PROCESS FOR CONTROLLING THE MWD OF A BROAD/BIMODAL RESIN PRODUCED IN A SINGLE REACTOR

A bimetallic catalyst produces broad or bimodal molecular weight distribution polyolefin resin whose composition depends on the ratio of metal concentration of the two metals of the catalyst producing the HMW and LMW components. The bimetallic catalyst produces a broad MWD resin whose HMW and LMW components depend on the relative productivity of each of the transition metal sites of the catalyst. Water and/or carbon dioxide are co-fed to the polymerization reactor at levels necessary to modify the weight fractions of the HMW and LMW components, thus achieving a target molecular weight distribution, MWD. The invention allows the resin MWD to be adjusted in the reactor. The weight fraction of the high molecular weight component decreases with the addition of the water and/or the carbon dioxide and the FI of the overall product increases with a decrease in the HMW component weight fraction in the product.
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PROCESS FOR CONTROLLING THE MWD OF A
BROAD/BIMODAL RESIN PRODUCED IN A SINGLE REACTOR

The invention relates to a catalytic process and a catalytic preparation of bimodal molecular weight distribution polymers and copolymers of ethylene, in one reactor, in the presence of a bimetallic catalyst. A water and/or carbon dioxide feed to the reactor is used to control the proportion of different weight fractions in broad or bimodal molecular weight distribution olefin resin product, produced by the bimetallic catalyst during polymerization or copolymerization.

The bimetallic catalyst contains two different transition metal compounds, each having different hydrogen response characteristics. Because of the different hydrogen response of each of the two sources of transition metal in the bimetallic catalyst, each will produce a different molecular weight component under identical olefin polymerization conditions. In preferred embodiments below, the LMW component is produced by the Zr site while the HMW component is produced by the Ti site.

The bimetallic catalyst produces broad or bimodal molecular weight distribution polyolefin resin whose composition depends on the ratio of the concentration of the two transition metal catalyst components producing the HMW and LMW components. Thus the product of olefin polymerization in the presence of such a catalyst will comprise at least two fractions each of different molecular weight, and one having a relatively high molecular weight (hereinafter HMW) relative to a second fraction of relatively lower molecular weight (LMW).

In that product, the weight fractions of the HMW and LMW components in the final product are fixed by the relative concentration of the two metal species in the bimetallic catalyst.
In bimodal molecular weight distribution products, the weight fraction of the HMW component should be in the range of 0.10 to 0.90 for applications requiring broad molecular weight distribution resins. Another measurable property of the bimodal products is flow index, (FI or I$_{21}$, measured at 190° C in accordance with ASTM D-1238, Condition F.) The FI of the bimodal molecular weight product should be in the range of 2 to 100. If the bimodal molecular weight distribution product has FI of less than 2, FI is too low for processability. On the other hand, if overall polymer FI is too high, then product toughness properties decrease. Hence, it is necessary to control polymer FI in the polymerization reactor. Product MFR values are preferably in the range of 30 - 250. MFR is defined herein as the ratio of the flow index (FI or I$_{21}$) divided by the melt index, i.e.,

\[
\text{MFR} = \frac{I_{21}}{I_{2.16}}
\]

Smaller MFR values indicate relatively narrow molecular weight distribution polymers.

Because of the different hydrogen response of each of the two sources of transition metals in the bimetallic catalyst, each will produce a different molecular weight component under identical olefin polymerization conditions. In preferred embodiments below, the metal of highest hydrogen response will be present in amounts of 0.1 to 0.8 weight percent; in preferred embodiments that metal is zirconium. The metal of lowest hydrogen response will be present in amounts of 0.5 to 3.0 weight percent; in preferred embodiments that metal is titanium. This catalyst system of the invention is catalytically effective to produce bimodal molecular weight distribution product containing 0.05 to 0.95 weight percent of the high molecular weight component.
Olefins are polymerized with catalysts according to the present invention by any suitable process. Such processes include polymerizations carried out in suspension, in solution or in the gas phase. Gas phase polymerization reactions are preferred, e.g., those taking place in stirred bed reactors and, especially, fluidized bed reactors. The polymerization is carried out at relatively low temperatures, e.g., from 30 to 115°C. Preferably, polymerization pressures are less than 10,000 psi (70,000 kPa), preferably less than 1000 psi (7,000 kPa), and most preferably in the range of 689.476 kPa to 2413.66 kPa [100 to 350 psig].

A particularly desirable method for producing polyethylene polymers according to the present invention is in a fluid-bed reactor. The polymer produced in such a reactor contains the catalyst particles because the catalyst is not separated from the polymer.

The molecular weight of the polymer may be controlled in a known manner, e.g., by using hydrogen. With the catalysts produced according to the present invention, molecular weight may be suitably controlled with hydrogen when the polymerization is carried out at relatively low temperatures, e.g., from 30 to 105°C. This control of molecular weight may be evidenced by a measurable positive change in melt index (I₂) of the polymer produced.

