes used in Comparative examples 15 and 16, with no problem of motor load. Physical properties of these films are shown in Table 24. Compared with the films of the high 20 pressure method polyethylenes, the films of the compositions prepared in Examples 36 and 37 had about same transparency but were superior in dart impact strength, Elmendorf tear strength (absolute value property and MD/TD balance), heat-sealing properties, tensile 25 strength, hot tack and heat sealing strength in contaminated condition. In case of the films of the compositions prepared in Examples 36 and 37, heat-sealing strengths and heat sealing strength in contaminated condition were at

1 about same levels, but in the films of the high pressure polyethylenes of Comparative example 16, heat sealing strength in contaminated condition were lower than heat-sealing strengths.

5 Comparative Examples 22, 23, 25

By mixing ethylene- α -olefin copolymers A obtained in Example 33 and ethylene- α -olefin copolymers B obtained in Example 34 at ratios as shown in Table 23, compositions of low density ethylene- α -olefin copolymers
10 of the conventional technique were prepared of which molecular weight distribution are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs and physical properties of
15 these compositions are shown in Table 23.

Comparative Example 24

By mixing an ethylene- α -olefin copolymer A obtained in Example 33 and an ethylene- α -olefin copolymer B obtained in Example 34 at a ratio shown in Table 23,
20 a composition of ethylene- α -olefin copolymers was prepared of which distribution index of S.C.B. meets the scope of this invention but of which lower molecular weight components have a too low intrinsic viscosity. Its density, MI, MFR and physical properties are shown in Table 23.

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Table 24

	Haze (%)	Dart impact strength (kg·cm/mm)	Elmendorf tear strength MD/TD (kg/cm)	Tensile strength MD/TD (kg/cm ²)	Heat- sealing strength (kg/15mm width)	Hot tack property (mm)	Heat sealing strength in contaminated condition
Example 36	5	500	90/120	410/380	1.2	2.0	o
Example 37	5	450	60/120	420/370	1.3	2.0	o
Comparative Example 15	4	270	80/50	250/210	0.7	4.0	Δ
Comparative Example 16	7	250	70/70	280/250	0.7	3.0	Δ

1 Example 45

Ethylene- α -olefin copolymers were synthesized using the catalyst produced in Example 1 and organo-aluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 25. Densities, intrinsic viscosities, and S.C.B. of these copolymers were shown in Table 25.

These copolymers are used in the following examples as higher molecular weight components.

10 Example 46

Ethylene- α -olefin copolymers were synthesized using the catalyst produced in Example 1 and organoaluminum compounds (co-catalyst) and employing α -olefins and other polymerization conditions as shown in Table 26. Densities, intrinsic viscosities and S.C.B. of these copolymers were shown in Table 26.

These copolymers are used in the following examples as lower molecular weight components.

Table 25

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg)
A-1	Slurry	65	131	TEA 100	C ₄ 6.0	C ₄ ' 6.14	0.45
A-2	"	65	145	TEA 50	"	"	0.59
A-3	"	65	310	TEA 100	"	"	0.70
A-4	"	65	125	"	"	"	1.8
A-5	Solution	1	25.3	DEAC 2.5	C ₇ 0.25	4-MP-1 0.11	0.1
A-6	"	1	24.5	"	C ₇ 0.30	4-MP-1 0.05	0.15
A-7	Slurry	65	121	TEA 50	C ₄ 6.0	C ₄ ' 6.14	0.98
A-8	"	65	320	TEA 100	"	"	3.0

-- Cont'd --

Note TEA = Triethyl aluminum C₄ = n-Butane
 DEAC = Diethyl aluminum chloride C₄' = Butene-1
 4-MP-1 = 4-Methylpentene-1 C₇ = n-Heptane

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Table 25 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties		
		Density (g/cm ³)	[η] (dl/g)	S.C.B.
5.0	50	0.899	2.6	38
6.7	50	0.906	2.6	29
7.8	50	0.912	2.6	24
18	50	0.923	2.6	9
20	140	0.904	2.5	23
20	140	0.920	2.5	10
6.5	50	0.907	2.2	30
20	50	0.928	2.2	8

