

Olefin Polymerization Catalyst and Methods
for the Preparation and Use Thereof

The invention relates to olefin polymerization catalysts, the preparation thereof and the use thereof in olefin polymerization processes.

5 In the production of polyolefins, such as for example polyethylene, polypropylene, ethylene-butene copolymers etc., an important aspect of the various processes and catalysts used to produce such polymers is the productivity. By productivity is meant the amount or yield of solid polymer that is obtained by employing a given quantity of catalyst. If the productivity is
10 high enough then the amount of catalyst residues contained in the polymer is low enough that the presence of the catalyst residues does not significantly affect the properties of the polymer and the polymer does not require additional processing to remove the catalyst residues. As those skilled in the art
15 are aware, removal of catalyst residues from polymer is an expensive process and it is very desirable to employ a catalyst which provides sufficient productivity so that catalyst residue removal is not necessary.

In addition, high productivities are desirable in order
20 to minimize catalyst costs. Therefore it is desirable to develop new and improved catalysts and polymerization processes which provide improved polymer productivities.

In particular, the present invention and olefin polymerization catalyst which is such that when used in an olefin

polymerization process not only does the catalyst provide improved polymer productivities as compared to prior art catalysts but the polymer produced also contains catalyst residues in such small amounts that catalyst residue removal is unnecessary.

5 In accordance with a principal aspect of this invention there is thus provided a method of preparing an olefin polymerization catalyst which comprises

 (A) reacting in an inert solvent or diluent a dihalide or hydroxyhalide of a metal from Group IIA or IIB of the Mendeleev
10 Periodic Table with a titanium compound in which the titanium metal is bonded to at least one atom of oxygen, nitrogen or sulfur, and said oxygen, nitrogen and sulfur atom(s) in turn being bonded to a carbon atom of a carbon containing radical;

 B) reacting the product of step A in the presence of the
15 same or different solvent or diluent with an organometallic compound of a metal from Group I, II or III of the Mendeleev Periodic Table thereby to precipitate a solid organometallo complex of said Group I, Group II or Group II metal; and

 C) separating the solid organometallic complex obtained
20 in Step B from the solvent or diluent medium, and treating the separated solid complex with a transition metal halide as a halide ion exchanging medium.

 As used herein the term "Mendeleev Periodic Table" is meant the Periodic Table of the Elements as shown in the inside front
25 cover of Perry, Chemical Engineer's Handbook, 4th Edition, McGraw Hill & Co. (1963).

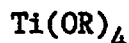
As noted above the first-mentioned reactant in step A is a dihalide or hydroxyhalide of the metal from Group IIA and Group IIB of the Periodic Table, such as for example beryllium, magnesium, calcium or zinc. Some suitable metal halide compounds include for example, beryllium dichloride, beryllium dibromide, beryllium hydroxyiodide, magnesium dichloride, magnesium dibromide, magnesium hydroxychloride, magnesium diiodide, magnesium difluoride, calcium dichloride, calcium dibromide, calcium hydroxybromide, zinc dichloride, zinc difluoride, and zinc hydroxychloride. Whilst metal hydroxyhalide compounds are known in the art, they are not as common and as readily available as metal dihalide compounds; therefore, metal dihalides are preferred.

Of the metal dihalides, magnesium dihalides, and particularly magnesium dichloride is preferred because it is readily available and relatively inexpensive and has provided excellent results. The metal dihalide component is generally used in the form of an anhydrous, particulate solid to facilitate its reaction with the transition metal compound. It is also noted that various techniques for converting a metal halide compound to a fine particulate form, such as for example roll milling, reprecipitating, etc., can be used to prepare the metal halide compound for use according to the present invention and that such additional preparation of the metal halide compound promotes the reaction of the metal halide compound with the titanium compound; however, it does not appear to make any difference in a catalyst of the present invention prepared from a composition of matter of the present invention if the metal halide compound is in a fine

particulate form, that is, polymer productivity for example is not a function of the size of the particles of the metal halide compound. Preparation of metal hydroxyhalide compounds are described in K. Soga, S. Katano, Y. Akimoto and T. Kagiya, "Polymerization of alpha-Olefins with Supported Ziegler-type Catalysts", Polymer Journal, Vol. 2, No. 5, pp. 128-134 (1973).

Hereinafter the titanium compound used in step A is generally referred to as "the transition metal compound" which term is not to be confused with the transition metal halide which is used in step C as the halide ion exchange medium, and which, as will be seen hereinafter, preferably is a titanium halide, although other transition metal halides can be used. As the transition metal compound used in step A there may be used for example titanium tetrahydrocarbyloxides, titanium tetraimides, titanium tetraamides and titanium tetramercaptides.

The titanium tetrahydrocarbyloxides are the preferred titanium compounds because they produce excellent results and are readily available. Suitable titanium tetrahydrocarbyloxide compounds include those expressed by the general formula



wherein each R is individually selected from an alkyl, cycloalkyl, aryl, alkaryl, and saturated aralkyl hydrocarbon radical containing from about 1 to about 20 carbon atoms per radical and each R can be the same or different. Titanium tetrahydrocarbyl oxides in which the hydrocarbyl group contains from about 1 to about 10 carbon atoms per radical are most often employed because they are more readily available. Suitable titanium tetrahydrocarbyl-

oxides include, for example, titanium tetramethoxide, titanium dimethoxydiethoxide, titanium tetraethoxide, titanium tetra-n-butoxide, titanium tetrahexyloxide, titanium tetradecyloxide, titanium tetraeicosyloxide, titanium tetracyclohexyloxide, titanium tetrabenzoyloxide, titanium tetra-p-tolyloxide and titanium tetraphenoxide.

Of the titanium tetrahydrocarbyloxides, titanium tetraalkoxides are generally preferred and titanium tetraethoxide is particularly preferred because of the excellent results obtained employing this material. Titanium tetraethoxide is also generally available at a reasonable cost.

The molar ratio of the transition metal compound to the metal halide (i.e. the Group IIA or Group IIB metal dihalide or hydroxyhalide) can be selected over a relatively broad range.

Generally the molar ratio is within the range of about 10:1 to about 1:10, however, the most common molar ratios are within the range of about 2:1 to about 1:2. When titanium tetrahydrocarbyloxide and magnesium dichloride are employed to form a composition of matter of the invention, a molar ratio of titanium to magnesium of about 2:1 is presently recommended as all the magnesium compound apparently goes into solution easily.

The metal halide compound and the transition metal

compound employed in the present invention are normally mixed together by heating, e.g. refluxing, these two components together in a suitable dry (essential absence of water) solvent or diluent, which is essentially inert to the these components and the product produced. By the term "inert" is meant that the solvent does not chemically react with the dissolved components such as to interfere with the formation of the product or the stability of the product once it is formed. Such solvents or diluents include, for example, n-pentane, n-heptane, methylcyclohexane, toluene, xylenes and the like. It is emphasized that aromatic solvents are preferred, such as for example xylene because the solubility of the metal halide compound and the transition metal compound is higher in aromatic solvents as compared to aliphatic solvents, particularly at low temperatures, which as described hereinafter, are preferred when mixing the metal halide compound and the transition metal compound in the solvent with an organo-metallic compound. Such mixing temperatures are generally within the range of from about 0° C to about -100° C and preferably from about -15° C to about -40° C. It is also noted that as compared to aliphatic solvents the use of aromatic solvents, such as for example xylene, appears to improve production of larger polymer particles and/or polymer particles with improved resistance to attrition when the composition resulting from the chemical combination of the metal halide compound and the transition metal compound is used to produce a polymerization catalyst as described herein. Generally the amount of solvent or diluent employed can be selected over a broad range. Usually the amount of solvent or diluent is within the range of about 20 to about 100 cc per gram of metal dihalide. The temperature employed during the heating step can also be selected over a broad range. Normally the heating temperature is within the range of about 15° C to about 150° C when the heating step is carried out at atmospheric pressure. Obviously the heating temperatures employed would be higher if the pressure employed is above atmospheric pressure. The pressure employed during the heating step does not appear to be a

significant parameter. In addition to the above noted solvents or diluents, more polar solvents or diluents such as nitrobenzene and halogenated hydrocarbons, e.g. methylene chloride, chlorobenzene and 1,2-dichloroethane can be used, particularly when
5 producing compositions of the invention having a molar ratio of the transition metal compound to the metal dihalide compound of other than 2:1. Generally, the time required for heating these two components together is within the range of about 5 minutes to about 10 hours, although in most instances a time within the
10 range of about 15 minutes to about 3 hours is sufficient. Following the heating operation, the resulting solution can be filtered to remove any undissolved material or extraneous solid, if desired. A first catalyst composition is thus produced which is in solution in the solvent or diluent. If desired this component can be
15 recovered from the solvent or diluent by crystallation or other suitable means.

