

PATENT SPECIFICATION

(11) 1 531 544

1 531 544

- (21) Application No. 7852/76 (22) Filed 27 Feb. 1976
(31) Convention Application No. 557 122
(32) Filed 10 March 1975
(31) Convention Application No. 648 971
(32) Filed 14 Jan. 1976 in
(33) United States of America (US)
(44) Complete Specification published 8 Nov. 1978
(51) INT CL² C08F 210/16//4/16, 4/24
(52) Index at acceptance
C3P 404 434 436 444 484 486 574 578 580 582 GG

(19)



(54) PREPARATION OF LOW AND MEDIUM DENSITY ETHYLENE POLYMER IN FLUID BED REACTOR

(71) We, UNION CARBIDE CORPORATION, a Corporation organised and existing under the laws of the State of New York, United States of America, of 270 Park Avenue, New York, State of New York, 10017, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The invention relates to the catalytic copolymerization of ethylene with other copolymerizable monomers in a fluid bed reactor to produce low (0.900 to 0.925 grams/cc) and medium (0.926 to 0.940 grams/cc) density ethylene copolymers.

The commercialization of low and medium density ethylene polymers is much more significant in the United States, and in the rest of the world, than is the commercialization of high density (>0.940 grams/cc) ethylene polymers. The low density polymers are usually made commercially by homopolymerizing ethylene with free radical catalysts under very high pressures (>15,000 psig) in tubular and stirred reactors, in the absence of solvents. The medium density polymers can also be made commercially by the high pressure process, or by blending high pressure polyethylene with high density polyethylene made in a low pressure process with transition metal-based catalysts.

The preparation of ethylene polymers in the absence of solvents under low pressures (~40 to 350 psig) in a fluid bed reactor, using various supported chromium-containing catalysts, is disclosed in United States Patent Specifications Nos. 3,023,203; 3,687,920; 3,704,287 and 3,709,853; Belgian Patent Specification No. 773,050 and published Netherlands Patent Application No. 72-10881. These publications also disclose that the ethylene polymers produced may be ethylene homopolymers or copolymers of

ethylene and one or more other alpha olefin.

The disclosures in these patent publications are primarily concerned with the preparation of high density ethylene polymers. Furthermore, because of the technical difficulties involved, it has not been possible, prior to the present invention, to provide a commercially useful process for the production of low and medium density ethylene polymers in a low pressure fluid bed process. In order to provide such a useful process, the catalyst employed must be one which can, simultaneously, copolymerize ethylene with other alpha olefins so as to yield the desired density range in the copolymer product; provide a polymer product having a particle size which is conducive to being readily fluidized in a fluid bed reactor; provide such a high degree of productivity that the catalyst residues in the polymer product are so small as to allow them to remain therein, and thus avoid the need for catalyst removal steps; provide a polymer product which can be readily molded in a variety of molding applications, i.e., provide a polymer product having a relatively wide melt index range; provide a polymer product which has a relatively small low molecular weight fraction content so as to allow the product to meet Federal Food and Drug Administration standards for extractables (<5.5 weight percent at 50°C. in *n*-hexane) for food contact applications; and be used in solid form to provide the required copolymer products under the operating conditions which can be readily achieved in a commercial sized fluid bed reactor.

Thus, attempts to use various prior art catalysts, for the purposes of attempting to make low to medium density ethylene polymers in a commercially useful fluid bed process have not been successful to date, since those catalysts do not provide the desired combination of features noted above. For example, certain Ziegler catalysts provide products which have a very narrow melt index

2

range (0.0 to $\sim$ 0.2), and are readily subject to catalyst poisoning and have a relatively low productivity as evidenced by a catalyst residue content of greater than about ten parts per million of transition metal. The Ziegler polymers thus usually have to undergo a catalyst residue removal operation.

The supported bis(cyclopentadienyl)chromium (II) catalysts disclosed in United States Patent Specifications Nos. 3,687,920 and 3,709,853 and in Belgian Patent Specification No. 773,050 do not readily allow for the copolymerization of enough of the suitable comonomers with ethylene to provide copolymers having densities below about 0.945.

Although the family of supported silyl chromate catalysts disclosed in United States Patent Specifications Nos. 3,324,095; 3,324,101 and 3,704,287 will provide ethylene copolymers of relatively low density, some of the catalysts in the family will provide polymer products which have a high content of small particle sizes which cannot be readily fluidized, and/or which have a narrow melt index range (0.0 to $\sim$ 0.2), and/or which have a relatively high *n*-hexane extractables content.

The supported chromium oxide catalysts disclosed in United States Patent Specifications Nos. 2,825,721 and 3,023,203 can be used to provide low and medium density ethylene copolymers provided that relatively high ratios of comonomer to ethylene are employed in the monomer feed stream. However, the copolymers produced have a relatively narrow melt index range (0.0 to $\sim$ 0.2). The supported titanated chromium oxide catalysts disclosed in United States Patent Specification No. 3,622,521 provide copolymers which have a significantly higher melt index range. Published Netherlands Patent Application No. 72-10881 discloses the use of a supported fluorided and titanated chromium oxide catalyst for ethylene polymerization purposes. However United States Patent Specification No. 3,622,521 and published Netherlands Patent Application No. 72-10881 do not disclose a practical method for making low to medium density ethylene copolymers in a commercially useful fluid bed process.

Thus, based on the technology known prior to the present invention, it was not possible to make low to medium density ethylene polymers having a relatively high melt index of >0.0 to 2.0, a relatively low *n*-hexane soluble fraction and a relatively low residual catalyst content at relatively low temperatures and pressures in the absence of solvent in a commercially useful fluid bed process.