Table 26

No.	Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst (mmol)	Solvent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)
B-1	Slurry	65	405	TEA 50	C ₄ 50	C ₄ ' 2.0	10.8
B-2	"	65	411	"	C ₄ 15.2	C ₄ ' 1.6	6.5
B-3	"	65	402	"	C ₄ 12.0	C ₄ ' 3.2	7.8
B-4	"	65	408	TEA 100	"	C ₄ ' 4.0	5.2
B-5	Solution	1	26.5	DEAC 2.5	C ₇ 0.28	4-MP-1 0.03	3.0
B-6	"	1	25.7	"	C ₇ 0.25	4-MP-1 0.05	2.5
B-7	Slurry	65	407	TEA 100	C ₄ 15.4	C ₄ ' 0.5	13.0
B-8	"	65	422	TEA 50	C ₄ 15.2	C ₄ ' 1.8	11.0

- Cont'd -

C₄ = n-ButaneC₄' = Butene-1C₇ = n-Heptane

Note TEA = Triethyl aluminum

DEAC = Diethyl aluminum chloride

4-MP-1 = 4-Methylpentene-1

Table 26 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Properties		
		Density (g/cm ³)	[η] (dl/g)	S.C.B.
8.3	70	0.912	0.83	15
5	70	0.935	0.83	20
6	70	0.929	0.85	24
4	50	0.910	0.82	35
10	140	0.938	0.50	13
10	140	0.912	0.52	22
5	70	0.953	0.62	9
5	70	0.934	0.61	22

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1 Example 47

A composition of ethylene- α -olefin copolymers was prepared in two stage polymerization. The first stage polymerization was carried out for 70 min. using the catalyst produced in Example 1 and triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 27. Successively, the second stage polymerization was conducted for 180 min. by changing only the hydrogen partial pressure and the ethylene partial pressure as shown in Table 27. In both stages, the liquid phase molar ratio of ethylene, butene-1 and hydrogen was kept constant at respective fixed levels. The polymerized quantities in each stage were calculated from the quantities of fed ethylene. The copolymer composition consisted of about 50% by weight of higher molecular weight components and about 50% by weight of lower molecular weight components. Immediately before the completion of the first stage polymerization, a part of the polymer was taken out and measured for its density, intrinsic viscosity and S.C.B. The whole polymer obtained after the second stage was also measured for the same test items. From the values of the first stage polymer and the whole polymer, the intrinsic viscosity and the number of branched short chains of the polymer formed in the second stage alone were calculated. These values were shown in Table 27. The whole polymer gave: density 0.921 g/cm³, MI 0.5 g/10 min., MFR 70, intrinsic viscosity 1.7 dl/g, S.C.B. 24, g_n^* 0.93. The whole polymer was subjected

1 to gel permeation chromatography and a curve of molecular weight distribution shown in Fig. 4 was obtained.

Because of bimodal distribution which has two peaks, the curve was divided into two parts using broken
5 lines. The areas of each part were calculated, and the lower molecular weight components and the higher molecular weight components were determined to be 48 and 52% by weight, respectively.

The whole polymer was divided into 30 fractions
10 using column chromatography. These fractions were divided into two parts (the lower molecular weight components and the higher molecular weight components) so that the former became 48% by weight and the latter 52% by weight. S.C.B., densities and intrinsic viscosities of each com-
15 ponent were shown in Table 29.

Flow characteristics and solid physical properties of the whole polymer were shown in Table 30.

In the following examples, ethylene- α -olefin copolymers as higher molecular weight components and
20 ethylene- α -olefin copolymers as lower molecular weight components were mixed at respective fixed ratios (total quantity 1 kg) and kneaded for 5 min. with a Banbury mixer (150 to 230 rpm). At that time, replacement by nitrogen was conducted completely and the polymer
25 temperatures were controlled not to exceed 250°C.

When sample quantities were small, mixing was made in xylene. After mixing, the whole solution was added into methanol to cause precipitation. After

1 filtration, the precipitate was completely dried in a vacuum drier and used as a copolymers composition sample.

Examples 48, 49, 50

Ethylene- α -olefin copolymers obtained in
5 Example 45 and ethylene- α -olefin copolymers obtained in Example 46 were kneaded with a Banbury mixer at ratios as shown in Table 28.

Thus, compositions of copolymers having densities, MIs, MFRs, intrinsic viscosities, S.C.B. and g_{η}^* shown in
10 Table 32 were obtained. These compositions had molecular weight distribution curves about equal to Fig. 4. With the same technique as used in Example 47, quantities of lower molecular weight components and higher molecular weight components were calculated, and they were both approximately
15 50% by weight as shown in Table 29. Physical properties of these compositions were shown in Table 30.