It is also emphasized that the first catalyst component is prepared in step A in an oxygen free system e.g., absence of air as well as a dry system i.e., absence of water. Generally
20 a dry box is employed as known in the art to prepare the compositions of the present invention usually employing a dry oxygen free nitrogen atmosphere.

The preparation of the first catalyst component is illustrated by the following procedure:

25 Anhydrous, powdered magnesium dichloride amounting to 4.758g (0.050 mole) was roll milled and mixed with 23.010 g (0.101 mole) of titanium tetraethoxide in 200 ml of dry n-heptane in a flask equipped for stirring and refluxing. Under a nitrogen

purge, the mixture was stirred, heated to refluxing temperature refluxed for 45 minutes and cooled to room temperature to yield a solution containing a very small amount of undissolved residue. The reaction mixture was suction filtered to remove the residue to obtain a clear, colorless solution. The solution contained in a flask was first cooled in an ice bath to a temperature of about 0° C and then to a temperature of about -22° C using a freezer to yield a relatively small crop of crystals. To increase the yield, the mother liquor was heated to boiling under a nitrogen purge to remove about 1/3 of the volume by evaporation. The resulting solution was cooled to room temperature, then to -22° C and finally to about -78° C in a dry ice-isopropanol bath for about 1 hour. The mother liquor was pumped off the crystals that had formed and the crystals were rinsed off with three 20 ml portions of dry n-hexane cooled to about -78° C. The liquid remaining after the last rinse was pumped off and the product was dried overnight under a nitrogen purge to obtain 23.6 g of white crystals amounting to 85% of the theoretical yield.

Elemental analysis of a portion of the composition was performed with the following results, in terms of wt. %.

	C	H	Cl	Mg	Ti	O
Calculated	34.84	7.32	12.85	4.41	17.37	23.21
Found	32.02	7.21	13.3	3.88	17.3	-

The results indicate that a composition having a formula consistent with $2\text{Ti}(\text{OC}_2\text{H}_5)_4 \cdot \text{MgCl}_2$ was formed and recovered. Thus the composition apparently had a molar ratio of two moles of titanium to one mole of magnesium.

A sample of the white crystals was analyzed by powder X-ray diffraction under conditions to exclude the presence of air and water. The sample revealed the following characteristics:

Table 1

	interplanar spacing (meter x 10^{-10})	relative intensity of spectrum
	10.77	weak
5	10.47	very strong
	9.28	very weak
	8.73	weak
	8.23	very strong
	8.10	moderate
10	7.91	very strong
	7.43	strong
	7.27	strong
	6.52	weak
	6.41	weak
15	6.10	weak
	4.90	very weak
	4.42	very weak
	4.40	very weak
	4.09	very weak
20	3.86	very weak

The interplanar spacing lines were sharp and in view of the above number of interplanar spacings it is apparent that the composition formed has essentially a crystalline structure.

The catalysts of the present invention are made up of two components. The first catalyst component comprises a composition of matter as described above and the second catalyst component comprises an organometallic compound. Particularly effective catalysts have been obtained by treating the above-described catalyst with a halide ion exchanging source, such as for example titanium tetrahalide. For convenience, the designation "catalyst A" refers to those catalysts which have not been treated with a halide

It is noted that the first component need not be recovered from the diluent or solvent, such as by crystallation, prior to using such material to produce the catalysts of the present invention. Good results have been obtained both by recovering the first component from the reaction medium and resuspending it in the same or different solvent or diluent prior to the reaction with the organometallic compound in step B), or by using the reaction product of step A) directly in the reaction of step B).

In the second step of the process of the present invention, the first component obtained as above is reacted with an organometallic compound of a metal from Group I, II or III of the Mendeleev Periodic Table. Some suitable organometallic compounds include, for example, lithium alkyls, Grignard reagents, dialkyl magnesium compounds, dialkyl zinc compounds, organoaluminum compounds, etc. The preferred organometallic compounds used in this step are organoaluminum halide compounds, which include for example, dihydrocarbylaluminum monohalides of the formula R'_2AlX , monohydrocarbylaluminum dihalides of the formula $R'AlX_2$ and hydrocarbylaluminum sesquihalides of the formula $R'_3Al_2X_3$ wherein each R' in the above formulas is individually selected from linear and branched chain hydrocarbyl radicals containing from 1 to about 20 carbon atoms per radical and can be the same or different and each X is a halogen atom and can be the same or different. Some suitable organoaluminum halide compounds include, for example, methylaluminum dibromide, ethylaluminum dichloride, ethylaluminum diiodide, isobutylaluminum dichloride, dodecylaluminum dibromide, dimethylaluminum bromide, diethylaluminum chloride, diisopropylaluminum chloride, methyl-n-propylaluminum

bromide, di-n-octylaluminum bromide, diphenylaluminum chloride, dicyclohexylaluminum bromide, dieicosylaluminum chloride, methylaluminum sesquibromide, ethylaluminum sesquichloride, ethylaluminum sesquiodide, and the like. Ethylaluminum sesquichloride, ethylaluminum dichloride, and diethylaluminum chloride have been employed with good results and are preferred. The most preferred organoaluminum halide compound is ethylaluminum sesquichloride, which produced the best results.

In step B the product of step A, either still in its original solution, or separated and redissolved in a fresh solvent is reacted with the organometallic compound preferably itself in a hydrocarbon solvent. A solid reaction product is thus formed which precipitates out of the solution.

The molar ratio of the transition metal compound of the first catalyst component to the organometallic compound used in step B can be selected over a relatively broad range. Generally, the molar ratio of the transition metal of the first catalyst component to the organometallic compound is within a range of from about 10:1 to about 1:10 and more generally within a range of about 2:1 to about 1:3 since a molar ratio within the latter range usually produces a catalyst which can be employed as an especially active ethylene polymerization catalyst.

The temperature employed in step B can be selected over a broad range. Generally the temperature employed is within a range of about -100°C to about 50°C or higher, while temperatures within the range of -10°C to about 30°C were most often employed, additional investigation has surprisingly established that the use of a temperature within the range of about -100°C to about

0°C in step B results in the production of larger polymer particles and/or polymer particles with improved resistance to attrition as compared to polymer produced with a catalyst where step B is carried out at temperatures above 0°C. As the data hereinafter indicates polymer particles of good size are produced employing temperatures of from -15°C to -40°C in step B and accordingly temperatures within this range are preferred. Since the reaction involved in step B is exothermic, the mixing rate of the two reactants is adjusted as required and additional cooling is employed in order to maintain a relatively constant reaction temperature. It is noted with respect to mixing of the reactants in step B the order of addition is not important and either reactant can be added to the other. After completing the mixing, the resulting slurry is stirred or agitated for a sufficient time, generally within a range of about 15 minutes to about 5 hours to insure that reaction is complete. It is recommended that the stirring or agitation be carried out whereby the slurry is maintained at the mixing temperature for the first 10 to about 30 minutes after mixing and then gradually raising the temperature of the slurry to ambient temperature for the remainder of the stirring or agitation period. Thereafter, stirring is discontinued and the solid product recovered by filtration, decantation, and the like. The product is then preferably washed with a suitable material such as a hydrocarbon, e.g., n-pentane, n-heptane, cyclohexane, benzene, xylenes and the like, to remove any soluble material which may still be present.

In the final step of the invention, the solid organometallic complex obtained in step B is treated with a halide of a transition

metal as a halide ion exchanging source in order to produce the catalyst of the present invention. Some examples of suitable halide ion exchanging sources that have been employed are titanium tetrachloride, vanadium oxychloride (VOCl_3) and zirconium tetrachloride.

5 Because titanium tetrachloride is readily available and produced excellent results after somewhat extensive experimentation, it is preferred.