When a fluid-bed reactor is employed, the catalyst modifier of the invention can be introduced separately. The catalyst modifier is added continuously to the reactor. In the presence of the catalyst described below and used in accordance with the invention, water and/or carbon dioxide decrease the weight fraction of the HMW component, with the result that the relative weight fraction of LMW component increases; the effect of decreasing the amount of HMW component is to increase FI of broad or bimodal molecular weight distribution resin. The amount of the catalyst modifier can range from 0.1 to 1000 ppm (based on
ethylene), and preferably from 0.1 to 50 ppm (based on ethylene). For example, when CO₂ is employed the CO₂ feed will range from 0.1 ppm to 50 ppm (based on ethylene); generally, 0.1 to 20 ppm CO₂ (based on ethylene) has been employed. The water cofeed can range from 0.1 ppm to 1000 ppm based on ethylene; generally 0.1 to 50 ppm water, based on ethylene, is employed. Although the catalyst modifier can be added separately, it can also be added as a mixture, a cofeed, with ethylene or hydrogen. The presence of the modifier acts to increase FI by at least 10%. The increase in FI depends on the level of modifier employed and the composition of the catalyst system. Increase in FI can range from 10 to 2000%, preferably 20 to 100% over that of a resin produced in the absence of the modifier.

The linear polyethylene polymers prepared in accordance with the present invention are homopolymers of ethylene or copolymers of ethylene with one or more C₇–C₁₀ alpha-olefins. Thus, copolymers having two monomeric units are possible as well as terpolymers having three monomeric units. Particular examples of such polymers include ethylene/1-butene copolymers, ethylene/1-hexene copolymers, ethylene/1-octene copolymers, ethylene/4-methyl-1-pentene copolymers, ethylene/1-butene/1-hexene terpolymers, ethylene/propylene/1-hexene terpolymers and ethylene/propylene/1-butene terpolymers. When propylene is employed as a comonomer, the resulting linear low density polyethylene copolymer preferably has at least one other alpha-olefin comonomer having at least four carbon atoms in an amount of at least 1 percent by weight of the polymer. Accordingly, ethylene/propylene copolymers are possible, but not preferred. The most preferred comonomer is 1-hexene. The linear low density polyethylene polymers produced in accordance with the present invention preferably contain at least 80 percent by weight of ethylene units.
Preferred bimetallic catalysts employed in the process of the invention contain at least two transition metals, one in the form of a metalloocene and one transition metal in the form of a non-metalloocene, and have an activity of at least 1000 g polymer/g catalyst or 50 kg polymer/g of each transition metal. The bimetallic catalysts are free of water.

The catalysts of the invention comprise a cocatalyst comprising an aluminum alkyl compound, such as a trialkyl aluminum, free of alumoxane and free of water, or oxygen-containing oligomers and polymers of the aluminum alkyl compound, and a catalyst precursor comprising a carrier, an alumoxane and at least one metalloocene; in one embodiment the catalysts further include a non-metalloocene transition metal source.

The carrier material is a solid, particulate, porous, preferably inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material is used in the form of a dry powder having an average particle size of from 1 micron to 500 microns, preferably from 10 microns to 250 microns. The surface area of the carrier is at least 3 square meters per gram (m²/g), and preferably at least 50 m²/g up to 350 m²/g. The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating at 100°C to 1000°C, preferably at 600°C. When the carrier is silica, it is heated to at least 200°C, preferably 200°C to 850°C and most preferably at 600°C. The carrier material must have at least some active hydroxyl (OH) groups to produce the catalyst composition of this invention.

In the most preferred embodiment, the carrier is silica which, prior to the use thereof in the first catalyst synthesis step, has been dehydrated by fluidizing it with nitrogen and heating at 600°C for 4-16 hours to achieve a surface hydroxyl group concentration of 0.7 millimoles per gram (mmol/g). The silica of the most
preferred embodiment is a high surface area, amorphous silica (surface area = 300 m²/g; pore volume of 1.65 cm³/g), and it is a material marketed under the tradenames of Davison 952 or Davison 955 by the Davison Chemical Division of W.R. Grace and Company. The silica is in the form of spherical particles, e.g., as obtained by a spray-drying process. As procured, these silicas are not calcined; and this must be dehydrated, as indicated above.

The catalyst synthesis is undertaken under inert conditions, in the absence of water and of oxygen. The carrier is dispersed in solvent to form a slurry.

The carrier material, having said (OH) groups, is slurried in a non-polar solvent and the resulting slurry is contacted with at least one organomagnesium compound having the empirical formula below. The slurry of the carrier material in the solvent is prepared by introducing the carrier into the solvent, preferably while stirring, and heating the mixture to 25 to 70°C, preferably to 40 to 60°C. Temperatures here are critical with respect to the non-metallocene transition metal which is subsequently added; that is temperatures in this slurry of 90°C result in deactivation of the transition metal added subsequently. Accordingly, all catalyst precursor synthesis steps are conducted below 90°C. The slurry is then contacted with the aforementioned organomagnesium compound, while the heating is continued as indicated.