With the same technique as used in Example 47, column fractionation was applied in order to divide into higher molecular weight components and lower molecular
20 weight components. Characteristics of the components were shown in Table 29.

In Tables 29 and 30 were also shown Example 47 using a composition of ethylene- α -olefin copolymers prepared in two stage polymerization and, for comparison,
25 Comparative example 26 using a high pressure method polyethylene of the conventional technique (commercial product Sumikathene[®] F 101-1 manufactured by Sumitomo

- 1 Chemical Co., Ltd.), Comparative example 27 using a composition of low density ethylene- α -olefin copolymers of the conventional technique and Comparative example 28 using a composition of low density ethylene- α -olefin
- 5 copolymers of the conventional technique of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.
- 10 As is obvious from Tables 29 and 30, when compared with the high pressure polyethylene, the copolymer compositions of this invention have about equivalent
- 15 Brabender torques (excellent in processability), and are largely excellent in tensile impact strength, rigidity, ESCR and tensile strength. Transparency is equally good, because distribution index of S.C.B. is in a certain range as defined by the present invention. When compared with the composition of low density ethylene- α -olefin copolymers of the conventional technique, the compositions of
- 20 this invention have far smaller Brabender torques (much better processability) and higher tensile impact strengths and tensile strengths.

 From comparison between Comparative examples 27 and 28 in Tables 29 and 30, it is learned that widening

25 of molecular weight distribution (larger MFR gives wider distribution) in the manufacture of a low density ethylene- α -olefin copolymer of the conventional technique with density and MI fixed results in large reduction in tensile impact strength and tensile strength.

Table 27

No.	Polymeri- zation method	Polymer- zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Solvent (g)	α -olefin (g)	H ₂ partial pressure (kg/cm ²)
1st stage	Slurry	5	24.3	5	C ₄ 1000	C ₄ ' 250	0.6
2nd stage	Slurry						10

- Cont'd -

Note C₄ = n-Butane TEA = Triethyl aluminum

C₄' = Butene-1 () = Calculated values

C₂' = Ethylene

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Table 27 (Cont'd)

C ₂ '- partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Polymeri- zation time (min)	Properties		
			Density (g/cm ³)	[η] (dl/g)	S.C.B.
4	50	70	0.912	2.6	24
5		180	-	(0.8)	(23)

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Table 28

	Higher molecular weight component		Lower molecular weight component	
	Designation	% by weight	Designation	% by weight
Example 48	A-1	50	B-1	50
Example 49	A-2	50	B-2	50
Example 50	A-3	50	B-3	50
Comparative Example 28	A-4	50	B-4	50

Table 29

	Properties of copolymer					
	Density (g/cm ³)	MI (g/10 min.)	MFR	[η] (dl/g)	S.C.B.	η_{sp} [#]
Example 47	0.921	0.5	70	1.7	24	0.96
Example 48	0.920	0.5	70	1.7	26	0.97
Example 49	0.920	0.5	70	1.7	25	0.93
Example 50	0.920	0.5	70	1.7'	24	0.97
Comparative Example 26	0.922	0.3	65	1.06	23	0.48
Comparative Example 27	0.920	0.5	30	1.7	23	0.95
Comparative Example 28	0.920	0.5	70	1.7	22	0.95

- Cont'd -

Degree of S.C.B. of higher
molecular weight componentDegree of S.C.B. of lower
molecular weight component* Distribution index =
of S.C.B.

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Table 29 (Cont'd)

GPC			
Length of main peak chain (A)		Ratio (% by weight)	
Lower molecular weight component	Higher molecular weight component	Lower molecular weight component	Higher molecular weight component
1.7 x 10 ³	3.4 x 10 ³	48	52
1.7 x 10 ³	3.4 x 10 ³	48	52
1.6 x 10 ³	3.5 x 10 ³	47	53
1.9 x 10 ³	3.4 x 10 ³	48	52
1.05 x 10 ³	6.5 x 10 ³	36	64
Uniform distribution (peak) 2.8 x 10 ³		50	50
1.6 x 10 ³	3.6 x 10 ³	49	51

- Cont'd -

Table 29 (Cont'd)

