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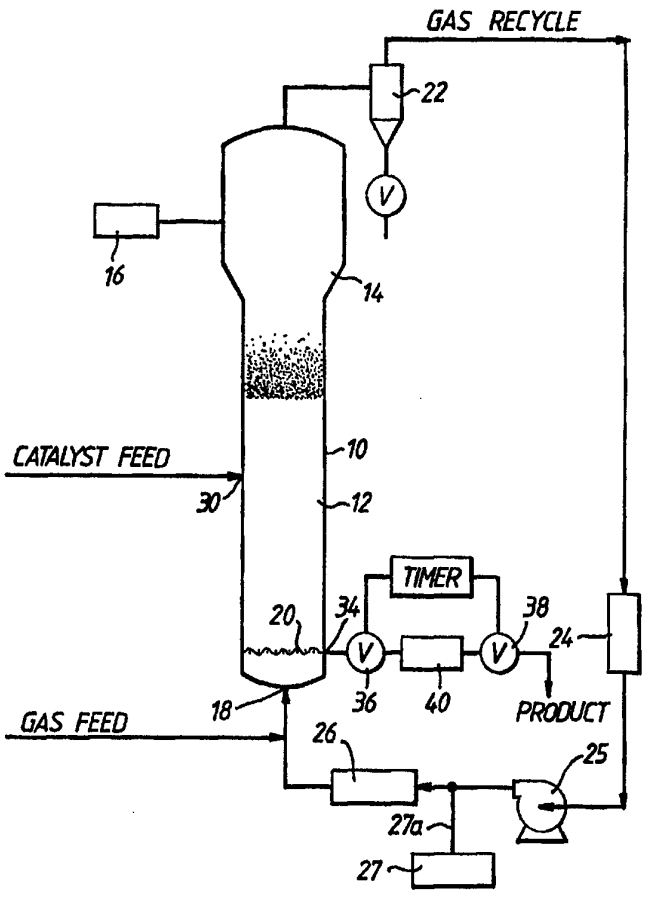
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(54) Title: CATALYST COMPOSITION FOR USE IN THE POLYMERIZATION AND COPOLYMERIZATION OF ETHYLENE

(57) Abstract

An ethylene polymerization catalyst comprising two transition metal components on a support with one of the two transition metals in the form of a metallocene. An aluminum alkyl activator for the non-metallocene transition metal component is also present. The support is an anhydrous material prepared by reacting (i) a silanol-containing silica impregnated with a magnesium alkyl with (ii) an alcohol. The catalyst produces ethylene copolymer in a single reactor with a bimodal molecular weight distribution. The polymerization is practiced in a reactor (10) comprising a reaction zone (12), a velocity reduction zone (14) and a distributor plate (20). The reaction zone (12) comprises a bed of growing polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components. The distribution plate diffuses the recycle gas. The recycle gas is separated in the cyclone separator (22) from the catalyst particles, passes through the cooler (24), and is further compressed in compressor (25), passes through a heat exchanger (26), combines with a fresh feed and enters the reaction zone (12) through the distributor plate (20). When a desirable degree of polymerization has been accomplished the polymer particles with bimodal molecular weight distribution are recovered from the reactor.



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Catalyst Composition for use in the Polymerization and Copolymerization of Ethylene

This invention relates to a catalyst composition for use in the polymerization and copolymerization of ethylene, particularly of bimodal molecular weight distribution high density and linear low density polymers and copolymers of ethylene.

Polyethylene is produced commercially in a gas phase reaction in the absence of solvents and in slurry by catalysis. To be commercially useful in the gas phase fluid bed process, the catalyst must exhibit high activity, with concomitant high catalyst productivity, because gas phase process systems do not include catalyst residue removal procedures. Accordingly, catalyst residue in the polymer product must be so small that it can be left in the polymer without causing any undue problems in the fabrication and/or to the ultimate consumer. To this end, the patent literature is replete with developments of new catalysts, of high activity with corresponding high productivity values.

The use of metallocene compounds of transition metals as catalysts for polymerization and copolymerization of ethylene is one of those developments. Metallocenes can be described by the empirical formula $Cp_xMA_yB_z$. These compounds in combination with methylalumoxane (MAO) compounds have been used to produce olefin polymers and copolymers, such as ethylene and propylene homopolymers, ethylene-butene and ethylene-hexene copolymers, e.g., see US-A-4542199 US-A-4404344.

More recently, as exemplified in US-A-5032562, metallocene catalysts containing a second transition metal, such as titaniu have been developed which produce bimodal molecular weig distribution products, having a high molecular weight componen and a relatively lower molecular weight component. The development of a catalyst which can produce bimodal products in a single reactor is significant per se. That development also provides a commercial alternative to processes which require two reactors to produce bimodal production with production of one of the molecular weight components in a first reactor and

transfer of that component to a second reactor and completion of the polymerization with production of the other component of different molecular weight.

Alumoxanes, e.g. methylalumoxane (MAO), are used as co-catalyst with metallocenes. The class of alumoxanes comprises oligomeric linear and/or cyclic alkylalumoxanes represented by the formula: $R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes; and $(-Al(R)-O-)_m$ for oligomeric cyclic alumoxanes wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl.

Methylalumoxane is commonly produced by reacting trimethylaluminum with water or with hydrated inorganic salts, such as $CuSO_4.5H_2O$ or $Al_2(SO_4)_3.5H_2O$. Methylalumoxane can be also generated in situ in polymerization reactors by adding to the reactor trimethylaluminum and water or water-containing inorganic salts. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene. While the MAO solutions remain liquid at fluid bed reactor temperatures, the MAO itself is a solid at room temperature.

Most of the experiments reported in the literature relating to methylalumoxane used as a cocatalyst with metallocene catalysts are undertaken in a slurry or solution process, rather than in a gas phase fluid bed reactor process.

Reactor fouling results when MAO solutions are fed directly into the gas phase reactor in large enough quantities to provide liquid contact with the metallocene component of the catalyst. The fouling occurs because the MAO solution forms a liquid film on the interior walls of the reactor. The catalyst is activated when it comes into contact with this liquid film, and the activated catalyst reacts with ethylene to form a polymer coating which grows larger in size until the reactor is fouled. In addition, since substantially all of the activation takes place on the walls, the MAO is not uniformly distributed to the catalyst particles. The resulting non-homogeneous polymerization gives low catalyst activity and poor product

properties.