Preferably, treating the catalyst with the halide ion exchanging source takes place in a suitable diluent such as a hydro-
10 carbon diluent, for example, n-pentane, n-heptane, cyclohexane, benzene, xylenes, and the like, to facilitate the treating process. The treating temperature can be selected over a relatively broad range and is normally within a range of about 0°C to about 200°C ; however, surprisingly it has also been found that employing a tempera-
15 ture within the range of about 80°C to about 180°C for step C results in the production of larger polymer particles and/or polymer particles with improved resistance to attrition as compared to polymer produced with catalysts prepared at a lower treating temperature in step C. In view of the above discovery the preferred
20 temperature for step C is from about 100°C to about 130°C when considering the over-all catalyst performance. While the use of treating temperatures in excess of 130°C , such as for example 150°C to about 180°C , produces catalysts that provide larger and/or more attrition resistant polymer particles as compared to polymer
25 particles produced with catalysts prepared at treating temperatures of 130°C and below, catalysts produced with treating temperatures of about 150°C to about 180°C also show a marked reduction in productivity as compared to catalysts prepared at treating

temperatures of 130°C and below.

The treatment time can also be selected over a broad range and generally is within the range of about 10 minutes to about 10 hours. While the weight ratio of the halide ion exchanging source to the solid complex can be selected over a relatively broad range, the weight ratio of the halide ion exchanging source to the complex is generally within a range of about 10:1 to about 1:10 and more generally from about 7:1 to about 1:4. Following the treatment of organometallic complex obtained in step B with the halide ion exchanging source the surplus halide ion exchanging source is removed by washing the final catalyst product with a dry (essential absence of water) liquid such as a hydrocarbon of the type previously disclosed, n-hexane, or xylene for example. The resulting product, i.e. the catalyst of this invention, can, after drying, be stored under dry nitrogen if so desired for a month or longer without any significant decrease in activity.

If desired, the catalyst can be admixed with a particulate diluent such as, for example, silica, silica-alumina, silica-titania, magnesium dichloride, magnesium oxide, polyethylene, polypropylene, and poly-(phenylene sulfide), prior to using the catalyst in a polymerization process. While the weight ratio of the particulate diluent to catalyst can be selected over a relatively wide range, the weight ratio of particulate diluent to catalyst generally is within the range of about 100:1 to about 1:100. More often, the weight ratio of particulate diluent to catalyst is within the range of about 20:1 to about 2:1 and use of a particulate diluent has been found effective to facilitate charging of the catalyst to the reactor.

While it may not be necessary in all instances to employ a cocatalyst with the catalyst of the present invention, the use of cocatalysts is recommended for best results. The organometallic cocatalysts suitable for use in accordance with the invention may be the same as the organometallic compounds used in the second step of the process of the present invention previously described as well as organometallic compounds represented by the general formulas $R''AlX_2$, R''_2AlX and $R''_3Al_2X_3$. Suitable cocatalysts also include compounds of the formula R''_3Al in which R'' is the same as R' defined above. Of the organometallic cocatalysts, the organoaluminum cocatalysts are preferred especially organoaluminum compounds of the formula R''_3Al for example, trimethylaluminum, triethylaluminum, triisopropylaluminum, tridecylaluminum, trieicosylaluminum, tricyclohexylaluminum, triphenylaluminum, 2-methylpentyl-diethylaluminum, and triisoprenylaluminum. Triethylaluminum is preferred since this compound produced excellent results in the runs hereafter described.

The molar ratio of the cocatalyst to the transition metal content of the principal catalyst is not particularly critical and can be selected over a relatively broad range. Generally, the molar ratio of the organometallic compound of the cocatalyst to the transition metal compound present the principal catalyst is within a range of about 1:1 to about 1500:1. However, it has been found that generally when relatively high amounts of the cocatalyst is employed in relation to the catalyst, larger and/or more attrition resistant polymer particles are produced. For example, larger and/or more attrition resistant particles are produced when the weight ratio of cocatalyst to catalyst employed is at least about

4:1 up to about 400:1 and higher; however, weight ratios of cocatalyst to catalyst within the range of about 6:1 to about 100:1 are generally recommended as the best compromise between particle size and/or attrition resistance and polymer production since it has been found that generally the higher the cocatalyst level the lower the polymer production per unit weight of catalyst.

A variety of polymerizable compounds are suitable for use in the process of the present invention. Olefins which can be homopolymerized or copolymerized with the invention catalysts include aliphatic mono-1-olefins. While the invention would appear to be suitable for use with any aliphatic mono-1-olefin, those olefins having 2 to 18 carbon atoms are most often used. The mono-1-olefins can be polymerized according to the present invention employing either a particle form process or a solution form process. Aliphatic mono-1-olefins can be copolymerized with other 1-olefins and/or with other smaller amounts of other ethylenically unsaturated monomers, such as butadiene 1,3, isoprene, pentadiene-1,3, styrene, alpha-methylstyrene, and similar ethylenically unsaturated monomers which do not impair the catalyst.

The catalysts of this invention can also be utilized to prepare homopolymers and copolymers of conjugated diolefins. Generally the conjugated diolefins contain 4 to 8 carbon atoms per molecule. Examples of suitable conjugated diolefins include 1,3-butadiene, isoprene, 2-methyl-1,3-butadiene, 1,3-pentadiene, and 1,3-octadiene. Suitable comonomers, besides the conjugated diolefins listed above include mono-1-olefins previously described and vinylaromatic compounds generally. Some suitable vinylaromatic compounds are those having from about 8 to about 14 carbon atoms per molecule, and include for example styrene and various alkylstyrenes, such as 4-ethylstyrene and such as 1-vinylnaphthalene.

The weight percent of the conjugated diolefin in the copolymerization mixture can be selected over a relatively broad range. Generally the weight percent of the conjugated diolefin is from about 10 to about 95 weight percent and the

other comonomers are from about 90 to about 5 weight percent. However, the weight percent of the conjugated diolefin is preferably from about 50 to about 90 weight percent and the other comonomers are from about 50 to about 10 weight percent.

In one aspect of the invention, the catalysts of the present invention have been found to be particularly effective for polymerization of mono-1-olefins such as ethylene as extremely high productivities have been obtained and thus mono-1-olefins such as ethylene are the preferred monomers for use with the catalysts of the present invention.

The polymerization process according to the present invention employing the catalysts and cocatalysts as above described can be performed either batchwise or continuously.

In a batch process, for example, a stirred autoclave is prepared by first purging with nitrogen and then with a suitable compound, such as isobutane for example. When the catalyst and cocatalyst are employed either can be charged to the reactor first or they can be charged simultaneously through an entry port under an isobutane purge. After closing the entry port, hydrogen, if used, is added, and then a diluent such as isobutane is added to the reactor. The reactor is heated to the desired reaction temperature, which for polymerizing ethylene, for example, is, for best results, generally within a range of about 50° C to about 120° C and the ethylene is then admitted and maintained at a partial pressure within a range of about 5/10 MPa to about 5.0 MPa (70-725 psig) for best results. At the end of the designated reaction period, the polymerization reaction is terminated and the unreacted olefin and isobutane are vented. The reactor is opened and the polymer, such as polyethylene, is collected as a free-flowing white solid and is dried to obtain the product.

In a continuous process, for example, a suitable reactor such as a loop reactor is continuously charged with suitable quantities of solvent or diluent, catalyst, cocatalyst, polymerizable compounds and hydrogen if any and in any desirable order. The reactor product is continuously

withdrawn and the polymer recovered as appropriate, generally by flashing the diluent (solvent) and unreacted monomers and drying the resulting polymer.

5 The olefin polymers made with the catalysts of this invention are useful in preparing articles by conventional poly-olefin processing techniques such as injection molding, rotational molding, extrusion of film, and the like. For example, polyethylene made with the catalysts of this invention is typically of narrow molecular weight distribution which is especially desirable for
10 injection molding applications. Furthermore, the polyethylene produced as described generally has a desirable high bulk density of about 0.44 g/cc as recovered from the polymerization zone. In addition, the polyethylene produced as described is characterized by a high degree of stiffness, e.g. high flexural modulus, which
15 is also desirable in many applications.

Hereinafter, the material identified as catalyst A is the solid product obtained at the end of step B and catalyst B is the catalyst of this invention, i.e. the product obtained by treating catalyst A with the halide exchange medium.

EXAMPLE 1 (comparative)

CATALYST A

20 All mixing and filtering operations were performed in a dry box (essential absence of air, i.e. oxygen, and water) under a dry nitrogen atmosphere employing dry n-heptane as the reaction medium. Anhydrous magnesium dichloride and titanium tetraethoxide (unless otherwise noted) were charged to a flask equipped for
25 refluxing and stirring the contents of the flask. The mixture was brought to reflux temperature (about 100°C), refluxed for the time shown in Table 2, cooled and filtered if extraneous or undissolved material was present. The product was cooled in an ice bath and the indicated organoaluminum halide compound was added
30 to the product at a rate sufficient to avoid a significant temperature rise to produce a slurry. The resulting slurry was stirred about 30 minutes after removal of the flask from the ice bath. The slurry was filtered to produce a filter cake which was washed

29

19

with portions of dry n-hexane and dried under a nitrogen purge to produce the product.