It has now been unexpectedly found that ethylene copolymers having a density of from 0.900 to less than 0.941 grams/cc and a melt index of >0.0 to 2.0 which have a relatively low *n*-hexane extractables content and residual catalyst content can be produced at relatively

high productivities for commercial purposes in a fluid bed process if the ethylene is polymerized in the process of the present invention with one or more C_3 to C_6 alpha olefins in the presence of a supported catalyst which has a specific particle size and which contains specific amounts of chromium, titanium and optionally fluorine.

It has now been found that the desired low to medium density ethylene copolymers may be readily produced with relatively high productivities in a low pressure fluid bed reaction process, if the comonomers are copolymerized under a specific set of operating conditions, as detailed below, and in the presence of a particulate activated supported catalyst which contains specific amounts of chromium, titanium, and optionally, fluorine as is also detailed below.

In accordance with the present invention there is provided a process for producing a solid ethylene polymer having a density of from 0.900 to less than 0.941 grams/cc and a melt index of >0.0 to 2.0 which process comprises copolymerizing ethylene with a sufficient amount of at least one C_3 to C_6 α -olefin monomer to provide from 1.0 to 15 mole percent of C_3 to C_6 monomer in the copolymer product in a fluid bed reactor substantially in the absence of catalyst poisons under a pressure of less than 1000 psig and at a temperature below the sintering temperature of the polymer by contacting the monomers with fluidized particles of a thermally activated supported catalyst having an average diameter of from 50 to 200 microns, and comprising, based on the total weight of the support and the catalyst, from 0.05 to 3.0 weight percent of chromium, from 1.5 to 9.0 weight percent of titanium, and from ≥ 0.0 to 2.5 weight percent of fluorine, wherein at least a portion of both the chromium and the titanium of the catalyst is in the form of their respective oxides, and wherein at least a portion of the chromium in the oxide is in its hexavalent state.

The copolymers which may be prepared in the process of the present invention are copolymers of a major mol percent ($\geq 85\%$) of ethylene, and a minor mol percent ($\leq 15\%$) of one or more C_3 to C_6 alpha olefins. These alpha olefins are preferably propylene, butene-1, pentene-1 or hexene-1.

The copolymers have a density of from 0.900 to 0.925 grams/cc for low density polymers and of from 0.926 to less than 0.941 grams/cc for medium density polymers. The density of the polymer, at a given melt index level for the polymer, is primarily regulated by the amount of the C_3 to C_6 comonomer which is copolymerized with the ethylene. In the absence of the comonomer, the ethylene would homopolymerize with the catalyst of the present invention to provide homopolymers having a density of ≥ 0.95

grams/cc. Thus, the addition of progressively larger amounts of the comonomers to the polymers results in a progressive lowering, in approximately a linear fashion, of the density of the polymer. The amount of each of the various C_3 to C_n comonomers needed to achieve the same result will vary from monomer to monomer, under the same reaction conditions.

Thus, to achieve the same results, in terms of a given density, at a given melt index level, larger molar amounts of the comonomers would be needed in the order of $C_3 > C_4 > C_5 > C_6$.

The melt index of a polymer is a reflection of its molecular weight. Polymers having a relatively high molecular weight, have a relatively low melt index. Ultra-high molecular weight ethylene polymers have a high load melt index (HLMI) of about 0.0 and very high molecular weight polymers have a high load melt index (HLMI) of from 0.0 to 1.0. These high molecular weight polymers are difficult, if not impossible, to mold in conventional injection molding equipment. The copolymers made in the process of the present invention, on the other hand, can be readily molded, in this equipment. They have a standard or normal load melt index of >0.0 to 2.0, and preferably from 0.1 to 1.5, and a high load melt index (HLMI) of from 1 to 100. The melt index of the polymers which are made in the process of the present invention is a function of a combination of the polymerization temperature of the reaction, the density of the polymer and the titanium content of the catalyst. Thus, the melt index is raised by increasing the polymerization temperature and/or by decreasing the density of the polymer (by increasing the comonomer/ethylene ratio) and/or by increasing the titanium content of the catalyst.

The copolymers made in the process of the present invention have a *n*-hexane extractables content (at 50°C.) of less than 12 percent, and preferably of less than 5.5 percent. Increasing the fluorine content of the catalyst improves the rate of incorporation of the C_3 to C_6 comonomer in the copolymer. An increase in fluorine content, however, also tends to lower the melt index of the polymers.

The copolymers made in the process of the present invention have a residual catalyst content, in terms of parts per million of chromium metal, of the order of less than ten parts per million, and preferably of the order of less than three parts per million. This catalyst residue content is primarily a function of the productivity of the catalyst. The productivity of the catalyst is primarily a function of the chromium content thereof.

The copolymers of the present invention generally have an average particle size of from 0.005 to 0.06 inches, and preferably of from 0.01 to 0.05 inches, in diameter. The

particle size is important for the purposes of readily fluidizing the polymer particles in the fluid bed reactor, as described below.

The catalyst used in the process of the present invention is a chromium oxide (CrO_3) based catalyst which is formed, in general, by depositing a suitable chromium compound, a titanium compound and optionally a fluorine compound on a dried support, and then activating the resulting composite composition by heating it in air or oxygen at a temperature of usually from 300° to 900°C., and preferably at from 700° to 850°C., usually for at least two hours, and preferably for from 5 to 15 hours. The chromium compound and titanium compound are usually deposited on the support from solutions thereof, and the fluorine compound, when used, is usually dry blended with the supported titanium and chromium compounds, and in such quantities as to provide, after the activation step, the desired levels of Cr, Ti and F in the catalyst. After the compounds are placed on the support and it is activated, there results a powdery, free-flowing particulate material. From 0.005 to 1 weight percent of the composite catalyst is usually employed per pound of polymer produced.