According to the present invention, there is provided a catalyst composition for producing bimodal molecular weight distribution high density and linear low density polymers and copolymers of ethylene, comprising:

(a) an aluminum alkyl non-oxygen containing activator; and

(b) a dry, anhydrous, support containing composition comprising an activated metallocene compound of a transition metal and a non-metallocene transition metal activated by said aluminum alkyl activator,

wherein the support is the reaction product of:

(1) silica having OH groups, impregnated with $R_mMgR'_n$, wherein each of R_m and R_n is alkyl group containing 1 to 12 carbon atoms, each of m and n is 0, 1 or 2 provided that m+n is equal to the valency of Mg, and $R_mMgR'_n$ is present in an amount to provide a $R_mMgR'_n$:OH molar ratio of 0.5:1 to 4:1; and

(2) an organic alcohol reagent providing alkoxy groups having a formula R''O-, wherein R'' is alkyl group containing 1 to 12 carbons; said alkoxy groups being effective to displace the R_m and R'_n of said $R_mMgR'_n$; and said reagent being used in an amount effective to provide an alcohol:Mg molar ratio of 0.5 to 2.0.

In an embodiment said alkyl aluminum activator activates said non-metallocene transition metal.

In a preferred embodiment, the reaction product is formed by

(i) providing a slurry of a non-polar solvent and a solid porous silica having -OH groups;

(ii) impregnating said silica, with said $R_mMgR'_n$, to form an intermediate (ii), wherein the Mg:-OH groups ratio is less than 2, wherein said $R_mMgR'_n$ is soluble in said non-polar solvent;

(iii) treating the intermediate from step (ii) with an amount of R''OH, which amount is effective to provide a R''OH:$R_mMgR'_m$ molar ratio of 0.5 to

2.0.

It is preferred that this embodiment includes further steps, after (iii), comprising:

(iv) treating the product of step (iii) product with $TiCl_4$ to form a titanium containing intermediate; and

(v) combining the titanium containing intermediate with a said activator.

As explained above, the catalyst comprises at least two transition metal components on a support; one of the two transition metal components is provided in the form of a metallocene. The supported transition metals are activated by an aluminum compound, free of water and of oligomeric and polymeric oxygen-containing compounds of aluminum. Polymerization products comprise two components of different molecular weight, thus one being of higher molecular weight than the other. The film products exhibit excellent Drop Dart Impact (DDI) and excellent bubble stability in high stalk extrusion.

The invention relates to a catalyst and its use in the preparation of bimodal molecular weight distribution polymers and copolymers of ethylene, which can be prepared in one reactor. The catalyst comprises at least two transition metal components on a support; one of the two transition metal components is provided in the form of a metallocene. The supported transition metals are activated by a non-oxygen containing aluminum compound. In accordance with the invention, no alumoxane (e.g. methylalumoxane) feed to the reactor (slurry or gas phase fluid bed) is required for the activation of the transition metal provided as a metallocene.

Catalysts which contain at least two transition metals, one in the form of a metallocene and one transition metal in the form of a non-metallocene, have an activity of at least about 1000 g polymer/g catalyst or about 200 kg polymer/g of each transition metal.

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 metallocene; in one embodiment the catalysts further include a non-metallocene transition metal source.

The carrier material may be a solid, particulate, porous, preferably inorganic material, such as an oxide of silicon and/or of aluminum. The carrier material may be used in the form of a dry powder having an average particle size of from about 1 micron to about 500 microns, preferably from about 10 microns to about 250 microns. The surface area of the carrier may be at least about 3 square meters per gram (m^2/g), and preferably at least about 50 m^2/g up to about 350 m^2/g. The carrier material should be dry, that is, free of absorbed water. Drying of the carrier material can be effected by heating at about 100°C to about 1000°C, preferably at about 600°C. When the carrier is silica, it is heated to at least 200°C, preferably about 200°C to about 850°C and most preferably at about 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 about 600°C for about 16 hours to achieve a surface hydroxyl group concentration of about 0.7 millimoles per gram (mmols/g). The silica of the most preferred embodiment is a high surface area, amorphous silica (surface area = 300 m^2/g; pore volume of about 1.65 cm^3/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. This 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, may be 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 about 25 to about 70°C, preferably to about 40 to about 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 about 90°C result in deactivation of the transition metal added subsequently. Accordingly, all catalyst precursor synthesis steps are preferably 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

$$R_mMgR'_n$$

where R and R' are the same or different C_1 to C_{12} alkyl groups, preferably C_2-C_{12} alkyl groups, more preferably C_4-C_{10} alkyl groups, more preferably C_4-C_8 normal alkyl groups, and most preferably both R and R' are mostly n-butyl groups; m and n are each 0, 1 or 2, providing that m + n is equal to the valence of Mg.

Suitable non-polar solvents are materials in which all of the reactants may be used herein, i.e., the organomagnesium compound, and the transition metal compound, are at least partially soluble and which are liquid at reaction temperatures. Preferred non-polar solvents are alkanes, such as isopentane, 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 preferably to ensure 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 is greater 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 is preferably not 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-metallocene transition metal compound, thereby forming a precipitate outside of the support which is detrimental in the synthesis of our catalyst: this is generally undesirable. 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 as a solution in the solvent.

For example, for the silica carrier heated at about 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 about 0.5:1 to about 4:1, preferably

about 0.8:1 to about 3:1, more preferably about 0.9:1 to about 2:1 and most preferably about 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 (ROH) containing RO- 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 ROH: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-transition metal (e.g. titanium), and is much more active with respect to the product component produced with the metallocene-transition metal component.