The quantities of the materials employed, weight and mole ratios of reactants charged and results obtained are given in Table 2.

TABLE 2

PREPARATION OF CATALYSTS (Catalyst A)

Catalyst Designation	A-1	A-2	A-3	A-4	A-5	A-6	A-7	A-8	A-9	A-10
<u>MgCl₂</u>										
Grams	0.950	9.518	0.955	2.856	2.856	0.952	0.952	9.516	0.952	0.952
mole (1)	0.010	0.100	0.010	0.030	0.030	0.010	0.010	0.100	0.010	0.010
<u>Ti(OR)₄</u>										
grams	4.460	45.59	4.554	13.673	13.673	4.540	4.540	45.60	3.403	4.54
mole	0.0196	0.200	0.020	0.060	0.060	0.020	0.020	0.200	0.010	0.02
<u>2nd Catalyst Component</u>										
Type	EASC (2)	EASC (2)	EADC (3)	EADC (3)	DEAC (4)	DEAC (4)	1-BADC (5)	EASC (2)	EASC (2)	EASC (2)
ml	17.5	250	13.5	27	52	26.5	16.7	250	12.5	12.0
mole	0.0140	0.200	0.020	0.040	0.0393	0.020	0.020	0.200	0.010	0.01
<u>Reaction Diluent (7)</u>										
ml	30	550	60	150	150	60	60	530	60	50
Reflux, Min	20	45	60	60	60	60	60	60	80	45
<u>Wash Liquid (6)</u>										
ml	50	600	40	50	50	60	50	250	30	30
<u>Mole Ratios</u>										
Ti/Mg	1.96:1	2:1	2:1	2:1	2:1	2:1	2:1	2:1	1:1	2:1
Ti/2nd catalyst comp.	1.4:1	1:1	1:1	1.5:1	1.53:1	1:1	1:1	1:1	1:1	2:1
<u>Recovered Product</u>										
grams	2.948	25.54	2.925	3.136	2.868	2.615	2.828	29.440	1.350	3.250
Color	off-white	brown	white	pink-brown	lt. brown	cream	white	lt. brown	lt. brown	lt. yellow

Notes:

- (1) Ti(OR)₄ in catalysts A-1 through A-8 and A-10 was Ti(OC₂H₅)₄. In catalyst A-9, it was Ti(O n-C₄H₉)₄.
 (2) EASC is ethylaluminum sesquichloride, 25 wt. % in n-heptane.
 (3) EADC is ethylaluminum dichloride, 25 wt. % in n-hexane.
 (4) DEAC is diethylaluminum chloride, 12.96 wt. % in n-hexane.
 (5) 1-BADC is isobutylaluminum dichloride, 25.4 wt. % in n-hexane.
 (6) n-Hexane.
 (7) n-Heptane.

EXAMPLE 22Catalyst PreparationsCATALYST B

5 All mixing and filtering operations were conducted in
a dry box under a nitrogen atmosphere employing dry n-hexane
as the reaction medium. To a flask equipped for stirring
was charged the n-hexane, catalyst A, ^{as obtained in Example 1} and titanium tetra-
chloride. Generally, each mixture was stirred about 1 hour
at ambient temperature, e.g., about 25° C, and then fil-
10 tered. The filter cake was washed with portions of dry n-
hexane and dried under a nitrogen purge. The dry powdery
product was sieved through a 50 mesh screen to remove the
larger particles.

The quantities of components employed, weight ratios of
15 catalyst A to TiCl_4 and results obtained are given in Table
3.

TABLE 3

PREPARATION OF CATALYSTS (Catalyst B)

Catalyst Designation	Catalyst A No.	Catalyst A grams	TiCl ₄ grams	Weight Ratio TiCl ₄ /Catalyst A	Hydrocarbon Used ml.		Reaction Time Min.	Recovered Product	
					Diluent	Wash		grams	Color
B-1 (8)	A-1	1.014	4.992	4.9:1	20	20	60	0.796	grayish
B-2	A-2	25.140	129.450	5.1:1	460	500	75	25.540	brown
B-3	A-3	1.000	5.000	5:1	20	30	60	0.771	grayish
B-4	A-4	0.984	5.000	5.1:1	20	30	25	0.790	grayish
B-5	A-5	1.000	5.000	5:1	20	30	60	1.025	lt. brown
B-6	A-6	1.000	5.000	5:1	20	30	60	0.870	grayish
B-7 (9)	A-7	1.000	5.000	5:1	20	30	60	0.695	white
B-8	A-8	25.440	146.710	5.8:1	550	300	60	27.498	brown
B-9	A-9	1.210	6.000	5:1	20	20	60	1.095	lt. brown
B-10	A-10	2.000	10.000	5:1	40	45	60	1.639	yellow-brown

Notes:

- (8) 21.040 grams of recovered product were diluted with 84.054 grams of 50 mesh polyethylene fines dried in a vacuum oven and the mixture was roll milled overnight (approx. 13 hours). Mixed catalyst consists of about 1 part by weight active component and 4 parts by weight diluent. The mixture was kept under N₂.
- (9) 27.498 grams of recovered product were diluted with 108.502 grams of dry polyethylene fines and processed as described in footnote (8). The mixture was kept under N₂. Mixed catalyst consists of about 1 part by weight active component and 3.95 parts by weight diluent.

Elemental analyses of catalysts A-2 and B-2 (not mixed with polyethylene fines) were performed and the results obtained are shown below in terms of wt. % of each element:

	<u>Element</u>	<u>Catalyst A-2</u>	<u>Catalyst B-2</u>
5	Carbon	17.5	10.1
	Hydrogen	5.0	2.6
	Chlorine	39.4	54.7
	Oxygen ¹⁰	16.2	10.9
	Titanium	11.9	13.0
10	Magnesium	7.6	7.2
	Aluminum	2.4	1.5

¹⁰The amount of oxygen was determined by subtracting total weight of other components from the total weight of the catalyst sample.

15 The results indicate that treating catalyst A compositions with TiCl_4 has some effect on the amount of the elements making up the compositions. The Ti concentration increased 1.1 wt. % and chlorine concentration increased 15.3 wt. % at the expense of carbon, hydrogen and oxygen in particular.

20 From the above results it is believed that the halide ion exchanging source, which in this instance was titanium tetrachloride, caused an exchange of chloride for ethoxide groups in the catalyst.

25 Catalysts A-2 and B-2 were also examined by powder X-ray diffraction and X-ray photoelectron spectroscopy to measure the surface composition and bulk crystalline phases.

30 The results indicated no significant differences in the elemental composition of the surface within experimental error. However, Catalyst B-2 appeared to be amorphous whereas catalyst A-2 appeared to have a highly crystalline component present with a low surface area.

EXAMPLE 13

Ethylene Polymerization

35 A 3.8 liter, stirred, stainless steel reactor was employed for ethylene polymerization. The reactor was conditioned for each run by charging to it 3 liters of

dry n-heptane, closing the port, and heating the reactor and contents at 175° C for 30 minutes. The reactor was drained and residual heptane purged with dry nitrogen. The reactor was then closed and cooled under nitrogen pressure.

5 The conditioned reactor was purged with dry isobutane vapor and 3 ml of the cocatalyst solution containing 15 wt. % triethylaluminum (TEA) in dry n-heptane (2.8 mmoles TEA) was charged followed by addition of the catalyst. The reactor was closed, about 2.1 liters of dry isobutane was
10 charged, the reactor and contents were heated to 80° C and the ethylene and hydrogen, if used, was added.

Each run was terminated by flashing the ethylene and isobutane and hydrogen, if present, from the reactor. The polymer was then recovered, dried and weighed to obtain the
15 yield.

Each polymer yield was divided by the weight of catalyst employed to determine the calculated catalyst productivity which is expressed as kilograms (kg) polyethylene per gram (g) catalyst per hour. In some runs of less than
20 60 minutes duration, a productivity figure is calculated for 60 minutes in which the reasonable assumption is made based on past experience that the activity of the catalyst remains unchanged during at least the first 60 minutes of each run. When the catalyst is diluted, a calculated productivity
25 based on kg polyethylene produced per gram diluted catalyst per hour is given as well as kg polyethylene produced per gram catalyst contained in the mixture per hour.