Characteristics of components fractionated by column fractionation						
Lower molecular weight component			Higher molecular weight component			Distribution index of S.C.B.*
S.C.B.	Density (g/cm ³)	[η] (dl/g)	S.C.B.	Density (g/cm ³)	[η] (dl/g)	
30	0.920	0.8	18	0.915	2.6	0.6
27	0.924	0.8	25	0.910	2.6	0.9
28	0.923	0.7	20	0.914	2.5	0.7
30	0.920	0.8	18	0.915	2.5	0.6
27	0.916	0.6	19	0.926	1.4	0.7
38	0.906	1.1	8	0.925	2.4	0.2
37	0.907	0.8	7	0.926	2.6	0.2

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Table 30

	Physical properties of copolymer						
	Tensile impact strength (kg-cm/cm ²)	Olsen's Flexural modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Haze (%)	Torque (kg-m)	ESCR P50 (hr)	Tackiness
Example 47	340	2800	280	5	2.0	>1000	o
Example 48	450	2600	320	20	2.0	>1000	o
Example 49	400	2700	300	8	2.0	>1000	o
Example 50	350	2800	280	5	2.0	>1000	o
Comparative Example 26	200	2200	180	6	2.2	30	o
Comparative Example 27	280	3200	260	8	3.5	>1000	o
Comparative Example 28	150	3300	210	12	2.0	>1000	x

1 Example 51.

Compositions of ethylene- α -olefin copolymers were prepared by mixing ethylene- α -olefin copolymers obtained in Example 45 and ethylene- α -olefin copolymers 5 obtained in Example 46 at ratios shown in Table 31. Densities, MIs, MFRs, $[\eta]$, S.C.B. and g_n^* of these compositions were shown in Table 32. Their physical properties were shown in Table 33.

Molecular weight distributions of Example 51 10 showed "one almost symmetrical mountain" curves. Column fractionation was applied with the same technique as used in Example 47. Its results were shown in Table 32.

In Tables 32 and 33 were also shown low density ethylene- α -olefin copolymers of the conventional technique (Comparative examples 29 and 30) of which molecular 15 weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B.

20 Curves of molecular weight distributions of Comparative examples 29 and 30 were similar to that of Example. 51. As seen from Tables 32 and 33, in the compositions of this invention, S.C.B. of higher molecular weight components and those of lower molecular 25 weight components are nearly equal (compare Example 51 with Comparative example 29), therefore, the compositions

- 1 of the present invention are far superior to the copolymers of the conventional technique in tensile impact strength and tensile strength.

Comparative Example 26

- 5 A commercial high pressure polyethylene (Sumikathene[®] F 101-1 manufactured by Sumitomo Chemical Co., Ltd.) was subjected to measurements of physical properties and. Results were shown in Table 30.

- This polyethylene has low g_n^* of 0.48 and it suggests that this sample has many long chain branches. Its molecular weight distribution curve was shown in Fig. ⁵7. Column fractionation was applied with the same technique as used in Example 47. The fractions obtained were divided into two groups so that the lower molecular weight component group and the higher molecular weight component group became about 36 and 64% by weight, respectively. Densities, S.C.B. and intrinsic viscosity of each group were measured and results were shown in Table 29.

20 Comparative Example 27

- A low density ethylene- α -olefin copolymer of the conventional technique was synthesized using the catalyst produced in Example 1, triethyl aluminum (co-catalyst) and other polymerization conditions as shown in Table 34. The copolymer gave: density 0.920 g/cm^3 , MI 0.5 g/10 min. , MFR 30, intrinsic viscosity 1.7 dl/g ,

- 1 S.C.B. 23, g_n^* 0.95. Its physical properties were shown in Table 30. Its molecular weight distribution showed "one almost symmetrical mountain" curve, as seen in Fig. 1. From the area ratio, the lower molecular weight components and the higher molecular weight components were determined to be both 50% by weight. Column fractionation was applied with the same technique as used in Example 47 and results were shown in Table 29.

Comparative Example 28

- 10 By mixing the ethylene- α -olefin copolymer A-4 obtained in Example 45 and the ethylene- α -olefin copolymer B-4 obtained in Example 46 at the ratio as given in Table 28, a composition of low density ethylene- α -olefin copolymers of the conventional technique was prepared of which molecular weight distribution is made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Its density, MI, MFR, $[\eta]$, and g_n^* were shown in Table 29. The molecular weight distribution curve of this composition was almost equal to that in Fig. 4. With the same technique as used in Example 47, the ratio of the lower and higher molecular weight components was determined. Column fractionation was also conducted. These results were shown in Table 29.
- 25 Physical properties of this composition were shown in Table 30.