The organomagnesium compound has the empirical formula RMgR'

where R and R' are the same or different C₂-C₁₂ alkyl groups, preferably C₄-C₁₀ alkyl groups, more preferably C₄-C₈ alkyl groups, and most preferably both R and R' are mostly n-butyl and sec-butyl groups.

Suitable non-polar solvents, which are liquid at reaction temperatures, are materials in which all of the reactants used herein, i.e., the organomagnesium compound, and the non-metallocene transition metal compound, are at
least partially soluble. Preferred non-polar solvents are alkanes, such as isopentane, isohexanes, hexane, n-heptane, octane, nonane, and decane, although a variety of other materials including cycloalkanes, such as cyclohexane, aromatics, such as benzene, toluene and ethylbenzene, may also be employed. The most preferred non-polar solvent is isopentane. Prior to use, the non-polar solvent should be purified, such as by percolation through silica gel and/or molecular sieves, to remove traces of water, oxygen, polar compounds, and other materials capable of adversely affecting catalyst activity.

In the most preferred embodiment of the synthesis of this catalyst it is important to add only such an amount of the organomagnesium compound that will be deposited - physically or chemically - onto the support since any excess of the organomagnesium compound in the solution may react with other synthesis chemicals and precipitate outside of the support. The carrier drying temperature affects the number of sites on the carrier available for the organomagnesium compound - the higher the drying temperature the lower the number of sites. Thus, the exact molar ratio of the organomagnesium compound to the hydroxyl groups will vary and must be determined on a case-by-case basis to assure that only so much of the organomagnesium compound is added to the solution as will be deposited onto the support without leaving any excess of the organomagnesium compound in the solution. Furthermore, it is believed that the molar amount of the organomagnesium compound deposited onto the support may be greater than or less than the molar content of the hydroxyl groups on the support. Thus, the molar ratios given below are intended only as an approximate guideline and the exact amount of the organomagnesium compound in this embodiment must be controlled by the functional limitation discussed above, i.e., it must not be greater than that which can be deposited onto the support. If greater than that amount is
added to the solvent, the excess may react with the non-
metalloocene transition metal compound, thereby forming a
precipitate outside of the support which is detrimental in
the synthesis of our catalyst and must be avoided. The
amount of the organomagnesium compound which is not greater
than that deposited onto the support can be determined in
any conventional manner, e.g., by adding the
organomagnesium compound to the slurry of the carrier in
the solvent, while stirring the slurry, until the
organomagnesium compound is detected in the solvent.
For example, for the silica carrier heated at 600°C,
the amount of the organomagnesium compound added to the
slurry is such that the molar ratio of Mg to the hydroxyl
groups (OH) on the solid carrier is 0.5:1 to 4:1,
preferably 0.8:1 to 3:1, more preferably 0.9:1 to 2:1 and
most preferably 1:1. The organomagnesium compound
dissolves in the non-polar solvent to form a solution from
which the organomagnesium compound is deposited onto the
carrier.
It is also possible to add such an amount of the
organomagnesium compound which is in excess of that which
will be deposited onto the support, and then remove, e.g.,
by filtration and washing, any excess of the
organomagnesium compound. However, this alternative is
less desirable than the most preferred embodiment described
above.
The organomagnesium treated support is contacted with
an organic alcohol reagent, R"OH, containing R"O- groups
which are reactive or capable of displacing alkyl groups on
the magnesium. The amount of this organic alcohol reagent
is effective to provide a R"OH:Mg ratio of 0.5 to 2.0,
preferably 0.8 to 1.5.
Contact of the silica supported magnesium compound,
with the organic alcohol reagent is undertaken in the
slurry. Contact is undertaken at a temperature ranging
from 25°C to 80°C, preferably 40°C to 70°C.
The alkyl group in the organic alcohol reagent can contain 1 to 12 carbon atoms, preferably 1 to 8; in the embodiments below, it is an alkyl containing 2 to 4 carbon atoms, particularly of 4 carbon atoms (butyl). The inclusion of the alcohol reagent step in the catalyst synthesis of the invention produces a catalyst which, relative to the absence of this step, is much more active, requires much less non-metallocene transition metal and provides a more active metallocene-transition metal component in the bimetallic catalyst.

After the addition of the organic alcohol reagent to the slurry is completed, the slurry is contacted with a non-metallocene transition metal compound, free of substituted or unsubstituted cyclopentadienyl groups. The slurry temperature must be maintained at 25 to 70°C, preferably to 40 to 60°C. As noted above, temperatures in this slurry of 80°C or greater may result in deactivation of the non-metallocene transition metal. Suitable non-metallocene transition metal compounds used herein are compounds of metals of Groups 4, and 5, of the Periodic Chart of the Elements, as published by Chemical and Engineering News, 63(5), 27, 1985, providing that such compounds are soluble in the non-polar solvents. Non-limiting examples of such compounds are titanium and vanadium halides, e.g., titanium tetrachloride, TiCl₄, vanadium tetrachloride, VCl₄, vanadium oxytrichloride, VOCl₃, titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl radical of 1 to 20 carbon atoms, preferably 1 to 6 carbon atoms.