The order of the addition of the chromium compound, the titanium compound and, when used, the fluorine compound to the support is not critical, provided that all of the compounds are added before the activation of the composite catalyst and the support is dried before the titanium compound is added thereto.

After the activation of the supported catalyst it contains, based on the combined weight of the support and the chromium, titanium and fluorine therein,

from 0.05 to 3.0, and preferably from 0.2 to 1.0, weight percent of chromium (calculated as Cr),

from 1.5 to 9.0, and preferably from 4.0 to 7.0, weight percent of titanium (calculated as Ti), and

from >0.0 to 2.5, and preferably from 0.1 to 1.0, weight percent of fluorine (calculated as F).

The chromium compounds which may be used include CrO_3 , or any compound of chromium which is ignitable to yield CrO_3 under the activation conditions employed so that at least a portion of the chromium is in the form of its oxide. At least a portion of the chromium in the oxide in the supported, activated catalyst must, in addition, be in the hexavalent state. Chromium compounds other than CrO_3 which may be used are disclosed in United States Patent Specifications Nos. 2,825,721 and 3,622,521 and include chromic acetyl acetonate, chromic nitrate, chromic acetate, chromic chloride, chromic sulfate, and ammonium chromate.

Water-soluble compounds of chromium,

such as CrO_3 , are the preferred compounds for use in depositing the chromium compound on the support from a solution of the compound. Organic solvent-soluble chromium compounds may also be used.

The titanium compounds which may be used include all those which are ignitable to yield TiO_2 under the activation conditions employed so that at least a portion of the titanium is in the form of its oxide. These compounds include those disclosed in United States Patent Specification No. 3,622,521 and published Netherlands Patent Application No. 72-10881. Examples of these compounds are those having the structures:



where m is 1, 2, 3 or 4; n is 0, 1, 2 or 3 and $m+n=4$, and,



where R is a C_1 to C_{12} alkyl, aryl or cycloalkyl group, or a combination thereof, such as an aralkyl or alkaryl group;

R' is R , a cyclopentadienyl, or a C_2 to C_{12} alkenyl group, such as an ethenyl, propenyl, isopropenyl or butenyl group; and

X is a chlorine, bromine, fluorine or iodine atom.

The titanium compounds thus include titanium tetrachloride, titanium tetraisopropoxide and titanium tetrabutoxide. The titanium compounds are more conveniently deposited on the support from a hydrocarbon solvent solution thereof.

The titanium (as Ti) is usually present in the catalyst, with respect to the Cr (as Cr), in an atomic ratio of from 0.54:1 to 180:1, and preferably of from 4:1 to 35:1.

The fluorine compounds which may be used include HF , or any compound of fluorine which will yield HF under the activation conditions employed. Fluorine compounds other than HF which may be used are disclosed in published Netherlands Patent Application No. 72-10881. These compounds include ammonium hexafluorosilicate, ammonium tetrafluoroborate, and ammonium hexafluorotitanate. The fluorine compounds are conveniently deposited on the support from an aqueous solution thereof, or by dry blending the solid fluorine compounds with the other components of the catalyst prior to activation.

The inorganic oxide materials which may be used as the support in the catalyst compositions of the present invention are porous materials having a high surface area, that is, usually a surface area in the range of from 50 to 1000 square meters per gram, and a particle size of from 50 to 200 microns. The inorganic oxides which may be used include silica, alumina, thoria, zirconia and other comparable inorganic oxides, as well as mixtures of two or more of these oxides.

The catalyst support which may have the

chromium and/or fluorine compound deposited thereon should be dried before it is brought into contact with the titanium compound. This is normally done by simply heating or pre-drying the catalyst support with a dry inert gas or dry air prior to use. It has been found that the temperature of drying has an appreciable effect on the molecular weight distribution and the melt index of the polymer produced. The preferred drying temperature is from 100 to 300°C.

Activation of the supported catalyst can be accomplished at nearly any temperature up to its sintering temperature. The passage of a stream of dry air or oxygen through the supported catalyst during the activation step aids in the displacement of the water from the support. Activation temperatures of from 300°C. to 900°C. for a short period of six hours or so should be sufficient if well dried air or oxygen is used, and the temperature is not permitted to get so high as to cause sintering of the support.

Any grade of support can be used but microspheroidal intermediate density (MSID) silica having a surface area of 300 square meters per gram, and a pore diameter of about 200 Å, and an average particle size of about 70 microns (~ 0.0028 inches) (*W.R. Grace's G-952 grade*), and intermediate density (ID) silica having a surface area of about 300 m^2/gr , a pore diameter of about 160 Å and an average particle size of about 103 microns (~ 0.0040 inches) (*W.R. Grace's G-56 grade*) are preferred.

When incorporated in a porous support of high surface area, as described herein, the chromium forms active sites on the surface and in the pores of the support. Although the actual mechanism of the process is not entirely understood, it is believed that the polymers begin to grow at the surface as well as in the pores of the supported catalyst. When a pore grown polymer becomes large enough in the fluidized bed, it ruptures the support thereby exposing fresh catalyst sites in the inner pores of the support. The supported catalyst may thus subdivide many times during its lifetime in the fluidized bed and thereby enhance the production of low catalyst residue polymers, thereby eliminating the need for recovering the catalyst from the polymer particles. If the support is too large, it may resist rupture thereby preventing subdivision which would result in catalyst waste. In addition, a large support may act as a heat sink and cause "hot spots" to form.