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 is preferably be maintained at about 25 to about 70°C, more preferably at about 40 to about 60°C. As noted above, temperatures in this slurry of about 80°C or greater result in deactivation of the non-metallocene transition metal. Suitable

non-metallocene transition metal compounds used herein are compounds of metals of Groups 4A, and 5A, 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, $TiCl_4$, vanadium tetrachloride, VCl_4, vanadium oxytrichloride, $VOCl_3$, titanium and vanadium alkoxides, wherein the alkoxide moiety has a branched or unbranched alkyl radical of 1 to about 20 carbon atoms, preferably 1 to about 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 form preferably 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 $Cp_xMA_yB_z$ in which 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 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 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 $-CH_2-$, $-CH_2-CH_2-$, -CR'R"- and -CR'R"-CR'R"- where R' and R" are short alkyl groups or hydrogen, $-Si(CH_3)_2-$, $Si(CH_3)_2-CH_2-CH_2-Si(CH_3)_2-$ and similar bridge groups. If the A and B substituents in the above formula of the metallocene compound are halogen atoms, they belong to the group of fluorine, chlorine, bromine or iodine; and y + z is 3 or less, provided that x + y + 2 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 C_1-C_8 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 C_1-C_6 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(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 in aromatic hydrocarbons 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) mole 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:
$R-(Al(R)-O)_n-AlR_2$ for oligomeric, linear alumoxanes and
$(-Al(R)-O-)_m$ for oligomeric cyclic alumoxane
wherein n is 1-40, preferably 10-20, m is 3-40, preferably 3-20 and R is a C_1-C_8 alkyl group and preferably methyl. MAO is a mixture of oligomers with a very wide distribution of molecular weights and usually with an average molecular weight of about 1200. MAO is typically kept in solution in toluene. The MAO solutions remain liquid at fluid bed reactor temperatures.

Incorporation of the activated metallocene component onto the carrier can be accomplished in various ways. Incorporation of either or both the aluminoxane can be into the slurry resulting from the addition, i.e. after the addition, of the non-metallocene transition metal.

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 ensures that no slurry of silica is formed. Accordingly, if the pore volume of the carrier material is 1.65cm_3/g, then the volume of alumoxane will be equal to or less than 1.65 cm_3/gram 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 about 40°C and below about 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 about 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 metallocene 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 metallocene is the total pore volume of the carrier material sample. The mole ratio of alumoxane provided aluminum, expressed as Al, to metallocene metal expressed as M (e.g. Zr), preferably ranges from 50 to 500, more 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 metallocene compound are mixed together at a temperature of about 20 to 80°C, for 0.1 to 6.0 hours, prior to use in the infusion step. The solvent for the metallocene 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-metallocene transition metal and the activated metallocene, 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 preferably sufficient to give an Al:Ti molar ratio of about 10:1 to about 1000:1, more preferably about 15:1 to about 300:1, and most preferably about 20:1 to about 100:1. The catalyst exhibits high activity for long periods of time, and exhibits little deactivation.

The catalyst precursor of this invention comprises a metallocene compound and an alumoxane which is fed to the fluid bed reactor for gas phase polymerizations and copolymerizations of ethylene in particulate form. Moreover, in accordance with the invention, the cocatalyst or activator is fed to the fluid bed reactor for polymerizations and copolymerizations of ethylene in the absence of alumoxane solution.

The polymerization products produced using the catalyst according to the invention comprise two components of different molecular weight, with one MW component being of relatively higher molecular weight than the other. The relatively higher molecular weight component, of the bimodal molecular weight distribution product, has a relatively narrow molecular weight distribution. These resins exhibit better bubble stability than resins produced by other catalysts in which the MWD of the high MW component is relatively broad. Bubble stability is a prerequisite to use of the resin product in high stalk extrusion film equipment operating under commercially acceptable rates. (10-20 lb/hr.inch (0.18 to 0.36 Kg/hr.cm) die rate at thin gauge (< 1 mil (25 μ))).

The products exhibit excellent Dart Drop Impact (DDI) as measured by ASTM D 1709. The products exhibit Dart Drop Impact (DDI) in the range of 150 to 800g, preferably from 300 to 800g, and most preferably from 400 to 800g for a nominal 1 mil (25 μ) gauge film.

Ethylene polymers, as well as copolymers of ethylene with one or more C_3-C_{10} alpha-olefins, can be produced in accordance with the invention. 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 and ethylene/4-methyl-1-pentene copolymers.

Hydrogen may be used as a chain transfer agent in the polymerization reaction of the present invention. The ratio of hydrogen/ethylene employed will vary between about 0 to about 2.0 moles of hydrogen per mole of ethylene in the gas phase. Any gas inert to the catalyst and reactants can also be present in the gas stream.

Ethylene/1-butene and ethylene/1-hexene copolymers are the most preferred copolymers polymerized in the process of and with the catalyst of this invention. The ethylene copolymers produced in accordance with the present invention preferably contain at least about 80 percent by weight of ethylene units. The cocatalyst of this invention can also be used with the catalyst

precursor of this invention to polymerize propylene and other alpha-olefins and to copolymerize them.

In another embodiment of the invention, the catalyst of the invention exhibits high activity for polymerization of ethylene and higher alpha-olefins and allows the synthesis of ethylene polymers and copolymers with a broad molecular weight distribution and generally, bimodal molecular weight distribution with a relatively high molecular weight component and with a relatively lower molecular weight component in the resin blend. The molecular weight distribution of the bimodal resin, expressed as MFR, is about 70 to about 200.

Reference is now made to the accompanying drawings, in which:

Figure 1 is a gel permeation chromatogram of Example 4 product;

Figure 2 is a gel permeation chromatogram of Example 3 product;

Figure 3 is a gel permeation chromatogram of bimodal molecular weight distribution resin product, in which one component of the resin was produced under one set of polymerization conditions and the other component was produced under a second set of conditions; and

Figure 4 is a schematic drawing of a fluid bed reactor for gas phase polymerization (and copolymerization).

Referring to Figure 4, a reactor 10 consists of a reaction zone 12, a velocity reduction zone 14 and the distributor plate 20. Although fouling can occur in all of the cold areas (areas in a reactor at a temperature which is less than the temperature at which any component(s), in the gas phase reactor are liquid rather than gaseous) distributor plate fouling is the one most easily detected, since it results in a rapid increase in the pressure drop across the distributor plate due to flow restriction. Such flow restrictions also result in changing fluidization patterns and contribute to reactor wall fouling. The lowest temperature in the reactor loop is in the reactor inlet beneath the distributor plate. Other areas representing the coldest sections in the fluid bed reactor system include the

cooler and piping between the cooler and the bottom head.