The preferred transition metal compounds are titanium compounds, preferably tetravalent titanium compounds. The most preferred titanium compound is titanium tetrachloride. The amount of titanium or vanadium, in non-metallocene compound ranges from a Ti/Mg molar ratio of 0.3 to 1.0, preferably from 0.50 to 0.80.
Mixtures of such non-metallocene transition metal compounds may also be used and generally no restrictions are imposed on the transition metal compounds which may be included. Any transition metal compound that may be used alone may also be used in conjunction with other transition metal compounds.

After the addition of the non-metallocene transition metal compound is complete, the slurry solvent is removed by evaporation or filtering to obtain a free-flowing powder. Next, incorporation of the metallocene can be undertaken. The metallocene is activated with an alumoxane.

The metallocene compound has the formula \( \text{Cp}_x\text{MA}_y\text{B}_z \) in which \( \text{Cp} \) is an unsubstituted or substituted cyclopentadienyl group, \( M \) is zirconium or hafnium and \( A \) and \( B \) belong to the group including a halogen atom, hydrogen atom or an alkyl group. In the above formula of the metallocene compound, the preferred transition metal atom \( M \) is zirconium. In the above formula of the metallocene compound, the \( \text{Cp} \) group is an unsubstituted, a mono- or a polysubstituted cyclopentadienyl group: and \( x \) is at least 1. The substituents on the cyclopentadienyl group can be preferably straight-chain \( C_1-C_6 \) alkyl groups. The cyclopentadienyl group can be also a part of a bicyclic or a tricyclic moiety such as indenyl, tetrahydroindenyl, fluorenyl or a partially hydrogenated fluorenyl group, as well as a part of a substituted bicyclic or tricyclic moiety. In the case when \( x \) in the above formula of the metallocene compound is equal to 2, the cyclopentadienyl groups can be also bridged by polymethylene or dialkylsilane groups, such as \(-\text{CH}_2-, -\text{CH}_2-\text{CH}_2-, -\text{CR'}R"- \) and \(-\text{CR'}R"-\text{CR'}R"- \) where \( R' \) and \( R" \) are short alkyl groups or hydrogen atoms, \(-\text{Si(CH}_3)_2-, \text{Si(CH}_3)_2-\text{CH}_2-\text{CH}_2-\text{Si(CH}_3)_2- \) and similar bridge groups. The \( A \) and \( B \) substituents in the above formula of the metallocene compound may be halogen atoms; and \( y + z \) is 3 or less, provided that \( x + y + z \)
equals the valence of M. If the substituents A and B in
the above formula of the metallocene compound are alkyl
groups, they are preferably straight-chain or branched C₁-C₈
alkyl groups, such as methyl, ethyl, n-propyl, isopropyl,
n-butyl, isobutyl, n-pentyl, n-hexyl or n-octyl.

Suitable metallocene compounds include
bis(cyclopentadienyl)metal dihalides,
bis(cyclopentadienyl)metal hydridohalides,
bis(cyclopentadienyl)metal monoalkyl monohalides,
bis(cyclopentadienyl)metal dialkyls and bis(indenyl)metal
dihalides wherein the metal is zirconium or hafnium, halide
groups are preferably chlorine and the alkyl groups are C₁-
C₈ alkyls. Illustrative, but non-limiting examples of
metallocenes include bis(cyclopentadienyl)zirconium
dichloride, bis(cyclopentadienyl)hafnium dichloride,
bis(cyclopentadienyl)zirconium dimethyl,
bis(cyclopentadienyl)hafnium dimethyl,
bis(cyclopentadienyl)zirconium hydridochloride,
bis(cyclopentadienyl)hafnium hydridochloride, bis(n-
butylcyclopentadienyl)zirconium dichloride, bis(n-
butylcyclopentadienyl)hafnium dichloride, bis(n-
butylcyclopentadienyl)zirconium dimethyl, bis(n-
butylcyclopentadienyl)hafnium dimethyl, bis(n-
butylcyclopentadienyl)zirconium hydridochloride, bis(n-
butylcyclopentadienyl)hafnium hydridochloride,
bis(dimethylcyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)zirconium dichloride,
bis(pentamethylcyclopentadienyl)hafnium dichloride, bis(n-
butylcyclopentadienyl)zirconium dichloride,
cyclopentadienyl-zirconium trichloride,
bis(indenyl)zirconium dichloride, bis(4,5,6,7-tetrahydro-1-
indenyl)zirconium dichloride, and ethylene-[bis(4,5,6,7-
tetrahydro-1-indenyl)] zirconium dichloride. The
metallocene compounds utilized within the embodiment of
this art can be used as crystalline solids, as solutions or
in a supported form.
The alumoxane can be impregnated into the carrier at any stage of the process of catalyst preparation. In this embodiment, the amount of Al, provided by alumoxane, is sufficient to provide an Al:transition metal (provided by metallocene) molar ratio ranging from 50 to 500, preferably 75 to 300.