After the activated catalyst has been formed, the copolymerization reaction is conducted by contacting a stream of the comonomers, in a fluid bed reactor as described below, and substantially in the absence of catalyst poisons such as moisture, oxygen, carbon monoxide and acetylene, with a catalytically effective amount of the catalyst at a

temperature and at a pressure sufficient to initiate the polymerization reaction. The catalyst of the present invention can be used in the presence of up to 200 parts per million

5 CO₂.

In order to achieve the desired density ranges in the copolymers it is necessary to copolymerize enough of the C₃—C₆ comonomers with ethylene to achieve a level of from 10 1.0 to 15 mol percent of the C₃ to C₆ comonomer in the copolymer. The amount of comonomer needed to achieve this result will depend on the particular comonomer(s) being employed and on the fluoride content of the 15 catalyst. Some increased fluoride content of the catalyst improves the comonomer incorporation. Further, the various intended comonomers have different reactivity rates, when compared to the reactivity rate of ethylene,

with respect to the copolymerization thereof 20 with the catalysts of the present invention. Therefore, the amount of comonomer used in the stream of monomers fed to the reactor will also vary depending on the reactivity of the comonomer. 25

There is provided below a listing of the amounts, in mols, of various comonomers that must be copolymerized with ethylene in order to provide polymers having the desired density range at any given melt index. The listing also indicates the concentration, in 30 mol %, of these comonomers which must be present in the gas stream of monomers which is fed to the reactor, based on the total amount of ethylene plus comonomer in the gas stream, regardless of any other gases which 35 may be present in the gas stream.

Comonomer	mol % needed in copolymer	mol % needed in gas stream
propylene	3.0 to 15	6 to 30
butene-1	2.5 to 12	6 to 25
pentene-1	2.0 to 9.0	4 to 18
hexene-1	1.0 to 7.5	3 to 15

40 A fluidized bed reaction system which can be used in the practice of the process of the present invention is illustrated in the Figure. With reference thereto the reactor 10 consists of a reaction zone 12 and a velocity reduction zone 14.

45 The reaction zone 12 comprises a bed of growing polymer particles, formed polymer particles and a minor amount of catalyst fluidized by the continuous flow of polymerizable and modifying gaseous components in the form of make-up feed and recycle gas 50 through the reaction zone. To maintain a viable fluidized bed, mass gas flow through the bed must be above the minimum flow required for fluidization, preferably from 1.5 to 10 times G_{mf} and more preferably from 55 3 to 6 times G_{mf}. G_{mf} 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 to 111 (1966).

60 It is essential that the bed always contains particles to prevent the formation of localized "hot spots" and to entrain and distribute the powdery catalyst throughout the reaction zone. On start up, the reaction zone is usually 65 charged with a base of particulate polymer

particles before gas flow is initiated. These particles may be identical in nature to the polymer to be formed or different therefrom. When different, they are withdrawn with the desired formed polymer particles as the first product. Eventually, a fluidized bed of the desired particles replaces the start-up bed. 70 75

The supported catalyst used in the fluidized bed is preferably stored for service in a reservoir 32 under a nitrogen blanket.

Fluidization is achieved by a high rate of gas recycle to and through the bed, typically in the order of 50 times the rate of feed of make-up gas. The fluidized bed has the general appearance of a dense mass of viable particles in possibly free-vortex flow as created by the percolation of gas through the bed. The pressure drop through the bed is equal to or slightly greater than the mass of the bed divided by the cross-sectional area. It is thus dependent on the geometry of the reactor. 80 85 90

Make-up gas is fed to the bed at a rate equal to the rate at which particulate polymer product is withdrawn. The composition of the make-up gas is determined by a gas analyzer 16 positioned above the bed. The gas analyzer determines component deficiency in the gas being recycled and the composition of the make-up gas is adjusted accordingly to 95

73
14
6

maintain an essentially steady state gaseous composition within the reaction zone.

To ensure complete fluidization, the recycle gas and, where desired, part of the make-up gas are returned to the reactor at point 18 below the bed. There exists a gas distribution plate 20 above the point of return to aid fluidizing the bed.

The portion of the gas stream which does not react in the bed constitutes the recycle gas which is removed from the polymerization zone, preferably by passing it into a velocity reduction zone 14 above the bed where entrained particles are given an opportunity to drop back into the bed. Particle return may be aided by a cyclone 22 which may be part of the velocity reduction zone or exterior thereto. Where desired, the recycle gas may then be passed through a filter 24 designed to remove small particles at high gas flow rates to prevent dust from contacting heat transfer surfaces and compressor blades.

The recycle gas is then passed through a heat exchanger 26 where it is stripped of the heat of reaction before it is returned to the bed. By constantly removing heat of reaction, no noticeable temperature gradient appears to exist within the upper portion of the bed. A temperature gradient will exist in the bottom 6 to 12 inches of the bed, between the temperature of the inlet gas and the temperature of the remainder of the bed. Thus it has been observed that the bed acts almost immediately to adjust the temperature of the recycle gas above this lower 6 to 12 inch bed zone to make it conform to the temperature of the bed thereby maintaining itself at an essentially constant temperature under steady state conditions. After passing through the heat exchanger the recycle gas is then compressed in a compressor 28 and returned to the reactor at its base 18 and to the fluidized bed through distribution plate 20. The compressor 28 can also be placed upstream of the heat exchanger 26.