The quantity of each catalyst employed, run time, pressures employed, and results obtained are presented in
30 Table 4.

TABLE 4
ETHYLENE POLYMERIZATION AT 80° C
2.8 MMoles TEA (3 ml) as Cocatalyst in Each Run

Run No.	Catalyst Designation	Run Time min.	Yield grams	Catalyst Productivity kg polymer/g catalyst/hour	Reaction Pressures			
					Avg. MPa	Total psig	Ethylene MPa	Hydrogen MPa psig
1	A-1	60	479	32.8	1.79	260	0.69	100 0
2	A-2	60	330	35.5	1.93	280	0.69	100 0
3	A-3	60	270	13.6	1.93	280	0.69	100 0
4	A-4	60	690	32.9	1.93	280	0.69	100 0
5	A-5	60	504	25.5	1.93	280	0.69	100 0
6	A-6	60	68	3.1	1.93	280	0.69	100 0
7	A-7	60	119	8.9	2.00	290	0.69	100 0
8	A-8	60	480	28.7	1.93	280	0.69	100 0
9	A-9	60	233	20.6	1.93	280	0.69	100 0
10	A-10	60	112	20.7	1.93	280	0.69	100 0
11	B-1 (11)	60	577	148	1.79	260	0.69	100 0
12	B-2 (12)	60	355	147 (29.33 kg/g cat)	2.00	290	0.69	100 0
13	B-3 (13)	30	631	109 (54.4 kg/30 min)	1.97	285	0.69	100 0
14	B-3 (14)	30	510	120 (60.0 kg/30 min)	1.93	280	0.69	100 0
15	B-4 (15)	40	424	125 (83.1 kg/40 min)	1.97	285	0.69	100 0
16	B-5 (16)	60	387	73.0	1.97	285	0.69	100 0
17	B-6 (17)	45	787	88.9 (66.7 kg/45 min)	2.00	290	0.69	100 0
18	B-7 (18)	60	538	37.4	2.41	350	1.0	150 0.41 60
19	B-8 (19)	60	162	36.4 (7.34 kg/g cat)	2.41	350	1.0	150 0.41 60
20	B-9 (20)	40	688	83.8 (55.9 kg/40 min)	1.93	280	0.69	100 0
21	B-10	60	610	210	1.97	285	0.69	100 0

Notes:

- (11) One part by weight catalyst diluted with 4 parts by weight polyethylene powder; calculated productivity is 5 x 29.3 or 147 kg polymer/g undiluted catalyst.
- (12) 30 minute run time, calculated productivity is 54.4 x 60 ÷ 30 kg/g cat or 109 kg/g cat/hour.
- (13) 30 minute run time, calculated productivity is 60 x 60 ÷ 30 kg/g cat or 120 kg/g cat/hour.
- (14) 40 minute run time, calculated productivity is 83.1 x 60 ÷ 40 kg/g cat or 125 kg/g cat/hour.
- (15) 45 minute run time, calculated productivity is 66.7 x 60 ÷ 45 kg/g cat or 88.9 kg/g cat/hour.
- (16) One weight part catalyst diluted with 3.95 parts by weight polyethylene powder; calculated productivity is 4.95 x 7.36 or 36.4 kg polymer/g undiluted catalyst.
- (17) 40 minute run time, calculated productivity is 55.9 x 60 ÷ 40 kg/g cat or 83.8 kg/g cat/hour.

The quantities of materials employed, weight and mole ratios of reactants charged and results obtained are presented in Table 5.

The results given in Table 4 indicate that the A catalysts, while relatively active for ethylene polymerization, are not nearly as active as the B catalysts which are formed from the corresponding A catalysts by a $TiCl_4$ treatment. In terms of kg polyethylene produced per g (undiluted) catalyst per hour, the indicated A catalysts generally produce from about 3 to 36 kg polymer whereas their B counterparts generally produce from about 36 to 210 kg polymer. It is also noted in this regard that catalysts B-6 and B-7 (runs 18 and 19) showed exceptionally high productivities as compared to their corresponding "A" catalysts, catalysts A-6 and A-7 (runs 6 and 7).

The best results under the conditions employed, were obtained in run 21 employing catalyst B-10 produced from catalyst A-10 composition prepared from a titanium ethoxide-magnesium dichloride reaction product treated with ethylaluminum sesquichloride. This catalyst was extremely active and produced 210 kg polyethylene per gram of catalyst per hour.

Example 84 (Comparative)

~~Catalyst Preparation~~

Catalyst A

All mixing and filtering operations were performed in a dry box under an argon atmosphere employing a dry hydrocarbon as the reaction medium. Anhydrous magnesium dichloride and titanium tetraethoxide were charged to a flask equipped for refluxing and stirring and containing the chosen reaction medium. Each mixture was heated at the temperature and for the time indicated in Table 5 and cooled to the temperature indicated for the dropwise addition of the 0.783 molar solution of ethylaluminum sesquichloride in n-heptane. The resulting slurry was generally stirred an additional 30 minutes after the reaction was completed, stirring was discontinued and the mixture allowed to warm to room temperature, if cooling had been employed. The slurry was suction filtered to produce a filter cake which was washed with portions of dry n-hexane and dried under an argon purge to produce the product.

Table 5
Preparation of Catalysts (Catalyst A)

Catalyst Designation	A-11	A-12	A-13	A-14	A-15	A-16(a)	A-17
MgCl ₂ grams mole	1.90 0.020	1.90 0.020	9.52 0.100	1.92 0.020	1.92 0.020	946 9.94	11.4 0.120
Ti(OC ₂ H ₅) ₄ grams mole	9.12 0.040	9.11 0.040	45.40 0.200	9.39 0.041	9.10 0.040	4309 18.9	55.5 0.244
Reaction Medium							
type	n-hexane	xylenes	xylenes	n-hexane	n-hexane	n-hexane	xylenes
ml	100	70	250	75	110	60.6 liters	100
temperature, °C	108	107	110	110	105	84	110
heating time, minutes	30	30	30	30	40	45	60
Ethylaluminum Sesquichloride							
ml	25	25	125	42	42	12.5 l	301(b)
mole	0.020	0.020	0.098	0.033	0.033	12.7	0.24
reaction temperature, °C	25	-18	-20 to -25	-25	-27	21 to 30	-23 to -25
reaction time, minutes	90	80	270	135	280	120	240
Wash Liquid							
ml	30	30	150	120	120	4,57 liter(d)	300(c)
Mole Ratios							
Ti/Mg	2:1	2:1	2:1	2:1	2:1	1.9:1	2:1
Ti/EASC	2:1	2:1	2:1	1.2:1	1.2:1	1.5:1	1:1
Recovered Product							
grams	5.21	4.51	20.95	6.33	6.25	not recovered	39.53
color	white	tan	white	tan	tan	not determined	light purple

(a) Several batches of catalysts were made under the conditions shown which were combined and are identified as A-16.

(b) Add to 200 ml of xylenes cooled to -26° C and resting in a CCl₄/dry ice bath, the solution of MgCl₂/Ti(OC₂H₅)₄ cooled to 25° C followed by the solution of EASC in a dropwise manner.

(c) Washed filter cake with 50 ml xylenes, then 250 ml of n-hexane.

(d) Used 4, 57 liter portions, decanting liquid off product after each addition.

Example 5Catalyst PreparationCatalyst B

5 All mixing and filtering operations were conducted in a dry box under an argon atmosphere employing dry n-hexane as the reaction medium. To a flask equipped for stirring and reflux was charged n-hexane, ^{obtained as in Example 4} the catalyst A ~~of Example 5~~ and titanium tetrachloride. Each mixture was stirred at the temperature and for the time indicated in Table 6, cooled to
10 room temperature, if needed, and then suction filtered. The filter cake was washed with portions of dry n-hexane and dried under an argon purge.

The quantities of components employed, weight ratios of catalyst A to TiCl_4 and results obtained are given in Table
15 6.