The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula: R-(Al(R)-O)ₙ-AlRₙ for oligomeric, linear alumoxanes and (-Al(R)-O-)ₙ for oligomeric cyclic alumoxane wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C₁-C₈ alkyl group and preferably methyl to provide methylalumoxane (MAO). MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of 1200. MAO is typically kept in solution in toluene. The MAO solutions remain liquid at fluid-bed reactor temperatures.

Incorporation of the metallocene component onto the carrier can be accomplished in various ways. Incorporation of either or both the alumoxane and the metallocene compound can be into the slurry resulting from the addition, i.e. after the addition, of the non-metallocene transition metal. The alumoxane and metallocene can be added in any order, or together, to that slurry or to the isolated intermediate of that slurry.

Alternatively, and in accordance with the unique method of infusion of alumoxane into the pores of the carrier, the carrier slurry can be stripped of solvent, after the addition of the non-metallocene transition metal compound, to form a free-flowing powder. The free flowing powder can then be impregnated by determining the pore volume of the carrier and providing an alumoxane (or metallocene-alumoxane) solution in a volume equal to or less than the total pore volume of the carrier, and
recovering a dry catalyst precursor. The resulting free-flowing powder, referred to herein as a catalyst precursor, is combined with an activator (sometimes referred as a cocatalyst).

The volume of the solution comprising a solid alumoxane and a solvent therefor can vary. In a preferred embodiment, of alumoxane incorporation into the carrier, one of the controlling factors in the alumoxane incorporation into the carrier material catalyst synthesis is the pore volume of the silica. In this preferred embodiment, the process of impregnating the carrier material is by infusion of the alumoxane solution, without forming a slurry of the carrier material, such as silica, in the alumoxane solution. The volume of the solution of the alumoxane is sufficient to fill the pores of the carrier material without forming a slurry in which the volume of the solution exceeds the pore volume of the silica; accordingly and preferably, the maximum volume of the alumoxane solution is, does not exceed, the total pore volume of the carrier material sample. That maximum volume of the alumoxane solution insures that no slurry of silica is formed. Accordingly, if the pore volume of the carrier material is 1.65 cm³/g, then the volume of alumoxane will be equal to or less than 1.65 cm³/g of carrier material.

As a result of this proviso, the impregnated carrier material will appear dry immediately following impregnation although the pores of the carrier will be filled with *inter alia* solvent.

Solvent may be removed from the alumoxane impregnated pores of the carrier material by heating and/or under a positive pressure induced by an inert gas, such as nitrogen. If employed, the conditions in this step are controlled to reduce, if not to eliminate, agglomeration of impregnated carrier particles and/or crosslinking of the alumoxane. In this step, solvent can be removed by evaporation effected at relatively low elevated
temperatures of above 40°C and below 50°C to obviate agglomeration of catalyst particles and crosslinking of the alumoxane. Although solvent can be removed by evaporation at relatively higher temperatures than that defined by the range above 40°C and below 50°C, very short heating times schedules must be employed to obviate agglomeration of catalyst particles and crosslinking of the alumoxane.

In a preferred embodiment, the metalloocene is added to the solution of the alumoxane prior to impregnating the carrier with the solution. Again, as noted above, the maximum volume of the alumoxane solution also including the metalloocene is the total pore volume of the carrier material sample. The molar ratio of alumoxane provided aluminum, expressed as Al, to metalloocene metal expressed as M (e.g. Zr), ranges from 50 to 500, preferably 75 to 300, and most preferably 100 to 200. An added advantage of the present invention is that this Al:Zr ratio can be directly controlled. In a preferred embodiment the alumoxane and metalloocene compound are mixed together at a temperature of 20 to 80°C, for 0.1 to 6.0 hours, prior to use in the infusion step. The solvent for the metalloocene and alumoxane can be appropriate solvents, such as aromatic hydrocarbons, halogenated aromatic hydrocarbons, ethers, cyclic ethers or esters, preferably it is toluene.

The catalyst precursor component formed from the organomagnesium compound, the non-metalloocene transition metal and the activated metalloocene, must now be activated with a cocatalyst, which is an alkyl aluminum compound, free of water and free of oxygen-containing oligomers.

The cocatalyst can be a trialkylaluminum, free of an alumoxane. Preferably, trimethylaluminum (TMA) is the cocatalyst or activator. The amount of the TMA activator is sufficient to give an Al:Ti molar ratio of 10:1 to 1000:1, preferably 15:1 to 300:1, and most preferably 20:1 to 100:1. The catalyst exhibits high activity for long periods of time, and exhibits little deactivation.
A make-up catalyst can be fed to the polymerization together with the bimetallic catalyst but is a minor component of the catalyst system. The make-up catalyst includes one of the two different sources of transition metals, which are contained in the bimetallic component of the catalyst system; it is effective to increase the amount of one of the two polymer components, HMW or LMW; and to alter polymer FI and MFR values. In embodiments below, it is effective to increase FI and MFR. The minor component of the catalyst system comprises only 0.1% to 30%, preferably 1% to 15% of the catalyst system. The minor component will itself contain 0.1 to 3 weight percent of the transition metal.