The reaction zone 12 comprises a bed of growing polymer particles and a minor amount of catalyst particles fluidized by the continuous flow of polymerizable and modifying gaseous components. To maintain a viable fluidized bed, the mass gas flow rate through the bed must be above the minimum flow required for fluidization, and preferably from about 1.5 to about 10 times Gmf and more preferably from about 3 to about 6 times Gmf. Gmf is used in the accepted form as the abbreviation for the minimum mass gas flow required to achieve fluidization, C. Y. Wen and Y. H. Yu, "Mechanics of Fluidization", Chemical Engineering Progress Symposium Series, Vol. 62, p. 100-111 (1966). The distribution plate 20 serves the purpose of diffusing recycle gas through the bed at a rate sufficient to maintain fluidization at the base of the bed. Fluidization is achieved by a high rate of gas recycle to and through the bed, typically in the order of about 50 times the rate of feed of make-up gas. Make-up gas is fed to unity to drop back into the bed, through a cyclone 22, through a filter 24 (optionally) and is compressed in a compressor 25, passes through a heat exchanger 26 and is returned to the bed. The distribution plate 20 serves the purpose of diffusing recycle gas through the bed at a rate sufficient to maintain fluidization. The plate may be a screen, slotted plate, perforated plate, a plate of the bubble cap type, and the like. The elements of the plate may all be stationary, or the plate may be of the mobile type disclosed in US-A-3298792.

It is generally important to operate the fluid bed reactor at a temperature below the sintering temperature of the polymer particles. For the production of ethylene copolymers in the process of the present invention an operating temperature of about 30° to 115°C is preferred, and a temperature of about 75° to 95°C is most preferred. Temperatures of about 75° to 90°C are used to prepare products having a density of about 0.91 to 0.92 g/cm^3, and temperatures of about 80° to 100°C are used to prepare products having a density of about 0.92 to 0.94 g/cm^3, and temperatures of about 90° to 115°C are used to prepare

products having a density of about 0.94 to 0.96 g/cm^3.

The fluid bed reactor is operated at pressures of up to about 1000 psi (6.9 MPa), and is preferably operated at a pressure of from about 150 to 350 psi (1.0 to 2.4 MPa), with operation at the higher pressures in such ranges favouring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

The partially or completely activated catalyst is injected into the bed at a point above the distribution plate at a rate equal to its consumption. Since the catalysts used in the practice of this invention are highly active, injection of the fully activated catalyst into the area below the distribution plate may cause polymerization to begin there and eventually cause plugging of the distribution plate. Injection into the bed, instead, aids in distributing the catalyst throughout the bed and precludes the formation of localized spots of high catalyst concentration.

The production rate of polymer in the bed is controlled by the rate of catalyst injection. Since any change in the rate of catalyst injection changes the rate of generation of the heat of reaction, the temperature of the recycle gas is adjusted to accommodate the change in rate of heat generation. Complete instrumentation of both the fluidized bed and the recycle gas cooling system is, of course, necessary to detect any temperature change in the bed so as to enable the operator to make a suitable adjustment in the temperature of the recycle gas.

Since the rate of heat generation is directly related to product formation, a measurement of the temperature rise of the gas across the reactor (the difference between inlet gas temperature and exit gas temperature) is determinative of the rate of particulate polymer formation at a constant gas velocity.

Under a given set of operating conditions, the fluidized bed is maintained at essentially a constant height by withdrawing a portion of the bed as product at a rate equal to the rate of formation of the particulate polymer product.

Examples

(I) CATALYST PREPARATION

The titanium component of the catalyst was prepared first and isolated as a free-flowing powder. The zirconium component of the catalyst was prepared using a "dry" impregnation method described above.

Example 1

(A) Titanium Catalyst Component Preparation: 541 grams of Davison grade 955-[600°C calcination temperature] silica was weighed into a two-gallon (0.008 m^3) stainless steel autoclave containing a stirring paddle. Next, about 4.8 litres 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, 546 cm^3 of dibutylmagnesium (0.713 mmol/ml) was added to the slurry. The contents of the autoclave were stirred for 60 minutes. Then, 35.6 cm^3 of neat 1-butanol were added and stirring was continued for one hour. Finally, 21.4 cm^3 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 tan free-flowing powder. Ti found 1.48 wt.%; Mg found 1.48 wt.%.

(B) Small-Scale Catalyst Preparation: Solution (A): 0.0850 grams of $(BuCp)_2ZrCl_2$ was transferred to a 30 cm^3 serum-bottle and 4.5 cm^3 of a 4.67 Molar (13.7 wt.% Al) solution of methylalumoxane were added. The bottle was shaken for about one minute to form a yellow solution which was used immediately as described below.

Under an inert atmosphere, 2.508 grams of the titanium-containing catalyst described above [(A) Titanium Catalyst Component Preparation] was added to a 300 cm^3 pear flask containing a magnetic stirring bar which was used to agitate the catalyst powder vigorously. Then at room temperature, 3.76 cm^3 of solution (A) described above, was added dropwise to the flask over a 12 minute period. The total volume of solution (A) used was such that the titanium containing catalyst always appeared dry during the entire addition time. However, during this

addition time, the light tan titanium-containing catalyst turned a dark brown colour. Finally, the pear flask was placed into an oil bath set at 55-60°C, and the residual toluene from solution (A) was removed with a nitrogen purge to give a dry, tan, free-flowing powder.

Example 2

Large-Scale Catalyst Preparation: Solution B: 12.95 grams of $(BuCp)_2ZrCl_2$ was transferred to a one-litre bottle and 687 ml of a 4.67 Molar (13.7 wt.% Al) solution of methylalumoxane were added. The bottle was shaken for about one minute to form a yellow solution which was transferred into a 1.5 litre stainless steel hoke bomb and used immediately as described below.