Table 6
Preparation of Catalyst (Catalyst B)

Catalyst Designation	Catalyst A No.	Catalyst A Grams	Weight Ratio		Reaction Condition		n-Hexane, ml		Recovered Product	
			TiCl ₄ Grams	TiCl ₄ / Catalyst A	Time Min.	Max. Temp. °C	Reaction Medium	Wash	Grams	Color
B-11	A-11	2.22	8.9	4:1	60	112	11	30(a)	1.70	lt. purple
B-12	A-12	2.05	8.0	3.9:1	60	116	10	30(a)	1.83	lt. purple
B-13-0	A-13	3.00	12.0	4:1	60	182	15	50	2.58	yellow
B-13-1	A-13	3.00	12.0	4:1	80	80	15	30	2.55	white
B-13-2	A-13	3.00	12.0	4:1	75	132	15	30	2.71	lt. yellow
B-13-3	A-13	2.00	7.7	3.85:1	60	25	10	30(a)	1.61	white
B-14	A-14	2.19	7.7	3.5:1	60	122	15	30	2.10	brown
B-15	A-15	2.03	7.7	3.8:1	60	105	10	30(a)	1.99	lt. purple
B-16	A-16	5255(a)	9072	1.7:1	60	25	18.9 1. 4, 57 1. portions		2470(a)	brown
B-17	A-17	39.53	154.0	3.9:1	55	110	200	200	33.36	lt. purple
B-18	A-11	0.79	3.4	4.3:1	60	25	5	30(a)	0.69	grayish

Note: (a) Estimated

Example 6Ethylene Polymerization

A 3.8 liter, stirred, stainless steel reactor as described and conditioned in Example 3 was employed for ethylene polymerization.

The conditioned reactor for each run was purged with dry isobutane vapor and 1 ml of the cocatalyst solution containing 15 wt. % triethylaluminum (TEA) in dry n-heptane (0.93 mmoles TEA) was charged followed by addition of the catalyst. The reactor was closed, about 2 liters of dry isobutane was charged, the reactor and contents were heated to 80°C and the ethylene was added. Hydrogen was not present in any of the runs, thus each of the polymers produced had a melt index of less than 0.5. Unless indicated to the contrary in Table 7, a run time of 60 minutes was observed in each run.

Each run was terminated and the polymer recovered as described in Example 3. If a run time of less than 60 minutes was employed, a calculated productivity figure for 60 minutes is employed as described in Example 3.

The particle size distribution of the recovered polymer as made and/or ground in a Waring Blendor was determined by placing about 100 grams of the polymer on a set of mechanically agitated sieves. The sieve set consisted of sieves having the mesh sizes (U.S. Sieve Series) of 30, 50, 80, 100, 200 (0.59, 0.30, 0.18, 0.15 and 0.074 mm, respectively) and the bottom pan. Agitation was conducted for 30 minutes unless indicated otherwise and the amount of polymer remaining on each sieve and in the pan was determined by weighing. The ground samples were agitated for 2 minutes at high speed at room temperature in a Waring Blendor. The purpose of grinding the as made polymer is to simulate the attrition polymer particles appear to receive in a large scale reactor such as a loop reactor, for example, since commercially formed polymer particles are generally subjected to substantial agitation which results in the production of finer particles as compared to those made on the bench scale.

Grinding the polymer in a Waring Blendor as referred to above and throughout this application is carried out by grinding 100 grams of the polymer fluff in a dry condition at room temperature (25° C) for 2 minutes using the highest speed on a Waring Blendor Model 31DL42 manufactured by Waring Products Division, Dynamics Corporation of America, New Hartford, Connecticut. Although most any grinder or blender suitable for vigorously agitating relatively small quantities of polymer can be used, the Waring Blendor described above worked very well.

The ground fluff is then screened for 15 minutes. An electric Ro-Tap Sieve Shaker manufactured by the U. S. Tyler Manufacturing Company, Cleveland, Ohio, was used; however, most any sieve shaker could be used or the polymer could be sieved by hand.

The quantity of each catalyst employed and results obtained are given in Table 7.

In each run the initial ethylene pressure was 0.69 MPa (98.5 psig), and the average total pressure was 1.9 MPa (271.4 psig) for all runs except runs 24 and 26 in which it was 2.0 MPa (285.7 psig).

43

Table 7
Effect of Catalyst Formation Conditions
on Polymer Particle Size and Productivity

Run No.	Catalyst Formation			Catalyst		Calculated Productivity Kg/g/hr (a)	Yield Grams	Polymer	
	Reaction Medium	EASC °C	TiCl ₄ °C	Weight Grams	No.			Wt. % Than 100 Mesh	Coarser Ground
22	n-hexane	25	112	0.0023	B-11	193.5	445	82	59
23	n-hexane	-25	122	0.0050	B-14	107.8	539	81(d)	54(d)
24	n-hexane	-25	105	0.0034	B-15	248.5(b)	507	-(e)	46(d)
25	xylenes(f)	-24	25	0.0036	B-13-3	161.7	582	95	82
26	xylenes	-24	80	0.0068	B-13-1	97.5	663	93	-
27	xylenes	-18	116	0.0053	B-12	162.1(c)	573	91	85
28	xylenes	-24	132	0.0067	B-13-2	82.7	554	96	89
29	xylenes	-25	180	0.0099	B-13-0	19.8	196	99.8	95
30	n-hexane	25	25	0.0045	B-18	144	647	-(e)	34

(a) kg polymer per g catalyst per hour.

(b) Run time of 36 minutes giving 507 g polymer. Productivity for 60 minutes is calculated to be 149.1 kg/g/36 min. x 60 min. + 36 min. or 248.5 kg/g/60 min.

(c) Run time of 40 minutes giving 573 g polymer. Productivity for 60 minutes is calculated to be 108.1 kg/g/40 min. x 60 min. + 40 min. or 162.1 kg/g/60 min.

(d) Sieve agitation for 15 minutes was employed.

(e) A dash signifies no determination was made.

(f) Analytical reagent quality, 137°-144°C boiling point range.

Inspection of the results presented in Table 7 shows that the reaction conditions employed in forming the catalyst are of importance from a productivity standpoint of polymer produced per unit catalyst weight per hour as well as from a particle size distribution of the polymer. The most productive catalysts appear to result as shown in runs 22-24 when catalyst A is formed in a paraffin reaction medium at temperatures ranging from about -25° to about 25° C and the final catalyst (catalyst B) is formed by contact of catalyst A with TiCl_4 at temperatures ranging from about 100° to about 125° C. These catalysts form relatively coarse polymer as made consisting approximately of 80 wt. % coarser than 100 mesh^(0.15mm). The polymer is somewhat friable in nature, however, since after grinding it in a Waring Blendor for 2 minutes the amount of coarse polymer remaining consists of about 45 to 60 wt. % coarser than 100 mesh^(0.15mm).

When catalyst A is made in an aromatic reaction medium at about -20° to -25° C and catalyst B is formed by contact of catalyst A with TiCl_4 at temperatures ranging from about 80° to 180° C the particle size of as made polymer and ground polymer is coarser in nature as the results of runs 25-29 demonstrate. The coarsest, most attrition resistant polymer was made with catalyst B formed by contact with TiCl_4 at 180° C. However, the productivity of this catalyst was substantially lower as compared to the other catalysts of runs 25-29. The data in runs 25-29 indicate that when catalyst A is formed at about -25° C and catalyst B is formed from catalyst A at about 80° to about 130° C said catalyst B is capable of producing coarse, attrition resistant polymer at high rates in a slurry polymerization process.

All of the polymers shown in Table 7 have relatively low melt index values, i.e., less than about 0.5, as determined in accordance with the procedure of ASTM D1238-65T, condition E.

Example 87

Ethylene Polymerization - Effect of Cocatalyst Level

A 3.8 liter, stirred, stainless steel reactor as described and conditioned in Example 4³ was employed for ethylene polymerization.

45

The conditioned reactor for each run was purged with dry isobutane, the indicated quantity of cocatalyst solution containing 15 wt. % triethylaluminum (TEA) in dry n-heptane (1 molar) was charged followed by addition of the catalyst.

5 A portion of catalyst B-16 was used in each run. The reactor was closed, about 2 liters of dry isobutane was charged, the reactor and contents were heated to 100° C and the ethylene and hydrocarbon were charged. Run times of 60 minutes were employed.

10 Each run was terminated and the polymer recovered as described in Example A³. The particle size distribution of the as made and/or ground polymer was determined as described in Example 7⁶.

15 The quantity of each catalyst and cocatalyst employed, the melt index of each polymer and the results obtained are given in Table 8.

20 In each run, the initial hydrogen pressure was 0.34 MPa (50 psig), the initial ethylene pressure was 1.4 MPa (200 psig) and the total pressure attained during polymerization was 3.4 MPa (500 psig) except for run 35 which it was 3.3 MPa (485 psig).