1 Comparative Examples 29, 30

By mixing ethylene- α -olefin copolymers obtained in Example 45 and ethylene- α -olefin copolymers obtained in Example 46 at ratios as shown in Table 31, compositions of low density ethylene- α -olefin copolymers of the conventional technique were prepared of which molecular weight distributions are made wider and of which lower molecular weight components have larger S.C.B. and of which higher molecular weight components have smaller S.C.B. Densities, MIs, MFRs, $[\eta]$, S.C.B. and g_{η}^* of these compositions were shown in Table 32. Physical properties of these compositions were shown in Table 33.

Table 31

	Higher molecular weight component		Lower molecular weight component	
	Designation	% by weight	Designation	% by weight
Example 51	A-5	60	B-5	40
Comparative Example 29	A-6	60	B-6	40
Comparative Example 30	A-8	50	B-8	50

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Table 32

	Properties of copolymer					
	Density (g/cm ³)	MI (g/10 min)	MFR	[η] (dl/g)	S.C.B.	η^*
Example 51	0.920	0.5	70	1.7	19	0.91
Comparative Example 29	0.919	0.5	70	1.7	17	0.96
Comparative Example 30	0.929	1.2	70	1.4	17	0.93

- Cont'd -

Degree of S.C.B. of higher
molecular weight component

* Distribution index =
of S.C.B.

Degree of S.C.B. of lower
molecular weight component

Table 32 (Cont'd)

GPC			
Length of main peak chain (Å)		Ratio (% by weight)	
Lower molecular weight component	Higher molecular weight component	Lower molecular weight component	Higher molecular weight component
Uniform distribution (peak) 2.5 x 10 ³		57	43
Uniform distribution (peak) 2.5 x 10 ³		58	42
Uniform distribution (peak) 1.6 x 10 ³		48	52

- Cont'd -

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Table 32 (Cont'd)

Characteristics of components fractionated by column fractionation						
Lower molecular weight component			Higher molecular weight component			Distribution index of S.C.B.*
S.C.B.	Density (g/cm ³)	[n] (dl/g)	S.C.B.	Density (g/cm ³)	[n] (dl/g)	
22	0.933	0.5	15	0.920	2.4	0.7
24	0.930	0.5	7	0.927	2.4	0.3
29	0.922	0.6	6	0.930	2.1	0.2

Table 33

	Physical properties of copolymer			
	Tensile impact strength (kg·cm/cm ²)	Olsen's Flexural modulus (kg/cm ²)	Tensile strength (kg/cm ²)	Tackiness
Example 51	480	2600	320	o
Comparative Example 29	200	3100	200	x
Comparative Example 30	70	4500	200	o

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Table 34

Poly-meri-zation method	Poly-meri-zation vessel capacity (l)	Catalyst quantity (mg)	Co-catalyst TEA (mmol)	Sol-vent (kg)	α -olefin (kg)	H ₂ partial pressure (kg/cm ²)	C ₂ ' partial pressure (kg/cm ²)	Polymeri-zation temperature (°C)	Polymeri-zation time (min)
Slurry	65	202	100	C ₄ 7.0	C ₄ ' 7.16	3.0	10	50	90

Note TEA = Triethyl aluminum

C₄ = n-Butane

C₂' = Ethylene

C₄' = Butene-1

1 Reference Example 1

An ethylene- α -olefin copolymer was synthesized from ethylene and butene-1, using the catalyst produced in Example 1, diethyl aluminum monochloride (co-catalyst) 5 and other polymerization conditions as shown in Table 35. Properties of this copolymer were shown in Table 36. By applying column fractionation, the copolymer was fractionated into fractions of different molecular weights. Then, distribution of S.C.B. against molecular 10 weight was examined as shown in Fig. ⁶7.