Under an inert atmosphere, 465 grams of the titanium-containing catalyst described above [(A) Titanium Catalyst Component Preparation] was added to a 2-gallon (0.008 m^3, glass-reactor vessel containing a helical stirrer to agitate the catalyst powder and a temperature jacket which was set at about 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 cm^3 aliquots every 30-60 seconds over a 45 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 light tan titanium-containing catalyst turned a dark brown colour. 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, 0.99 wt.%; Ti, 0.96 wt.%; Al, 11.09 wt.% and Zr, 0.43 wt.%.

Example 3

Polymerization - Slurry

Ethylene/1-hexene copolymer was prepared with the bimetallic (Ti/Zr) composition of Example 2 to produce HDPE with a relatively high molecular weight.

A 1.6 litre stainless steel autoclave, at about 47°C. was filled with 0.750 litres of dry hexane, 0.030 litres of dry 1-

hexene and 4.0 mmols of trimethylaluminum (TMA) was added while under a slow nitrogen purge. The reactor was closed, the stirring rate was set at about 900 rpm, the internal temperature was increased to 85°C. and the internal pressure was raised from 7 psi to 13 psi (48 to 90 KPa) with hydrogen. Ethylene was introduced to maintain the reactor pressure at about 200 psi (1.4 MPa). Next, 0.0244 grams of catalyst composition of Example 2 was introduced into the reactor with ethylene over-pressure and the temperature was increased and held at 95°C. The polymerization was continued for 60 minutes, and then the ethylene supply was stopped and the reactor allowed to cool to room temperature. 36.6 grams of polyethylene were collected. The HLMI of the polymer was 4.3 indicating a relatively high molecular weight and the GPC chromatogram is shown in Figure 2.

Example 4

Polymerization - Gas Phase Fluid-bed Reactor

The catalyst of Example 2 was added to a fluid-bed gas phase reactor under the following conditions:

Ethylene	185 psi (1.28 MPa)
H_2/C_2	0.009
Hexene/ethylene	0.013
Reactor Temp.	90°C
Cocatalyst	TMA (trimethylaluminum) 300 ppm based on ethylene feed

Example 5

Product - Alpine Film Line:

Polymer produced in Example 4 with a HLMI of 5.9, MFR of 128, which gave a GPC chromatogram with a HMW/LMW ratio of 64.2/35.8 as shown in Figure 1, was fabricated into HDPE film at 0.5 and 1.0 mil (13 and 25 μ). The impact data is shown below:

RESIN	FI/MFR*	1.0 mil Dart Drop (25μ)	0.5 mil Dart Drop (13μ)
Example 4 herein	5/111	752	415
Tandem	7/110	275	395

* values for pellets obtained after stabilizer package was

added to granular resin

The molecular weight distribution (MWD) of polymer produced in Example 4 from the gas phase reactor and polymer from the slurry reactor (Example 3) were examined by Gel Permeation Chromatography (GPC), and the results clearly show that both polymers have a bimodal MWD (Figures 1 and 2). Figure 3 shows the GPC chromatogram for a HDPE polymer prepared in tandem gas phase reactors. Comparison of the GPC chromatograms shows that the polymer prepared in a single reactor (either gas phase or slurry) with the catalyst of this invention has a bimodal MWD similar to the polymer prepared in tandem reactors.

Presently, commercial samples of HDPE with a bimodal MWD are produced with a tandem reactor process. In such a process, the catalyst is exposed to one reactor in the presence of very low levels of hydrogen as chain transfer agent, and then transferred into a second reactor with relatively large amounts of hydrogen. The first reactor produces the high-molecular weight component, while the second reactor produces the low-molecular weight component.

Film toughness properties, as measured by Dart Drop Impact (DDI), show that the resin prepared with the bimetallic catalyst in a single reactor has significantly better properties than the resin produced in tandem gas phase reactors. The polymer of this invention also exhibited good film bubble stability without having to tailor the resin in an extruder prior to the film forming process.

Claims

1. An catalyst composition for producing bimodal molecular weight distribution high density and linear low density polymers and copolymers of ethylene, comprising:

(a) an aluminum alkyl non-oxygen containing activator; and

(b) a dry, anhydrous, support containing composition comprising an activated metallocene compound of a transition metal and a non-metallocene transition metal activated by said aluminum alkyl activator,

wherein the support is the reaction product of:

(1) silica having OH groups, impregnated with $R_mMgR'_n$, wherein each of R_m and R_n is alkyl group containing 1 to 12 carbon atoms, each of m and n is 0, 1 or 2 provided that m+n is equal to the valency of Mg, and $R_mMgR'_n$ is present in an amount to provide a $R_mMgR'_n$:OH molar ratio of 0.5:1 to 4:1; and

(2) an organic alcohol reagent providing alkoxy groups having a formula R''O-, wherein R'' is alkyl group containing 1 to 12 carbons; said alkoxy groups being effective to displace the R_m and R'_n of said $R_mMgR'_n$; and said reagent being used in an amount effective to provide an alcohol:Mg molar ratio of 0.5 to 2.0.

2. A catalyst composition according to Claim 1, wherein each of R_m and R'_n is alkyl group containing 4 to 10 carbon atoms.

3. A catalyst according to Claim 2, wherein each of R_m and R'_n is a butyl group.

4. A catalyst according to Claim 2, wherein each of R_m and R'_n is n-butyl.

5. A catalyst according to any one of Claims 1 to 4, wherein R'' is an alkyl group containing 1 to 8 carbons atoms.

6. A catalyst according to any one of the preceding Claims, wherein the R''O- is provided as an alcohol.

7. A catalyst according to any one of the preceding Claims, wherein the reaction product is formed by

(i) providing a slurry of a non-polar solvent and a solid porous silica having -OH groups;

(ii) impregnating said silica, with said $R_mMgR'_n$, to form an intermediate (ii), wherein the Mg:-OH groups ratio is less than 2, wherein said $R_mMgR'_n$ is soluble in said non-polar solvent;

(iii) treating the intermediate from step (ii) with an amount of R''OH, which amount is effective to provide a $R''OH:R_mMgR'_m$ molar ratio of 0.5 to 2.0.

8. A catalyst according to Claim 7, which includes further steps, after (iii), comprising:

(iv) treating the product of step (iii) product with $TiCl_4$ to form a titanium containing intermediate; and

(v) combining the titanium containing intermediate with a said activator.