The distribution plate 20 plays an important role in the operation of the reactor. The fluidized bed contains growing and formed particulate polymer particles as well as catalyst particles. As the polymer particles are hot and possibly active, they must be prevented from settling, for if a quiescent mass is allowed to exist, any active catalyst contained therein may continue to react and cause fusion. Diffusing recycle gas through the bed at a rate sufficient to maintain fluidization at the base of the bed is, therefore, important. The distribution plate 20 serves this purpose and may be a screen, slotted plate, perforated plate or a plate of the bubble cap type. The elements of the plate may all be stationary, or the plate may be of the mobile type disclosed in United States Patent Specification No. 3,298,792. Whatever its design, it must diffuse the recycle gas through the par-

ticles at the base of the bed to keep them in a fluidized condition; and also serve to support a quiescent bed of resin particles when the reactor is not in operation. The mobile elements of the plate may be used to dislodge any polymer particles entrapped in or on the plate.

Hydrogen may be used as a chain transfer agent in the polymerization reaction of the present invention in amounts varying from 0.001 to 10 moles of hydrogen per mole of ethylene and comonomer.

Also, if desired for temperature control of the system, any gas inert to the catalyst and reactants can also be present in the gas stream.

It is essential to operate the fluid bed reactor at a temperature below the sintering temperature of the polymer particles. For the production of the ethylene copolymers in the process of the present invention an operating temperature of from 30 to 105°C. is preferred, and a temperature of from 75 to 100°C. is most preferred. Temperatures of from 75° to 95°C. are used to prepare products having a density of from 0.900 to 0.920 grams/cc, and temperatures of from 85 to 100°C. are used to prepare products having a density of from 0.921 to less than 0.941 grams/cc.

The fluid bed reactor is operated at pressures of up to 1000 psi, and is preferably operated at a pressure of from 150 to 350 psi, with operation at the higher pressures favoring heat transfer since an increase in pressure increases the unit volume heat capacity of the gas.

The catalyst is injected into the bed at a rate equal to its consumption at a point 30 which is above the distribution plate 20. Preferably, the catalyst is injected at a point located from 1/4 to 3/4 of the way up the side of the bed. Injecting the catalyst at a point above the distribution plate is an important feature of this invention. Since the catalysts used in the practice of the invention are highly active, injection into the area below the distribution plate may cause polymerization to begin there and eventually cause plugging of the distribution plate. Injection into the viable bed, instead, aids in distributing the catalyst throughout the bed and tends to preclude the formation of localized spots of high catalyst concentration which may result in the formation of "hot spots".

An inert gas such as nitrogen is used to carry the catalyst into the bed.

The production rate of the bed is solely controlled by the rate of catalyst injection. The productivity of the bed may be increased by simply increasing the rate of catalyst injection and decreased by reducing the rate of catalyst injection.

Since any change in the rate of catalyst injection will change the rate of generation of the heat of reaction, the temperature of

the recycle gas is adjusted upwards or downwards to accommodate the change in rate of heat generation. This ensures the maintenance of an essentially constant temperature in the bed. 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.

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. 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 indicative of the rate of particulate polymer formation at a constant gas velocity.

The particulate polymer product is preferably continuously withdrawn at a point at or close to the distribution plate and in suspension with a portion of the gas stream which is vented before the particles settle to preclude further polymerization and sintering when the particles reach their ultimate collection zone. The suspending gas may also be used, as mentioned above, to drive the product of one reactor to another reactor.

The particulate polymer product is conveniently and preferably withdrawn through the sequential operation of a pair of timed valves defining a segregation zone. While valve 38 is closed, valve 36 is opened to emit a plug of gas and product to the zone 40 between it and valve 36 which is then closed. Valve 38 is then opened to deliver the product to an external recovery zone. Valve 38 is then closed to wait for the next product recovery operation.

Finally, the fluidized bed reactor is equipped with an adequate venting system to allow venting of the bed during start up and shut down. The reactor does not require the use of stirring means and/or wall scraping means.

The supported catalyst system of this invention generally yields a fluid bed product having an average particle size between 0.005 and 0.06 inches and preferably between 0.01 and 0.05 inches, wherein supported catalyst residue is unusually low.

The feed stream of gaseous monomer, with or without inert gaseous diluents, is fed into the reactor at a space time yield of from 2 to 10 pounds/hour/cubic foot of bed volume.

The following Examples are designed to illustrate the process of the present invention.

The properties of the polymers produced in the Examples were determined by the following test methods:

Density

ASTM D-1505 — Plaque is conditioned for one hour at 100°C. to approach equilibrium crystallinity.

Melt Index (MI)

ASTM D-1238 — Condition E — Measured at 190°C. — reported as grams per 10 minutes.

Flow Rate (HLMI)

ASTM D-1238 — Condition F — Measured at 10 times the weight used in the melt index test above.

Flow Rate Ratio (FRR) = Flow Rate

Melt Index

productivity

a sample of the resin product is burnt, and the weight % of ash is determined; since the ash is essentially composed of the supported catalyst, the productivity is thus the pounds of polymer produced per pound of total catalyst consumed.

n-hexane extractables

a sample of resin is lightly pressed into film samples and extracted with n-hexane at 50°C. for four hours.

Examples 1 to 21.

A. *Catalyst Preparation:* The catalysts used in Examples 1—21 were prepared as follows:

To a solution of the desired amount of CrO_3 in three liters of distilled water there was added 500 grams of a porous silica support having a particle size of about 70 microns and a surface area of about 300 square meters per gram. The mixture of the support, water and CrO_3 was stirred and allowed to stand for about 15 minutes. It was then filtered to remove about 2200—2300 ml of solution. The CrO_3 -loaded silica was then dried under a stream of nitrogen for about four hours at 200°C.