The effect of water and/or carbon dioxide can be augmented by adding the make-up catalyst. The make-up catalyst comprises a carrier, an alumoxane and at least one metalloocene. It is free-flowing and particulate in form comprising dry powder particles having a particle size of from 1 micron to 250 microns, preferably from 10 microns to 150 microns. The make-up catalyst which contains only one transition metal in the form of a metalloocene has an activity of at least 50 kg polymer/g of transition metal. The alumoxane and metalloocene loading on the carrier is such that the amount of aluminum, (elemental basis) provided by the alumoxane, on the carrier ranges from 1 to 40 weight percent, preferably from 5 to 30 weight percent, and most preferably from 5 to 15 weight percent. The optimum MAO loading is in the range of 3 to 15 mmol of Al per gram of silica carrier; if a silica carrier is overloaded with MAO, the catalyst activity is lower and the catalyst particles agglomerate with attendant problems of transferring the catalyst.

In the make-up catalyst the amount of metalloocene on the carrier ranges, on a transition metal elemental basis, from 0.001 to 10 weight percent, preferably from 0.05 to 0.4, and most preferably from 0.05 to 0.2 weight percent.
Accordingly the ratio of Al:Zr (on an elemental basis) in
the catalyst can range from 25 to 10,000, usually within
the range of from 70 to 980 but preferably from 70 to 350,
and most preferably from 100 to 200.

The carrier material is a solid, particulate, porous,
preferably inorganic material, such as an oxide of silicon
and/or of aluminum. The carrier material in the make-up
catalyst can be those used in the bimetallic catalyst, and
are described above. Both the metalloocene and the
alumoxane components are those used in the bimetallic
catalyst described above are used in both the bimetallic
catalyst and the make-up catalyst.

The polyolefin resin products of the invention can be
low density products of densities of less than 0.94 g/cc.
Preferably, the products are high density products with
densities of greater than 0.94. The products are broad or
bimodal molecular weight distribution products which
contain 0.10 to 0.90, preferably 0.30 to 0.70, most
preferably 0.50 to 0.65 weight percent of the high
molecular weight component.

The film products exhibit excellent Dart Drop Impact
strength (DDI) as measured by ASTM D 1709. The products
exhibit DDI in the range of 150 to 800 g, preferably from
300 to 800 g and most preferably from 400 to 800 g for a
nominal 1 mil gauge film.

The resins resulting from the process of the invention
exhibit FI values of 2 to 100, depending upon product
application. The FI is a measure of a resin's viscosity
which relates to its processability. Increase in resin FI
means lower viscosity which improves processability.
However, there is generally a trade-off with properties.
Typically, as FI values increase, properties deteriorate.
For most product applications, there is an optimum FI value
for maximized processability and properties, which also
depends upon MWD.
Example 1

(A) Titanium Catalyst Component Preparation. 425 gram of Davison grade 955[600°C calcination temperature] silica was weighed into a two-gallon stainless steel autoclave containing a stirring paddle. Next, ca. 4.8 liter of dry isopentane was added to the autoclave and the stirring rate was set at 100 rpm. The temperature of the silica/isopentane slurry was 54-58°C. Next, 406 ml of dibutylmagnesium (0.754 mmol/ml) was added to the slurry. The contents of the autoclave were stirred for 60 minutes. Then, 33.6 ml of neat 1-butanol were added and stirring was continued for one hour. Finally, 20.1 ml of titanium tetrachloride was added to the autoclave and stirring continued for 60 minutes. After this time, all solvents were removed by evaporation under a nitrogen purge. Catalyst yield was 496 grams of a white free-flowing powder. Ti found 1.60 wt.%; Mg found 1.37 wt.%.

Example 2

This example is described in Serial Number 08/151,664 filed November 15, 1993.

Solution B: 8.98 gram of (BuCp),ZrCl, was transferred to a one-liter bottle and 467 ml of a 4.75 Molar Al (14.1 wt.% Al) solution of methylalumoxane was added. The bottle was shaken for one minute to form a yellow solution which was transferred into a 1.5 liter stainless steel hoke bomb and used immediately as described below.

Under an inert atmosphere, 317 gram of the titanium-containing catalyst described in Example 1 was added to a 2-gallon, glass-reactor vessel containing a helical stirrer to agitate the catalyst powder and a temperature jacket which was set at 30°C. The stirrer was set at 125 rpm. Then, the contents of the hoke bomb (solution B) was added to the titanium-containing catalyst in approximately 5-10 ml aliquots every 30-60 seconds over a 55 minute period. The total volume of solution (B) used was such that the titanium containing catalyst always appeared "dry" during
the entire addition time. However, during this addition time, the white titanium-containing catalyst turned a dark brown color. After the addition of solution (B) was complete, the jacket temperature was set at 45°C and the residual toluene was removed with a nitrogen purge for 5 hrs. After this time the catalyst was a dark brown free-flowing powder. Analytical results: Mg, 0.85 wt.%; Ti, 1.04 wt.%; Al, 13.1 wt.% and Zr, 0.40 wt.%.