9. A catalyst according to any one of the preceding Claims, wherein the non-metallocene transition metal is titanium.

10. A catalyst according to Claim 9, wherein the non-metallocene transition metal is titanium tetrachloride.

11. A catalyst according to any one of the preceding Claims, wherein the activator is trimethylaluminum.

12. A catalyst according to any one of the preceding Claims, wherein the metallocene transition metal is provided as a compound which has the formula $Cp_xMA_yB_z$, wherein Cp is cyclopentadienyl unsubstituted or substituted by alkyl or

alkylene of 1 to 6 carbon atoms; x is at least 1; each of A and B is halogen or alkyl of 1 to 8 carbon atoms, and y plus z is 3 or less provided that x+y+z is equal to the valence of M; and M is selected from the group consisting of titanium or zirconium or hafnium.

13. A catalyst according to Claim 12, wherein the metallocene compound is selected from the group consisting of bis-(cyclopentadienyl) zirconium dichloride and bis-(n-butylcyclopentadienyl) zirconium dichloride.

14. A catalyst according to any one of the preceding Claims, wherein the metallocene compound is activated with a solution of methylalumoxane; wherein the silica has a pore volume in the range of 1.0 cm^3/g to 4.0 cm^3/g; and wherein the solution has a volume which is equal to the total pore volume.

15. A process for producing bimodal molecular weight distribution high density and linear low density polymers and copolymers of ethylene, comprising polymerizing ethylene in the presence of a catalyst as defined in any preceding Claim in a single reactor to produce bimodal molecular weight distribution high density and linear low density polymers of said ethylene.

16. A process according to Claim 15, wherein said ethylene is copolymerized with a C_3 to C_8 alpha olefin to produce bimodal molecular weight distribution high density and linear low density copolymers of said ethylene.