About 400 grams of the supported CrO_3 was then slurried in about 2000 ml of dry isopentane, and then a desired amount of tetraisopropyl titanate was added to the slurry. The system was then mixed thoroughly and then the isopentane was dried by heating the reaction vessel.

The dried material was then transferred to an activator (heating vessel) and a desired quantity of $(\text{NH}_4)_2\text{SiF}_6$ was added and admixed. The composition was then heated under N_2 at 50°C. for about one hour and then at 150°C. for about one hour to ensure that all the isopentane was removed and slowly to remove organic residues from the tetraisopropyl titanate so as to avoid any danger of a fire. The N_2 stream was then replaced with a stream of dry air and the catalyst composition was activated at 300°C. for about two hours and then at 750°C. or 825°C. for about eight hours. The activated

163

5 catalyst was then cooled with dry air (at ambient temperatures) to about 150°C. and further cooled from 150°C. to room temperature with N₂ (at ambient temperature). No significant change in particle size occurred during the course of the catalyst preparation.

10 The amounts of the chromium, titanium and fluorine compounds which were added to provide the desired levels of these elements in the activated catalyst are as follows:

	Weight % of compound added to support	Weight % of element in the activated catalyst
15	<u>CrO₃</u>	<u>Cr (as Cr)</u>
	0.8	0.4
	0.6	0.3
	0.53	0.26
	0.33	0.17
20	<u>0.13</u>	<u>0.07</u>
	<u>Ti(isopropyl)₄</u>	<u>Ti (as Ti)</u>
	35	5.6
	28	4.5
	25	4.1
25	<u>(NH₄)₂SiF₆</u>	<u>F (as F)</u>
	1.5	0.7
	0.6	0.3

B. Use of Catalysts in Examples 1 to 21

A series of 21 experiments were conducted in which ethylene was copolymerized with butene-1. Each of the reactions was conducted for 2 to 4 hours, after equilibrium was reached, in one or the other of two fluid bed reactor systems. One system, Reactor A, was as described in the drawing. It has a lower section 10 feet high and 13 1/2 inches in (inner) diameter, and an upper section which was 16 feet high and 23 1/2 inches in (inner) diameter. The other system, Reactor B, had the flared upper section of Reactor A replaced by a straight sided section which was 16 1/2 feet high and 13 1/2 inches in (inner) diameter. The lower section of Reactor B had the same dimensions as those of the lower section of Reactor A.

Examples 1 to 8.

Examples 1 to 8 were run in Reactor B under a gas velocity of 4 times G_{mf} and a pressure of 300 psig. The catalysts used in these Examples were prepared as disclosed above. After activation, at 825°C., each of the supported catalysts contained 0.4 weight % Cr, 4.5 weight % Ti, and 0.3 weight % of F. The other reaction conditions for Examples 1-8 are shown in Table I below:

TABLE I

Example	Temp. °C.	C ₂ H ₄ /C ₄ H ₆ mol ratio	H ₂ /C ₂ H ₄ mol ratio	Space Time Yield, lbs/hr/ft ³ of bed space
1	90	0.07	0.04	5.2
2	89	0.10	—	8.7
3	90	0.10	—	5.2
4	90	0.09	—	6.3
5	90	0.11	—	6.8
6	95	0.085	—	7.2
7	95	0.07	—	6.3
8	95	0.07	—	7.2

The copolymers produced in Examples 1-8 had the properties shown in Table II below:

TABLE II

Example	M.I.	HLMF	FRR	Den.	% Ash	Productivity	Wt. % n-hexane extract.	Average particle size inches
1	0.04	8.08	202	0.9237	0.013	7700	0.99	0.037
2	0.34	34.0	99.8	0.9166	0.012	8350	6.20	0.031
3	0.34	27.1	80	0.9176	0.017	5900	3.32	0.042
4	0.07	10.4	148.8	0.9222	0.016	6250	1.49	0.036
5	0.05	10.5	210.5	0.9233	0.008	12,500	1.96	0.021
6	0.08	13.8	172	0.9213	0.009	11,100	1.41	0.035
7	0.21	12.6	59.9	0.9250	0.007	14,300	1.38	0.027
8	0.08	12.1	151	0.9222	0.009	11,100	1.11	0.027

Examples 9 to 17.

Examples 9 to 15 were run in Reactor B, and Examples 16 and 17 were run in Reactor A, under a gas velocity of 4 times G_{mt} . The catalysts used in these examples were prepared as disclosed above. After activation, at 825°C.,

the supported catalysts contained 4.1 or 5.6 weight % of Ti, 0.3 or 0.7 weight % of F and 0.4, 0.26, 0.17 and 0.07 weight % of Cr. The variations in these catalysts, and the other reaction conditions for Examples 9 to 17 are shown in Table III below:

TABLE III

Example	Wt. % Cr	Wt. % Ti	Wt. % F	Temp. °C.	Press. psig.	C_4H_8/C_2H_4 mol ratio	H_2/C_2H_4 mol ratio	Space Time Yield lbs/hr/ft ³ of bed space
9	0.26	4.1	0.3	87.5	200	0.085	0	5.0
10	0.17	4.1	0.3	87.5	200	0.084	0	4.6
11	0.07	4.1	0.3	87.5	200	0.084	0	4.5
12	0.26	4.1	0.3	87.5	300	0.084	0	4.8
13	0.26	4.1	0.3	87.5	300	0.083	0.08	4.8
14	0.26	4.5	0.3	87.5	300	0.084	0	4.8
15	0.07	5.6	0.3	87.5	300	0.085	0	4.1
16	0.4	4.1	0.3	85	300	0.085	0	5.2
17	0.4	4.1	0.7	85	300	0.082	0	5.4