**Example 3**

493 g of silica (Davison 955), dehydrated at 250°C, was reacted with a solution of 6.986 g of (BuCp)₂ZrCl₂ dissolved in 670 gram of MAO in toluene. Gas evolution was observed. The addition of the solution was similar to that described inb Example 2. The MAO solution contained 13.7 wt.% Al. The Al/Zr molar ratio was 200:1. The catalyst was dried under flowing N₂ at 45°C for 5 hours. The catalyst contained 9.2 wt.% Al and 0.17 wt.% Zr.

**Example 4** was prepared in the same manner as Example 1 using 517 gram of silica, 522 ml of dibutylmagnesium (DBM) (0.713 Molar in Mg), 51.5 ml of 1-butanol and 20.4 ml of titanium tetrachloride.

**Example 5** was prepared in the same manner as Example 2 using 272 gram of the titanium-containing product prepared in Example 4, 7.70 gram of (BuCp)₂ZrCl₂ added to 408 ml of methylalumoxane (13.7 wt% Al).

**Example 6** was prepared in the same manner as Example 1 using 458 gram of silica, 462.5 ml of DBM (0.713 Molar in Mg), 28.7 ml of 1-butanol and 19.9 ml of titanium tetrachloride.

**Example 7** was prepared in the same manner as Example 2 using 554 gram of the titanium-containing product prepared in Example 6, 15.69 gram of (BuCp)₂ZrCl₂ added to 830 ml of Methylalumoxane (13.7 wt% Al).
Example 8
Ethylene/1-hexene copolymers were prepared with the bimetallic catalyst systems in a laboratory slurry reactor. The bimetallic catalyst system of Example 5 was tested with and without water in the reactor.

A 1.6 liter stainless steel autoclave under a slow nitrogen purge at 50°C was filled with 750 ml of dry heptane and 30 ml of dry 1-hexene, followed by the addition of 4.0 mmol of TMA and 2.8 mmol of H₂O. The stirring speed was set at 1000 rpm and the internal temperature was increased to 95°C. The internal pressure was raised 6 psi with hydrogen. Ethylene was introduced to maintain the pressure at 1549.26 kP (210 psig). The internal temperature was decreased to 85°C, 23.8 mg of bimetallic catalyst precursor of Example 5 was introduced into the reactor with ethylene over-pressure, and the internal temperature was increased and held at 95°C. The polymerization was continued for 60 minutes, then the ethylene supply was stopped, and the reactor was cooled to ambient temperature. The polyethylene was collected and dried. Yield of resin was 62.1 g.

A significantly higher resin flow index at a significantly higher catalyst productivity resulted in the presence of water.

<table>
<thead>
<tr>
<th>Water mmol</th>
<th>Flow Index</th>
<th>% Increase in FI</th>
<th>MFR</th>
<th>Productivity g/g-h</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>2.1</td>
<td>---</td>
<td>43</td>
<td>1670</td>
</tr>
<tr>
<td>2.8</td>
<td>39.4</td>
<td>1776</td>
<td>150</td>
<td>2610</td>
</tr>
</tbody>
</table>

Vapor phase hydrogen/ethylene molar ratio (H₂/C₂) was equal to 0.035 and ethylene partial pressure was equal to 185-188 psi.
Example 9
Polymerization in gas-phase fluid bed reactor.
This example illustrates the effect of cofeeding H₂O with the bimetallic catalyst of Example 7. A decrease in HMW fraction (XHMW) and a higher resin FI value were obtained with cofeeding H₂O.

<table>
<thead>
<tr>
<th>H₂O ppm</th>
<th>Density (g/cc)</th>
<th>FI</th>
<th>% Increase in FI</th>
<th>MFR</th>
<th>XHMW</th>
<th>Cat. Productivity (lb/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.938</td>
<td>4.7</td>
<td>0</td>
<td>71</td>
<td>0.68</td>
<td>3000</td>
</tr>
<tr>
<td>5-10</td>
<td>0.940</td>
<td>7.6</td>
<td>62</td>
<td>91</td>
<td>0.66-0.67</td>
<td>3180</td>
</tr>
</tbody>
</table>

Theoretical estimates, based on ethylene feed.
Constant: Reactor Temperature = 90°C, Ethylene Partial Pressure = 1310 kPa (190 psi), H₂/C₂ = 0.01, 200 ppm TMA

Example 10
Polymerization in gas-phase fluid-bed reactor.
This example illustrates the effect of cofeeding H₂O with the bimetallic catalyst of Example 2 and the catalyst of Example 3 (dual catalyst feed conditions of 92% of the catalyst in Example 2 and 8% of the catalyst in Example 3).
The resin’s high molecular weight fraction (XHMW) was reduced with 0.2 ppm of H₂O.