Fig.1

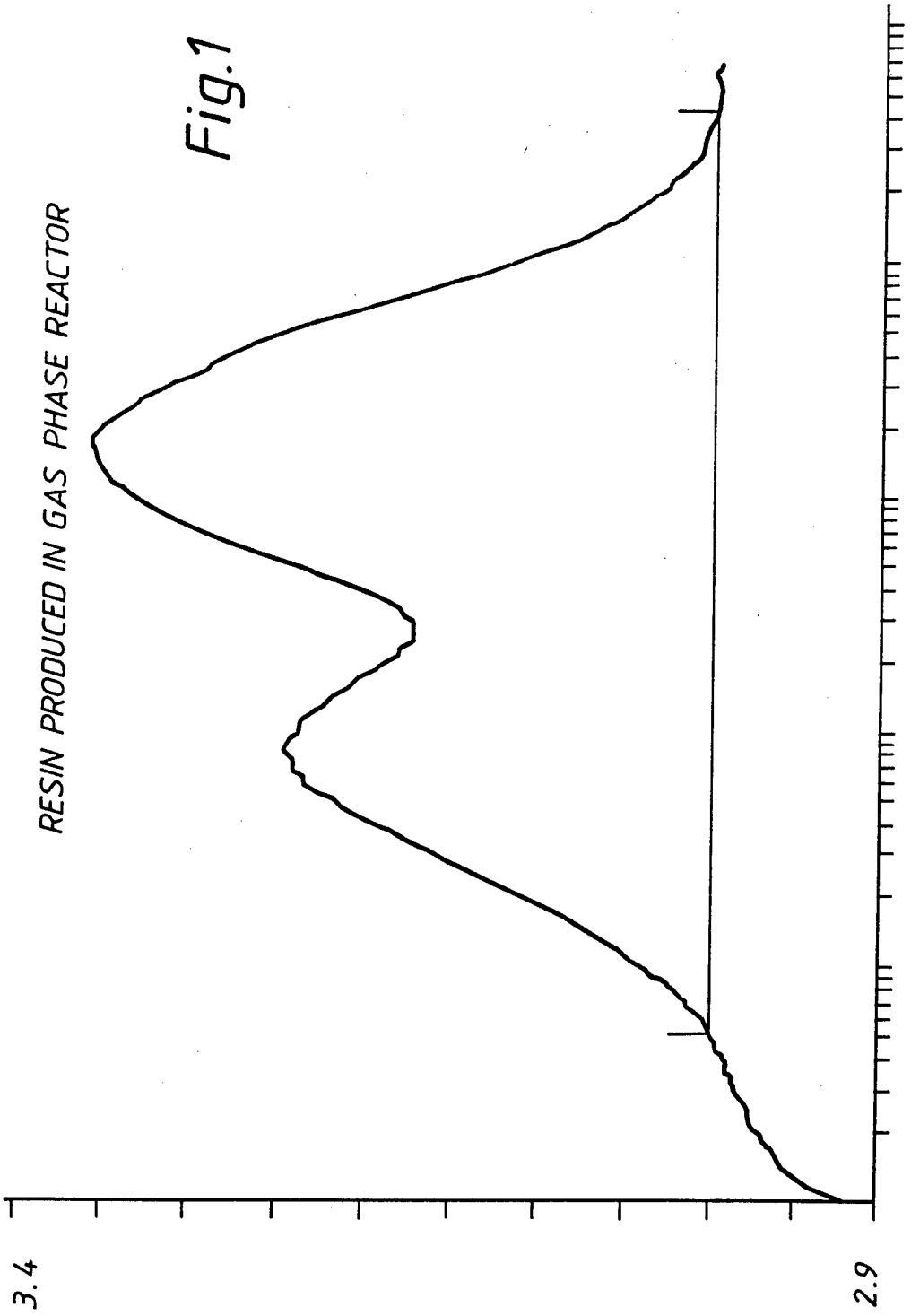


Fig. 2

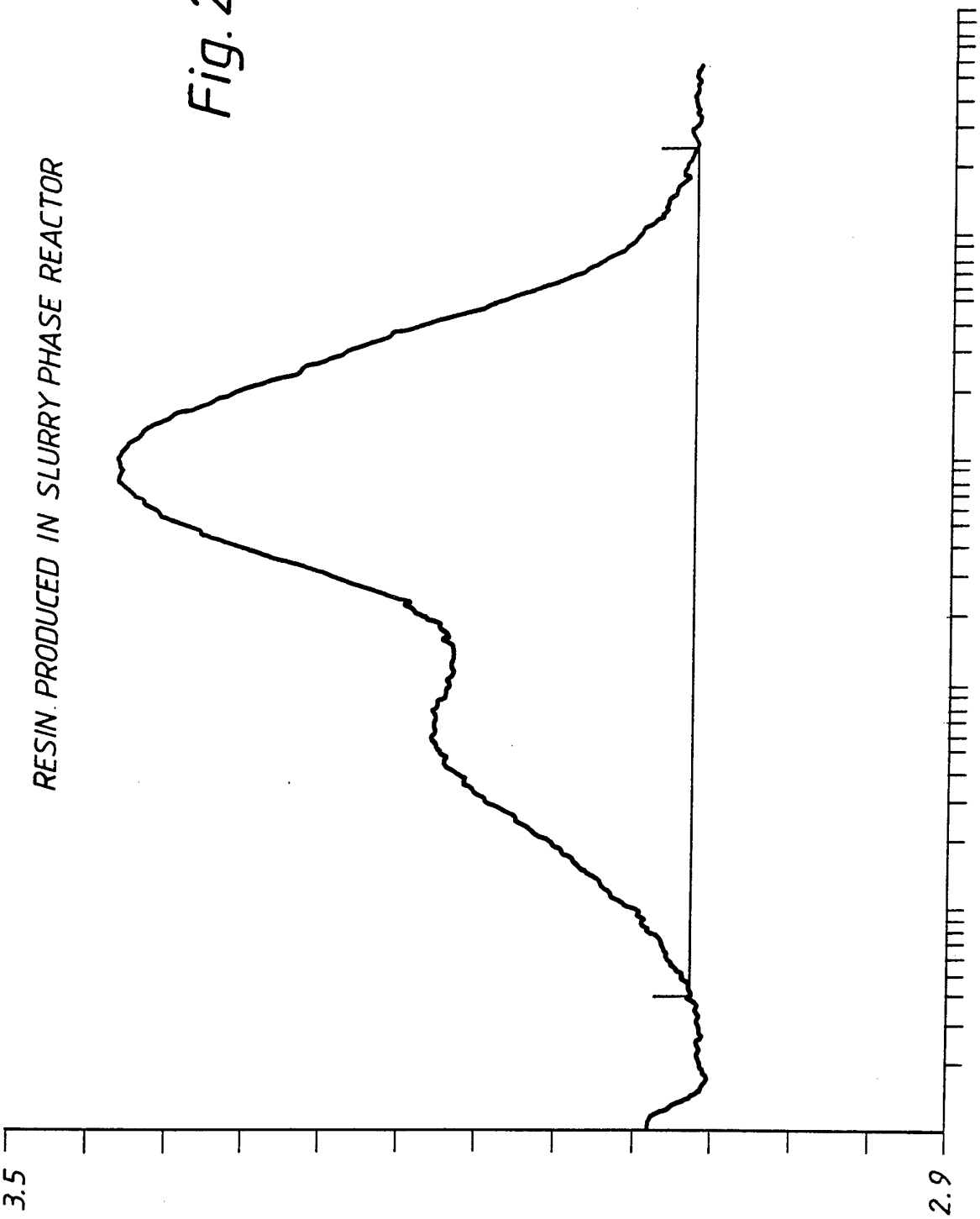
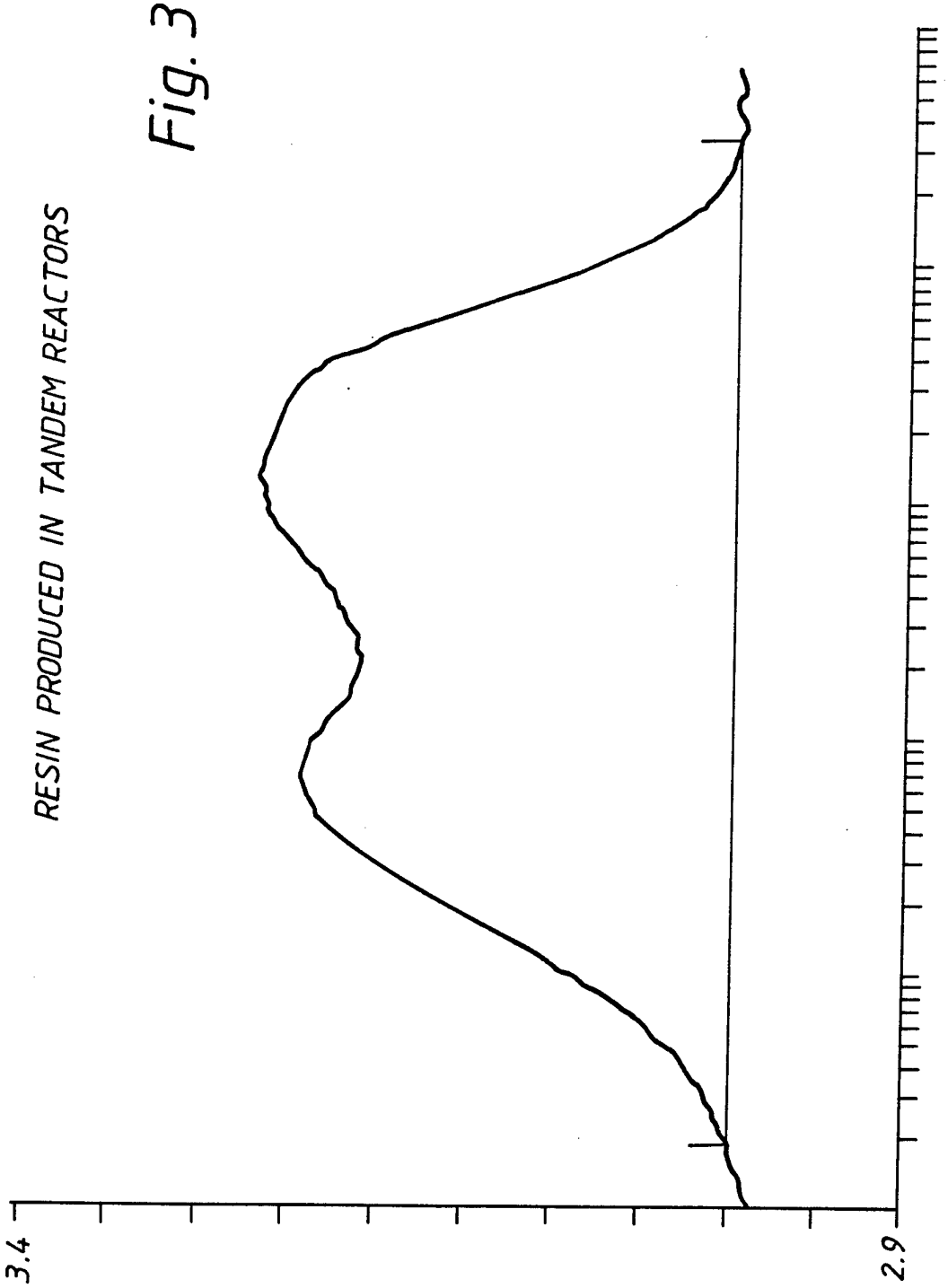