15 The copolymers produced in Examples 9 to 17 had the properties shown below in Table IV.

18

TABLE IV

Example	M.I.	HLMI	FRR	Den.	% Ash	Product-ivity	wt. % <i>n</i> -hexane extract.	Average particle size, inches
9	0.06	8.9	148	0.9228	0.009	11,100	3.32	0.035
10	0.09	11.9	132	0.9238	0.011	9,090	3.48	0.028
11	0.11	10.2	92.5	0.9211	0.015	6,680	3.26	0.037
12	0.08	10.6	132	0.9245	0.009	11,100	3.37	0.025
13	0.07	10.9	156	0.9242	0.013	7,700	3.45	0.032
14	0.08	10.6	132	0.9245	0.009	11,100	3.37	0.025
15	0.09	9.3	103	0.9232	0.011	9,100	1.55	0.035
16	0.11	17.9	163	0.9228	0.011	9,100	5.16	0.028
17	0.04	4.9	122	0.918	0.016	6,250	5.76	0.034

Examples 18 to 21.

5 Examples 18 to 21 were run in Reactor B under a pressure of 300 psig and a gas velocity of 4 times G_{mr} . The catalysts used in these examples were prepared as disclosed

above. After activation, at 825°C., each of the supported catalysts contained 0.4 weight %, Cr, 4.5 weight % of Ti and 0.3 weight % of F. The other reaction conditions for Ex-
10

TABLE V

Example	Temp. °C	C_2H_2 / C_2H_4 mol ratio	Space Time Yield lbs/hr/ft ³ of bed space
18	86	0.07	3.7
19	89	0.06	3.7
20	85	0.085	4.3
21	95	0.04	3.6

The copolymers produced in Examples 18 to 21 had the properties shown in Table VI below:

TABLE VI

Example	M.I.	HLMI	FRR	Den.	% Ash	Product-ivity	wt. % <i>n</i> -hexane extract.	Average particle size, inches
18	0.14	16.5	116	0.925	0.046	2200	1.75	0.02
19	0.23	24.1	105	0.925	0.005	20,000	1.65	0.02
20	0.51	36.7	72	0.917	0.021	4800	5.0	0.03
21	0.14	14.3	102	0.935	0.008	12,500	3.7	0.02

28
19

Examples 22 to 39.

A. *Catalyst Preparation:* The catalysts used in Examples 22 to 39 were prepared as were the catalysts for Examples 1 to 21.

5 The source of chromium was CrO_3 , the source of titanium was tetraisopropyl titanate and the source of F, when used, was $(\text{NH}_4)_2\text{SiF}_6$. In some cases, however, no source of fluorine was used in making the catalyst.

10 The supports used for all the catalysts was a porous silica support having a particle size of about 70 microns and a surface area of about 300 square meters per gram.

15 The catalysts of Examples 22 to 31 were activated by being heated at 750°C . in dry air for about eight hours, and the catalysts of Examples 32 to 39 were activated by being heated at 900°C . in dry air for about eight

hours. After activation, the catalysts contained various amounts of Cr, Ti, and, optionally, F, and these amounts are listed below in Table VII. 20

B. *Use of Catalysts in Examples 22 to 39*

The catalysts were used in each experiment to copolymerize butene-1 with ethylene at 91°C . in Reactor A under a pressure of 300 psig and at a gas velocity of about 4 times G_{mf} . The reactions were conducted using a mol ratio of $\text{C}_4\text{H}_8/\text{C}_2\text{H}_4$ of 0.080 ± 0.002 and a space time yield of 3.9 to 4.8 lbs/hr/ft³ of bed space. The exact values are shown below in Table VII. Table VII also discloses the productivity of the catalysts in each experiment, and various properties of the polymers that were produced. 25 30 35

TABLE VII
Examples 22 to 29

Example	Catalyst Components			Reaction Conditions		Catalyst Productivity		Product Properties		
	Wt. % Cr	Wt. % Ti	Wt. % F	$\frac{C_4H_8}{C_2H_4}$ mol ratio	Space Time Yield lbs/hr/ft ³ of bed space	lbs polymer/lb catalyst	Flow Rate (HLM) *	Density	Extractables %	Dp** inches
22	0.24	2.44	0	0.082	4.8	7,657	13.1	0.9248	4.9	0.0319
23	0.22	4.25	0	0.080	4.2	9,294	15.2	0.9278	3.7	0.0301
24	0.24	2.49	0.7	0.080	4.3	9,570	8.2	0.9230	4.9	0.0360
25	0.25	3.87	0.35	0.080	4.6	8,279	19.6	0.9260	4.3	0.0282
26	0.24	4.13	0.35	0.080	4.7	12,285	15.3	0.9232	3.9	0.0326
27	0.24	4.13	0.35	0.079	4.4	10,590	13.5	0.9258	4.0	0.0364
28	0.24	4.03	0.35	0.079	4.5	14,220	14.9	0.9235	3.0	0.0362
29	0.25	4.25	0	0.081	4.5	9,845	26.4	0.9244	4.3	0.0324
30	0.28	2.32	0.7	0.080	3.9	6,936	16.9	0.9231	5.3	0.0397
31	0.27	2.37	0	0.080	4.3	10,300	18.3	0.9245	3.9	0.0315
32	0.19	5.05	0	0.081	4.6	10,889	24.2	0.9260	3.6	0.0320
33	0.31	4.48	0	0.080	4.6	14,959	26.4	0.9261	3.5	0.0290
34	0.31	4.49	1.5	0.082	3.9	10,170	12.4	0.9200	5.6	0.0400
35	0.19	4.93	0	0.080	4.2	8,566	17.8	0.9262	2.8	0.0269
36	0.30	4.41	1.5	0.080	3.8	3,978	1.9	0.9215	1.9	0.0284
37	0.31	4.62	0	0.080	4.3	15,326	11.8	0.9256	2.4	0.0228
38	0.23	2.38	0	0.081	4.0	12,261	18.2	0.9267	3.1	0.0265
39	0.31	4.62	1.5	0.080	3.9	4,143	1.8	0.9215	2.7	0.0217

* The flow rate values shown correspond to melt index values in the range of 0.005 to 0.2.