<table>
<thead>
<tr>
<th>H₂O ppm</th>
<th>Density (g/cc)</th>
<th>FI</th>
<th>% Increase in FI</th>
<th>MFR</th>
<th>XHMW</th>
<th>Cat. Productivity (lb/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.948</td>
<td>5.3</td>
<td>0</td>
<td>86</td>
<td>0.58</td>
<td>3000</td>
</tr>
<tr>
<td>0.2</td>
<td>0.947</td>
<td>10.3</td>
<td>94</td>
<td>103</td>
<td>0.52</td>
<td>3300</td>
</tr>
</tbody>
</table>

* Based on ethylene feed, measured by a Du-Pont moisture analyzer. Constant: Reactor Temperature = 95°C, Ethylene Partial Pressure = 1241.06 kPa (180 psi), H₂/C₂=0.008, 200 ppm TMA.
Example 11
Polymerization in gas-phase fluid-bed reactor.
This example illustrates the effect of cofeeding CO₂ with the bimetallic catalyst of Example 2 and the catalyst of Example 3 (dual catalyst feed consisting of 90% of the catalyst of Example 2 and 10% of the catalyst of Example 3) with 2 ppm of CO₂ in the ethylene feed.

<table>
<thead>
<tr>
<th>CO₂ ppm</th>
<th>Density (g/cc)</th>
<th>FI</th>
<th>% Increase in FI</th>
<th>MFR</th>
<th>XHMW</th>
<th>Fl_{avg}</th>
<th>MI_{avg}</th>
<th>Cat. Productivity (lb/lb)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.947</td>
<td>5.5</td>
<td>0</td>
<td>84</td>
<td>0.59</td>
<td>0.6</td>
<td>1950</td>
<td>3600</td>
</tr>
<tr>
<td>2</td>
<td>0.947</td>
<td>7.8</td>
<td>42</td>
<td>94</td>
<td>0.55</td>
<td>0.6</td>
<td>7742</td>
<td>3360</td>
</tr>
</tbody>
</table>
CLAIMS:

1. A process for controlling the relative amount of a high molecular weight component and a low molecular weight component in a bimodal molecular weight distribution resin or a broad molecular weight distribution resin which comprises said high molecular weight component and said low molecular weight component, said process comprising contacting a feed comprising ethylene, under ethylene polymerization conditions, with a catalyst comprising a support containing two sources of transition metals, wherein the catalyst comprises a dry, anhydrous, support containing composition comprising an activated metallocene compound of a transition metal and a non-metallocene transition metal compound,

wherein the support is the reaction product of (1) silica having OH groups, impregnated with RMgR', wherein each of R and R' is alkyl of 4 to 10 carbon atoms, wherein RMgR' is present in an amount to provide a RMgR':OH molar ratio of 0.5:1 to 4:1; and (2) an organic alcohol reagent having a formula R"OH, wherein R" is an alkyl group of 1 to 12 carbon atoms; wherein said alcohol reagent is used in an amount effective to provide an alcohol/Mg molar ratio of 0.5 to 2.0; producing said bimodal molecular weight distribution resin or a broad molecular weight distribution resin product;

introducing additional feed for said contacting with said catalyst in which the activated metallocene compound exhibits a first productivity relative to the non-metallocene transition metal compound;
adding an amount of a reagent selected from the group consisting of water, carbon dioxide and admixtures thereof,

wherein the amount of reagent is effective to alter the first productivity relative to the non-metallocene transition metal compound; and

recovering a modified product which has a second relative ratio of said high molecular weight component and said low molecular weight component which second relative ratio differs from said relative amount.

2. The process of Claim 1 wherein the amount of reagent is effective to decrease the productivity of the non-metallocene transition metal compound.

3. The process of Claim 2, wherein the reagent effects a decrease in the amount of the high molecular weight component in the resin.

4. The process of Claim 1, which further comprises cofeeding a composition containing a single catalyst component which comprises silica and a metallocene.

5. The process of Claim 1, wherein the amount of the reagent ranges from 0-20 ppm H₂O based on ethylene; 0-10 ppm CO₂ based on ethylene.

6. The process of Claim 1, wherein the amount of reagent ranges from 0.1 to 1000 ppm H₂O based on ethylene or 0.1 to 50 ppm CO₂ based on ethylene.

7. The process of Claim 1, which is undertaken in the gas phase.
A. CLASSIFICATION OF SUBJECT MATTER
   IPC(6) :G08F 2/00, 4/42, 4/44, 4/646
   US CL  :526/78, 84, 86, 80, 81, 92, 114; 525/246, 270, 324
   According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED.
   Minimum documentation searched (classification system followed by classification symbols)
   U.S. : 526/78, 84, 86, 80, 81, 92, 114; 525/246, 270, 324

   Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

   Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

<table>
<thead>
<tr>
<th>Category*</th>
<th>Citation of document, with indication, where appropriate, of the relevant passages</th>
<th>Relevant to claim No.</th>
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<tr>
<td>Y</td>
<td>WO, A, 89/02448 (EXXON CHEMICAL PATENTS, INC) 23 March 1989, pages 4-5 and examples.</td>
<td>1-7</td>
</tr>
</tbody>
</table>

Date of the actual completion of the international search: 21 SEPTEMBER 1995

Date of mailing of the international search report: 12 OCT 1995