Fig. 3



4/4

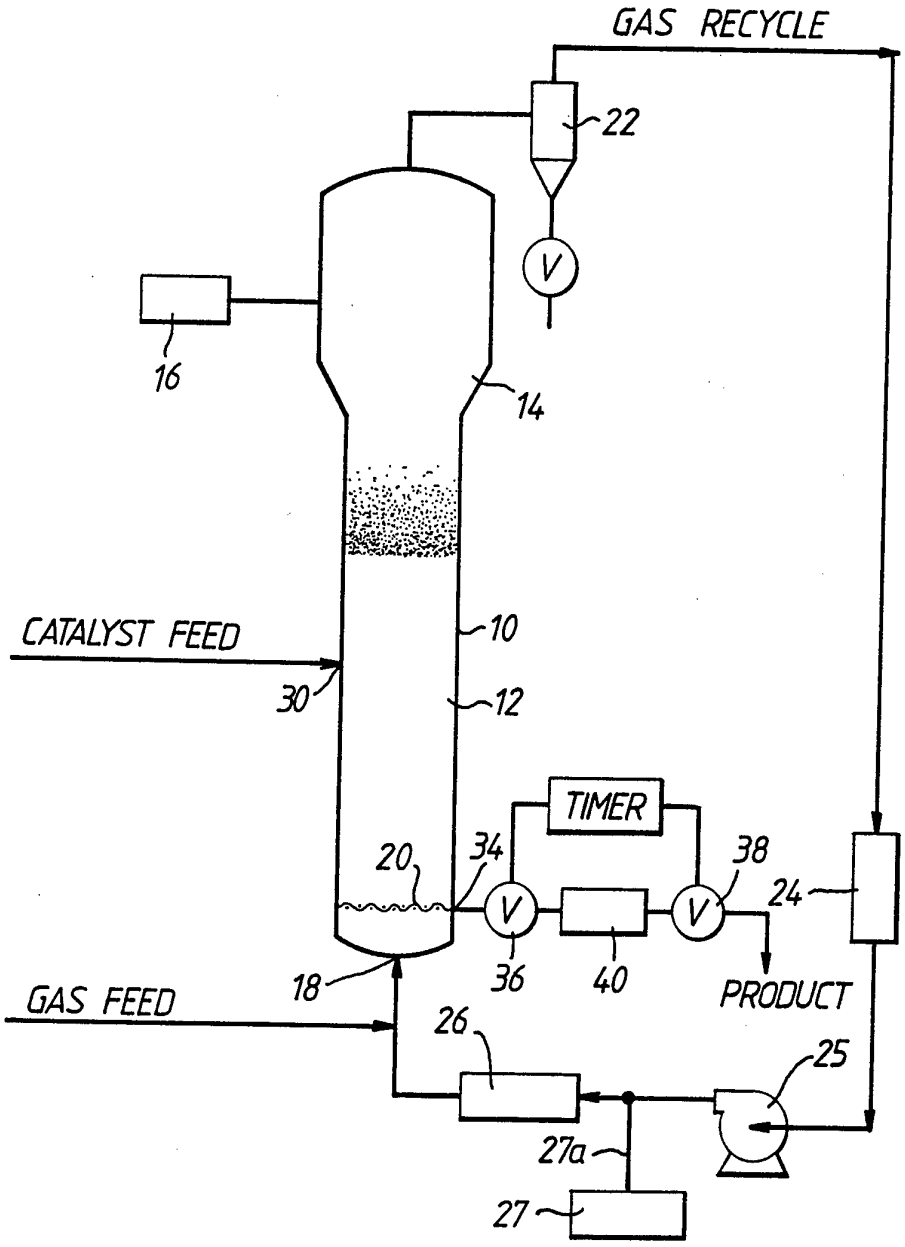

GAS RECYCLE
22
V
16
14
CATALYST FEED
30
10
12
TIMER
20
34
38
24
V
V
36
40
PRODUCT
GAS FEED
18
26
25
27a
27

Fig. 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US94/13128

A. CLASSIFICATION OF SUBJECT MATTER

IPC(6) :B01J 31/00, 31/12, 31/38, 37/00; C08F 4/42
US CL :502/104, 107, 113, 115, 117; 526/113, 118, 129
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. : 502/104, 107, 113, 115, 117; 526/113, 118, 129

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

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US, A, 4,530,914 (EWEN ET AL.) 23 July 1985, All pages	1-16
A	US, A, 4,578,373 (GRAVES) 25 March 1986, All pages	1-16
X	US, A, 5,032,562 (LO ET AL>) 16 July 1991, Columns 3-5, 7	1-16
X, P	US, A, 5,332,706 (NOWLIN ET AL.) 26 July 1994, All pages	1-16

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier document published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 11 JANUARY 1995	Date of mailing of the international search report 24 FEB 1995
Name and mailing address of the ISA/US Commissioner of Patents and Trademarks Box PCT Washington, D.C. 20231 Facsimile No. NOT APPLICABLE	Authorized officer ASOK PAL Denise Boyd 401 Telephone No. (703) 308-3809

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