** Dp is the average particle size (diameter) of the granules of polymer produced.



WHAT WE CLAIM IS:—

1. A process for producing a solid ethylene polymer having a density of from 0.900 to less than 0.941 grams/cc and a melt index of >0.0 to 2.0 which process comprises copolymerizing ethylene with a sufficient amount of at least one C_3 to C_6 α -olefin monomer to provide from 1.0 to 15 mole percent of C_3 to C_6 monomer in the copolymer product
10 in a fluid bed reactor substantially in the absence of catalyst poisons under a pressure of less than 1000 psig and at a temperature below the sintering temperature of the polymer by contacting the monomers with fluidized
15 particles of a thermally activated supported catalyst having an average diameter of from 50 to 200 microns and comprising, based on the total weight of the support and the catalyst, from 0.05 to 3.0 weight percent of chromium, from 1.5 to 9.0 weight percent of
20 titanium, and from ≥ 0.0 to 2.5 weight percent of fluorine, wherein at least a portion of both the chromium and the titanium of the catalyst is in the form of their respective oxides, and wherein at least a portion of the
25 chromium in the oxide is in its hexavalent state.
2. A process as claimed in claim 1 wherein the copolymerization is performed at a tem-
30 perature of from 30 to 105°C.
3. A process as claimed in claim 2 wherein the copolymerization is performed at a tem-
perature of from 75 to 100°C.
4. A process as claimed in any one of
35 claims 1 to 3 wherein the ethylene polymer contains from 3 to 15 mole percent of propylene.
5. A process as claimed in any one of
40 claims 1 to 3 wherein the ethylene polymer contains from 2.5 to 12 mole percent of butene-1.
6. A process as claimed in any one of
45 claims 1 to 3 wherein the ethylene polymer contains from 2 to 9 mole percent of pentene-1.
7. A process as claimed in any one of claims
1 to 3 wherein the ethylene polymer contains
50 from 1 to 7.5 mole percent of hexene-1.
8. A process as claimed in any one of the preceding claims wherein the ethylene and the α -olefin monomer are passed through the reactor at a mass flow rate of from 1.5 to 10 times the minimum gas mass flow rate re-
55 quired to achieve fluidization.
9. A process as claimed in claim 8 wherein the ethylene and the α -olefin monomer are passed through the reactor at a mass flow rate of from 3 to 6 times the minimum gas mass flow rate required to achieve fluidiza-
60 tion.
10. A process as claimed in any one of the preceding claims wherein hydrogen is additionally passed through the reactor in an amount of from 0.001 to 10 moles of hydrogen per mole of ethylene and comonomer. 65
11. A process as claimed in any one of the preceding claims wherein the copolymerization is performed at a pressure of from 150 to 350 psi.
12. A process as claimed in any one of the preceding claims wherein the supported catalyst is activated by heating in air or oxygen at a temperature of from 300 to 900°C. 70
13. A process as claimed in claim 12 wherein the supported catalyst is activated by heating in air or oxygen at a temperature of from 700 to 850°C. 75
14. A process as claimed in any one of the preceding claims wherein the activated supported catalyst contains from 0.2 to 1.0 weight percent of chromium. 80
15. A process as claimed in any one of the preceding claims wherein the activated supported catalyst contains from 4.0 to 7.0 weight percent of titanium. 85
16. A process as claimed in any one of the preceding claims wherein the activated supported catalyst contains from 0.1 to 1.0 weight percent of fluorine.
17. A process as claimed in any one of the preceding claims wherein the atomic ratio of titanium to chromium in the activated supported catalyst is from 0.54:1 to 180:1. 90
18. A process as claimed in claim 17 wherein the atomic ratio of titanium to chromium in the activated supported catalyst is from 4:1 to 35:1. 95
19. A process as claimed in any one of the preceding claims wherein the catalyst is supported on an inorganic oxide. 100
20. A process as claimed in claim 19 wherein the inorganic oxide has a surface area of from 50 to 1000 square meters per gram.
21. A process as claimed in claim 19 or claim 20 wherein the inorganic oxide is silica. 105
22. A process as claimed in claim 1 substantially as hereinbefore described with reference to and as illustrated in the accompanying drawing.
23. A process as claimed in claim 1 substantially as hereinbefore described in any one of Examples 1 to 21. 110
24. A process as claimed in claim 1 substantially as hereinbefore described in any one of Examples 22 to 39. 115
25. A solid ethylene polymer when produced by a process as claimed in any one of the preceding claims.
26. An article when molded from a solid ethylene polymer as claimed in claim 25. 120

2022



14

1,531,544

14

BOULT, WADE & TENNANT,
Chartered Patent Agents,
34 Cursitor Street,
London EC4A 1PQ.

Reference has been directed in pursuance
of section 9, subsection (1) of the Patents Act,
1949, to patent No. 1,429,174.

Printed for Her Majesty's Stationery Office by the Courier Press, Leamington Spa, 1978.
Published by the Patent Office, 25 Southampton Buildings, London, WC2A 1AY, from
which copies may be obtained.