Table 8

Effect of Cocatalyst Concentration on Polymer Particle Size

Run No.	Catalyst		g	mmoles	Wt. ratio		Yield g	Polymer		Weight Percent Conversion	
	Wt. g				Cocatalyst	Calculated Productivity		MI(b)	HLMI(c)	As Made	Than 100 Mesh Ground
						kg/g/hr				-(e)	
31	0.0059	0.2	0.023	21	3.9	51.4	303	1.1	29	99	66
32	0.0051	0.25	0.029	26	5.7	24.7	126	0.4	31	99	45
33	0.0052	0.3	0.035	31	6.7	63.5	330	0.6	31	-	87
34	0.0057	0.5	0.058	52	10	44.6	254	1.7	25	-	66
35	0.0099	0.5	0.058	52	5.9	39.7	393	1.6	27	99	88
36	0.0068	1.0	0.115	104	17	38.6	249	4.0	28	99	73
37	0.0071	2.0	0.230	208	32	38.7	275	2.1	29	-	84
38	0.0072	5.0	0.576	520	80	34.2	246	1.3	28	99	95

(a) Parts per million based on the weight of 2 liters of isobutane (1100g).

(b) MI is melt index, g/10 minutes, ASTM D1238-65T, condition E.

(c) HLMI is high load melt index, g/10 minutes, ASTM D1238-65T, condition F. The ratio, HLMI/MI, is believed to relate to molecular weight distribution. The higher the value, the broader the distribution.

(d) The levels of TEA cocatalyst employed in the runs can be related to an approximate mole ratio of TEA to Ti in the above catalysts ranging from about 10:1 to about 450:1.

(e) A dash signifies no determination was made.

(47)

The data given in Table 8 show that the coarse polymer, as made is produced at all of the cocatalyst levels employed. The trends observed in runs 31-38 indicates that more attrition resistant polymer is formed as the cocatalyst level increases based on the ground polymer results. At the same time, however, the productivity of the catalyst appears to diminish somewhat as the cocatalyst level increases. Since aluminum alkyl cocatalysts are relatively expensive materials it is desirable to use the least amount of cocatalyst consistent with high polymer production and low cocatalyst residues as well as the production of attrition resistant polymer. The results indicate that the objective is reached with the materials and conditions employed when the cocatalyst level ranges between about 20 to 200 ppm TEA (wt. ratio of cocatalyst to catalyst of about 4:1 to about 40:1), more preferably between about 30 to 100 ppm (wt. ratio of cocatalyst to catalyst of about 6:1 to about 35:1).

Melt index determinations of the produced polymer clearly show that commercially useful material was produced since many applications exist for polymers in the 0.4 to 4 melt index range including film, sheet, pipe, bottles, containers, and the like. The HLMI/MI ratios shown are indicative of relatively narrow molecular weight distribution polymer. Ethylene polymers with such molecular weight distribution are especially suitable for injection molding.

Example 8⁹

- A. Catalyst Preparation (Catalyst A)
- B. Catalyst Preparation (Catalyst B)
- C. Ethylene Polymerization in Presence of Hydrogen

A. A series of Catalyst A was prepared generally in the manner indicated previously as in Example 8⁴. The quantities of reactants employed, reaction conditions used, and results obtained are given in Table 9. B. Catalyst B was prepared generally in the manner described in Example 8⁵ by contacting a weighed portion of the Catalyst A series with TiCl_4 . The quantities of reactants employed, reaction conditions

utilized, and results obtained are shown in Table 9B. A series of ethylene polymerization runs were carried out generally as described in Example 7⁶ using each catalyst B shown in Table 9B; however each polymerization run was carried out in the presence of hydrogen in order to produce a higher melt index polymer. The polymers produced and the conditions employed are shown in Table 9C.

Table 9A

Preparation of Catalysts (Catalyst A)

Catalyst Designation	A-19	A-20	A-21	A-22
MgCl ₂				
grams	1.90	9.52	11.40	5.80
mole	0.020	0.100	0.120	0.061
Ti(OC ₂ H ₅) ₄				
grams	9.10	45.40	56.19	28.23
mole	0.040	0.200	0.246	0.124
Reaction Medium				
type	n-hexane	xylenes	xylenes	xylenes
ml	100	250	300	150
temp., °C	97	110	120	120
heating time, min.	30	30	40	35
Ethylaluminum Sesquichloride				
ml	25	125	220	77.5
mole	0.020	0.098	0.170	0.060
reaction temp., °C	+25	-20 to -25	-25 to -35	-21 to -27
reaction time, min.	95	270	8.6 hours	205
Wash Liquid	n-hexane	n-hexane	n-hexane	n-hexane
ml	100	100	400	1000(4-250 ml portions)
Mole Ratios				
Ti/Mg	2:1	2:1	2:1	2:1
Ti/EASC	2:1	2:1	1.4:1	2:1
Recovered Product				
grams	2.10	2.55	not determined	not determined
color	brown	white	brown	brown

utilized, and results obtained are shown in Table 9B. A series of ethylene polymerization runs were carried out generally as described in Example 7⁶ using each catalyst B shown in Table 9B; however each polymerization run was
5 carried out in the presence of hydrogen in order to produce a higher melt index polymer. The polymers produced and the conditions employed are shown in Table 9C.

Table 9A
Preparation of Catalysts (Catalyst A)

Catalyst Designation	A-19	A-20	A-21	A-22
MgCl ₂				
grams	1.90	9.52	11.40	5.80
mole	0.020	0.100	0.120	0.061
Ti(OC ₂ H ₅) ₄				
grams	9.10	45.40	56.19	28.23
mole	0.040	0.200	0.246	0.124
Reaction Medium				
type	n-hexane	xylene	xylene	xylene
ml	100	250	300	150
temp., °C	97	110	120	120
heating time, min.	30	30	40	35
Ethylaluminum Sesquichloride				
ml	25	125	220	77.5
mole	0.020	0.098	0.170	0.060
reaction temp., °C	+25	-20 to -25	-25 to -35	-21 to -27
reaction time, min.	95	270	8.6 hours	205
Wash Liquid	n-hexane	n-hexane	n-hexane	n-hexane
ml	100	100	400	1000(4-250 ml portions)
Mole Ratios				
Ti/Mg	2:1	2:1	2:1	2:1
Ti/EASC	2:1	2:1	1.4:1	2:1
Recovered Product				
grams	2.10	2.55	not determined	not determined
color	brown	white	brown	brown

3

Table 9B
Preparation of Catalysts (Catalyst B)

Catalyst Desig.	Catalyst A No.	Grams	TiCl ₄ Grams	Wt. Ratio TiCl ₄ /Cat. A	Reaction Conditions		N-Hexane, ml		Recovered Product	
					Time Min.	Max. Temp. °C	Reaction Medium	Wash Medium	Grams	Color
B-19	A-19	5.05	10.4	2.1:1	60	25	25	30	4.71	brown
B-20	A-20	3.00	12.	4:1	60	80	15	"	2.55	white
B-21	A-21	31.9(a)	128	4:1 est.	60	122	150	400 est.	32.55	lt. purple
B-22	A-12	2.11	7.9	3.7:1	60	25	10	45	1.90	gray

(a) Estimated yield based on previous experiments.

Table 9C

Ethylene Polymerization, Hydrogen Present, 1 Mmole TEA
Effect of catalyst Formation on Productivity and Polymer Particle Size

Run No.	Catalyst Formation		TiCl ₄ °C	Catalyst		Pressures, MPa(c)		Total Reactor	Calculated Productivity kg/g/hr	Yield Grams	Melt Index	Polymer Wt. % Coarser Than 100 Mesh (Ground)
	Reaction Medium	EASC °C		No.	Weight Grams	Ethylene	Hydrogen					
39	n-hexane	25	25	B-19	0.0212	1.48	0.446	3.41	21.7	461	3.6	57
40	"	"	"	"	0.0183	"	0.892	3.62	8.42(a)	154(a)	4.7	33
41	"	"	"	"	0.0195	"	"	"	26.6(b)	518(b)	13	58
42	"	"	"	"	0.0156	"	"	3.55	12.4	194	19	48
43	xylene	-18	25	B-22	0.0061	"	"	"	48.5	296	12	57
44	"	-25 to -35	122	B-21	0.0077	"	0.446	3.62	45.7	352	0.17	92.5
45	"	"	"	"	0.0117	"	0.892	3.76	36.4	426	3.2	67
46	"	"	"	"	0.0133	1.20	1.14	3.69	34.7	461	11	63
47	"	-20 to -25	80	B-20	0.0119	1.48	0.892	3.55	15.1	180	13	65

(a) Run time is 2 1/4 hours, productivity of kg/g/2 1/4 hours.