In column fractionation, about 5 g of the sample was placed in a fractionation column after being adsorbed on a carrier (Celite 745) in xylene. Then, the column was heated to 130°C, and butyl cellosolve and xylene 15 were passed through the column with the mixing ratio being gradually changed in order to obtain a gradual increase in solvency. Thus, all the copolymer fractions of lower to higher molecular weight were separated. To the eluates was added methanol to cause precipitation 20 of the copolymers. After recovery, the polymers were dried under reduced pressure and each copolymer fraction was obtained. In the above column fractionation process, in order to prevent the possible decomposition of the copolymers, 100 ppm of Irganox[®] 1076 was added to the 25 original sample and further air inside the column was replaced by nitrogen. Using each copolymer fraction, pressed sheets having about 100 to 300 μ thickness were prepared, and S.C.B. of each copolymer fraction were

- 1 calculated by conducting Fourier-transform infrared
absorption spectroscopy. Molecular weights of each
copolymer fraction were calculated, using intrinsic
viscosities $[\eta]$ measured in tetralin of 135°C and the
5 following formula.

$$[\eta] = 5.1 \times 10^{-4} \cdot \bar{M}_n^{0.725}$$

Reference Example 2

With ethylene- α -olefin copolymers of the conventional technique, a relationship between melt index
10 (MI) and tensile impact strength was examined with melt
flow ratio (MFR) used as a parameter. Results were shown
in Fig. ~~8~~⁹. It is revealed that widening of molecular
weight distribution results in remarkable reduction in
tensile impact strength. (In the figure, molecular weight
15 distribution was represented by MFR. Larger MFR means
wider molecular weight distribution.). These ethylene-
 α -olefin copolymers were subjected to molecular weight
fractionation with the same technique as used in
Reference Example 1. All the copolymers showed trends
20 similar to that of Reference Example 1. The fractions
were divided into two groups (lower molecular weight
group and higher molecular weight group) in such a way
that each group became about 50% by weight, and (S.C.B.
of higher molecular weight component/S.C.B. of lower
25 molecular weight component) was calculated. It was below
0.5 in all the copolymers.

1 Reference Example 3

With a high pressure method polyethylene of the conventional technique and a linear, high density polyethylene of medium to low pressure method, correlations
5 between melt index (MI) and intrinsic viscosity $[\eta]$ were examined and shown in Fig. ⁸ 8. The correlation lines of each sample are clearly divided by a partition line (broken line). It is learned that the high pressure polyethylene has much lower intrinsic viscosity than that
10 of the linear high density polyethylene of the same melt index.

A correlation between melt index and intrinsic viscosity was examined with the ethylene- α -olefin copolymers of the present invention. All of the copoly-
15 mers of the present invention fell in the zone of the linear, high density polyethylene.

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Table 35

Polymeri- zation method	Polymeri- zation vessel capacity (l)	Catalyst quantity (mg)	Solvent (g)	α -olefin (g)	H ₂ partial pressure (kg/cm ²)	C ₂ ' partial pressure (kg/cm ²)	Polymeri- zation tempera- ture (°C)	Polymeri- zation time (min)
Solution	1	25.1	C ₇ 300	C ₄ ' 40	3.5	20	140	90

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Table 36

Properties			
Density (g/cm ³)	MI (g/10 min)	MFR	S.C.B.
0.924	4	25	20



CLAIMS

1. An ethylene- α -olefin copolymer composition having a density of 0.915 to 0.929 g/cm³, a melt index of 0.02 to 50 g/10 min. and a melt flow ratio of 35 to 250, which comprises 10 to 70% by weight of an ethylene- α -olefin copolymer A and 90 to 30% by weight of an ethylene- α -olefin copolymer B; said copolymer A having higher molecular weight than copolymer B and being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 dl/g and a short chain branching ("S.C.B.") number per 1000 carbon atoms of 7 to 40 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; copolymer B being a copolymer of ethylene and an α -olefin of 3 to 18 carbon atoms and having a density of 0.910 to 0.949 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g and a S.C.B. of 5 to 35 and a (weight average molecular weight)/(number average molecular weight) value of 2 to 10; said copolymer A and said copolymer B being chosen such that (S.C.B. of copolymer A)/(S.C.B. of copolymer B) is 0.6 to 1.7.
2. A composition according to claim 1 wherein copolymer A and/or copolymer B is an ethylene-butene-1 copolymer.

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3. A composition according to claim 1 wherein copolymer A and/or copolymer B is an ethylene-4-methylpentene-1 copolymer.
4. A composition according to claim 1 wherein
5 copolymer A and/or copolymer B is an ethylene-hexene-1 copolymer.
5. A composition according to claim 1 wherein copolymer A and/or copolymer B is an ethylene-octene-1 copolymer.
- 10 6. A composition according to any one of the preceding claims prepared by a multi-stage polymerization.
7. A composition according to any one of claims 1 to 5, in which the copolymer components are mixed in a two-stage polymerization wherein, in the first stage,
15 copolymer A is polymerized and successively, in the second stage, copolymer B is polymerized under different conditions from the first stage polymerization apart from catalysts, until a required weight ratio of copolymers A and B is obtained.
- 20 8. A composition according to claim 1 substantially as hereinbefore described with reference to any one of Examples 18 to 23 and 35 to 43.
9. A composition of copolymers of ethylene and an α -olefin of 3 to 18 carbon atoms, having first and second
25 component groups, said first component group having a higher



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molecular weight than said second component group, having the following properties:

- (1) density of 0.915 to 0.929 g/cm³
- (2) intrinsic viscosity $[\eta]$ of 0.7 to 4.0 dl/g
- 5 (3) melt index of 0.02 to 50 g/10 min.,
- (4) S.C.B. being 5 to 45,
- (5) $[\eta]/[\eta]$ namely g_p^* being at least 0.8, where $[\eta]$ is an intrinsic viscosity of a linear polyethylene having the same weight average molecular weight measured by a light
- 10 scattering method, and
- (6) (S.C.B. of the higher molecular weight components)/(S.C.B. of the lower molecular weight components) being 0.6 to 0.8 where these two component groups are obtained by consolidating fractions obtained by column
- 15 fractionation in two portions of lower and higher molecular weight components, in order that the weight ratio of these two portions becomes closest to the weight ratio of lower and higher molecular weight components obtained in the gas permeation chromatography (GPC) curve,
- 20 (7) the second components have a density of 0.910 to 0.949 g/cm³, an intrinsic viscosity of 0.3 to 1.5 dl/g and S.C.B of 5 to 35,
- (8) the first components have a density of 0.895 to 0.935 g/cm³, an intrinsic viscosity of 1.2 to 6.0 - 166 -
- 25 dl/g and S.C.B of 7 to 40, and
- (9) the second components are 30 to 90% by weight and



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the first components are 70 to 10% by weight

10. A composition according to claim 9 which gives a two-peak or multi-peak molecular weight distribution curve when subjected to gel permeation chromatography, in which
5 curve the total lower molecular weight components contain at least one component having a peak chain length of 2×10^2 to 3.0×10^3 A and the total higher molecular weight components contain at least one component having a peak chain length of 1×10^3 to 6×10^4 A and the lower molecular weight
10 components represent 70 to 30% by weight and the higher molecular weight components represent 30 to 70% by weight of the total copolymers.

11. A composition according to claim 9 or 10 wherein the α -olefin is butene-1.

15 12. A composition according to claim 9 or 10 wherein the α -olefin is 4-methyl-pentene-1.

13. A composition according to claim 9 or 10, wherein the α -olefin is hexene-1.

20 14. A composition according to claim 9 or 10 wherein the α -olefin is octene-1.

15. A composition according to any one of claims 9 to 14 prepared by a multi-stage polymerization using a carrier-supported Ziegler catalyst.



16. A composition according to any one of Claims 9 to 15 which has a melt index of 0.04 to 10 g/10 min.

17. A composition according to any one of Claims 9 to 16 which has a melt flow ratio of 35 to 250.

5 18. A composition according to Claim 9 substantially as hereinbefore described with reference to any one of Examples 47, 49 and 50.

19. An extrusion processed material obtained from an ethylene- α -olefin copolymer composition as claimed
10 in any one of Claims 1 to 15 and 18 having a density of 0.915 to 0.929 g/cm³ and a melt index of 0.02 to 2.0 g/10 min.

20. A film obtained from an ethylene - α -olefin copolymer composition as claimed in any one of claims 1 to
15 15 and 18 having a density of 0.915 to 0.929 g/cm³ and a melt index of 0.02 to 5 g/10 min.

21. An injection molded material obtained from an ethylene- α -olefin copolymer composition as claimed in any one of Claims 1 to 15 and 18 having a density of 0.915
20 to 0.929 g/cm³, a melt index of 2.0 to 50 g/10 min. and melt flow ratio of 35 to 80 and being obtained by mixing a copolymer A as defined in Claim 1 having an intrinsic viscosity of 1.2 to 4.0 dl/g and a copolymer B as defined in Claim 1 having a density of 0.910 to 0.949 g/cm³ and an
25 intrinsic viscosity of 0.3 to 1.2 dl/g.