(b) Run time is 2 hours, productivity of kg/g/2 hours.

(c) Absolute pressures.

F

conditions favor the production of catalyst particles which are uniform in size and generally spherically shaped. An elevated temperature used to form catalyst B appears to set or harden catalyst A particles. The over-all effect results in a catalyst that is capable of producing large, attrition resistant polymer spheres at very high polymer productivities.

The effects of a low mixing temperature and a high treating temperature on the ~~modified~~ catalysts of the invention with respect to polymer particle size and attrition resistance are demonstrated in the results of the runs shown in Table 7 in which a low melt index polymer was produced and in invention runs 44-47 of Table 9C in which a relatively high melt index polymer was produced. It has been observed from past experience that grinding tests made on polymer formed with the catalysts of the present invention result in less coarse polymer (more fines) when the polymer melt index is above about 1. Also, a leveling effect appears to take place when the melt index ranges from about 5 to at least about 40. The amount of coarse polymer after grinding generally amounts from about 80 to about 95 wt. % for low melt index polymer and from about 60 to about 70 wt. % for high melt index polymer. Therefore, it is currently believed that a catalyst can be more accurately evaluated for potential commercial use (in absence of a commercial run) by preparing relatively high melt index polymer (about 5 to 40 melt index) as compared to a low melt index polymer on a bench scale.

A comparison of the results of runs 39-42 with runs 44-47 of Table 9C shows in general that catalysts prepared by contacting a solution of $\text{Ti(OR)}_4\text{-MgCl}_2$ contained in a paraffin, e.g. n-hexane, with an organoaluminum compound at about room temperature or lower and treating the isolated particulate product with TiCl_4 at room temperature or higher produce relatively less coarse polymer (more fines) as compared to the preferred catalysts of the invention.

Thus, the preferred catalysts of this invention which produce large and attrition resistant polymer particles are formed by employing an aromatic solvent and low temperatures (0°C to -100°C) to produce catalyst A and an elevated temperature (80°C to 180°C) to produce catalyst B. The low temperatures utilized in preparing catalyst A is beneficial in reducing fines (increasing coarser polymer particles) in polymerization runs with the finished catalysts. The



44

CLAIMS

1. A method of preparing an olefin polymerization catalyst which comprises

A) reacting in an inert solvent or diluent a dihalide or hydroxyhalide of a metal from Group IIA or IIB of the Mendeleev Periodic Table with a titanium compound in which the titanium metal is bonded to at least one atom of oxygen, nitrogen or sulfur, and said oxygen, nitrogen and sulfur atom(s) in turn being bonded to a carbon atom of a carbon containing radical;

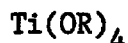
B) reacting the product of step A in the presence of the same or different solvent or diluent with an organometallic compound of a metal from Group I, II or III of the Mendeleev Periodic Table thereby to precipitate a solid organometallo complex of said Group I, Group II or Group III metal; and

C) separating the solid organometallic complex obtained in step B from the solvent or diluent medium, and treating the separated solid complex with a transition metal halide as a halide ion exchanging medium.

2. A method according to claim 1, wherein said transition metal halide used in step C) is titanium tetrachloride.

3. A method according to claim 1 or 2, wherein the titanium compound used in step A) is a titanium tetrahydrocarbyl oxide, titanium tetraimide, titanium tetraamide, or titanium tetramercaptide.

4. A method according to claim 3, wherein the titanium compound is represented by the general formula





45

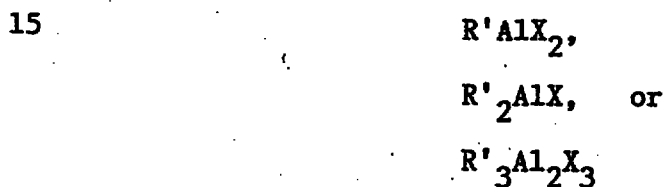
wherein each R is an alkyl, cycloalkyl, aryl, alkaryl or aralkyl hydrocarbon radical of up to 20 carbon atoms.

5. A method according to claim 4, wherein R is C_1-C_{10} alkyl.

5 6. A method according to claim 5, wherein said titanium compound is titanium tetraethoxide or tetrabutoxide.

7. A method according to any one of the preceding claims, wherein the metal dihalide used in step A) is magnesium dichloride, magnesium dibromide, zinc dichloride, beryllium dichloride, 10 beryllium dibromide, magnesium diiodide, magnesium difluoride, calcium dichloride, calcium dibromide or zinc difluoride.

8. A method according to any one of the preceding claims wherein the organometallic compound used in step B) is a hydro-carbylaluminum halide of the formulas



wherein each R' is a linear or branched chain hydrocarbyl radical of 1 to 20 carbon atoms and X is halogen.

20 9. A method according to claim 8, wherein said organo-metallic compound is ethylaluminum sesquichloride.

10. A method according to any one of claims 1-7, wherein the organometallic compound used in step B) is a dialkyl magnesium.

11. A method according to any one of the preceding claims, 25 wherein the step A) is conducted in a hydrocarbon solvent.



12. A method according to claim 11, wherein said hydrocarbon solvent is aromatic.

13. A method according to any one of the preceding claims, wherein step B) is carried out at a temperature in the range -100°C to 0°C.

14. A method according to claim 13, wherein said temperature is in the range -15°C to -40°C.

15. A method according to any one of the preceding claims, wherein step C) is conducted at a temperature in the range 80-180°C.

16. A method according to claim 15, wherein said temperature is in the range 100-130°C.

17. A method according to any one of the preceding claims, wherein the titanium compound and the metal dihalide or hydroxyhalide are reacted in step A) at a metal to metal mole ratio of 10:1 to 1:10 and, in step B), the molar ratio of said titanium metal to the organometallic compound is from 10:1 to 1:10.

18. A method according to claim 17, wherein said ratios are from 2:1 to 1:2 and to 2:1 to 1:3 respectively.

19. An olefin polymerization catalyst when prepared by a method claimed in any one of claims 1 to 18.

20. A catalyst according to claim 19, which is the reaction product in step C) of a titanium halide and a solid product obtained in accordance with steps A) and B), wherein step A) involved the reaction of magnesium dichloride and titanium tetraethoxide thereby producing as the product of step A) a solid material having, if isolated in a substantially crystalline form, a powder X-ray diffraction pattern, taken under conditions to exclude the presence of air and water, showing as characteristic features of the crystalline material interplanar spacings and relative

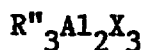
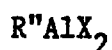


47

intensities as follows:

<u>interplanar spacing</u> <u>(meter x 10⁻¹⁰)</u>	<u>relative intensity of</u> <u>spectrum</u>
10.77	weak
10.47	very strong
9.28	very weak
8.73	weak
8.23	very strong
8.10	moderate
7.91	very strong
7.43	strong
7.27	strong
6.52	weak
6.41	weak
6.10	weak
4.90	very weak
4.42	very weak
4.40	very weak
4.09	very weak
3.86	very weak

21. A catalyst according to claim 19 or 20, further comprising as a cocatalyst an organoaluminum compound of the formula



wherein each R'' is a linear or branched chain hydrocarbyl radical containing from 1 to 20 carbon atoms and X is a halogen atom.

22. A catalyst according to claim 21, wherein said cocatalyst is triethylaluminum.

23. A catalyst according to claim 21 or 22, wherein the weight ratio of said cocatalyst to said titanium-containing catalyst



is in the range 4:1 to 40:1.

24. A process for producing olefin polymers which comprises contacting one or more aliphatic mono-1-olefins, conjugated diolefins or vinylaromatic compounds, under polymerization
5 conditions with a catalyst according to any one of claims 20-24.

25. A process according to claim 24, wherein the olefin comprises ethylene and optionally up to 10% by weight of propylene, 1-butene 2-butene, 1-hexene, 1,3-butadiene, isoprene, 1,3-pentadiene, styrene or α -methylstyrene.

The text of the specification has been reproduced by photocopying the applicants original typescript. It may contain a few amendments which are difficult to read. The original typescript containing these amendments may be inspected on the premises of the Patent Office.
