

POLYMERIZATION CATALYST AND PROCESS FOR
POLYMERIZING ALPHA-OLEFINS

The present invention relates to a catalyst and a polymerization process employing the catalyst.

In the field of catalytic polymerization of olefins, such as propylene, to produce useful solid polymers, a continuing objective is to increase productivity. By productivity is meant the amount of useful solid polymer that is obtained by means of a given quantity of catalytic materials. This is important because the removal of catalytic materials from the solid polymer is almost always necessary and is generally troublesome or expensive to carry out. Thus, improved polymerization processes are desired in which the productivity of the polymer per unit of the catalyst material is so great that the amount of catalyst residues remaining in the polymer is insignificant and the catalyst removal steps can be minimized or omitted. The present invention is directed to improved polymerization catalysts capable of yielding greater amounts of useable polymer per unit of catalyst.

Thus, the invention provides an olefin polymerization catalyst comprising the product which forms on mixing:

(A) a catalyst component A formed by milling

(1) magnesium halide or manganous halide with

(2) at least one catalyst adjuvant

to form a milled composite wherein the molar ratio of (1) to (2) is in the range from 4:1 to 100:1; and then treating the composite thus obtained from (1) and (2) with (3) a tetravalent titanium halide for a period of time sufficient to incorporate tetravalent titanium halide on at least a portion of the surface of said milled composite; and

(B) a cocatalyst component B comprising at least one of a trihydrocarbyl aluminium compound and an organoaluminium monohalide of the formula $(R')_2AlX$ in which R' is an alkyl group having 1-20 carbon atoms and X is bromine, chlorine or iodine, wherein the molar ratio of component B to titanium compound is in the range from 0.5:1 to 2000:1 and the amount of titanium present in the finished catalyst is in the range from 0.1 to 10 weight percent based on the dry composite, wherein said adjuvant A(2) is an aromatic organosphosphorus compound selected from

(a) aromatic organo phosphites of the formula

$$\begin{array}{c} R^2 - O \\ R^2 - O \end{array} \begin{array}{c} \diagup \\ \diagdown \end{array} P \begin{array}{c} H \\ O \end{array}$$

wherein each R^2 group is an aryl, aralkyl, alkaryl or haloaryl group having from 6 to 20 carbon atoms,

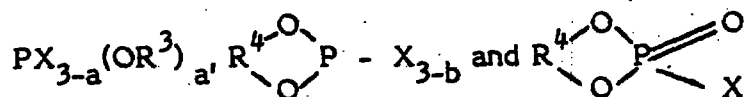
(b) triaryl phosphine oxides of the formula

$$R^{10} - \underset{\substack{| \\ R^{11}}}{\overset{\substack{R^9 \\ |}}{P}} O$$

wherein R^9 , R^{10} and R^{11} are each aromatic hydrocarbyl groups containing up to 20 carbon atoms,

(c) triarylphosphites having from 6 to 24 carbon atoms in each aryl group, and

(d) halogen-containing organo phosphorus compounds of the formulae



wherein R^3 is an aryl group of 6-20 carbon atoms, R^4 is an arylene group of 6-20 carbon atoms, X is a halogen, a is 1 or 2, and b is 0 or 2.

A broad range of olefins can be polymerized by the process and catalyst system of the present invention. Commercial value can be visualized presently with alpha-olefins which have from 2 to 10 carbon atoms. The invention finds particular usefulness with either ethylene or propylene which is polymerized to produce polyethylene or polypropylene, respectively. Mixtures of the alpha-olefins can be used. High ratios of polypropylene to catalyst were obtained employing the catalyst and process of the present invention.

As indicated above, catalyst component A is formed by milling or grinding together magnesium halide or manganous halide with suitable catalyst adjuvants. Magnesium dihalide is generally used, and magnesium

dichloride is a presently preferred magnesium halide.

Exemplary aromatic organophosphorus compounds A(2) contemplated in the preparation of catalyst component A are :

a) diphenyl phosphite, di(4-nonylphenyl) phosphite, di(2-methylphenyl) phosphite, di(4-chlorophenyl) phosphite and di(1-naphthyl)phosphite;

b) triphenyl phosphine oxide, tri-4-phenanthryl phosphine oxide and tris(7-phenyl-1-naphthyl) phosphine oxide;

c) tri-o-tolyl phosphite, tri-1-naphthyl phosphite, tri-9-anthryl phosphite, tri-4-phenanthryl phosphite, tri-p-cumenyl phosphite, tris(4-pentyl-1-naphthyl)phosphite, tris(5-decyl-2-phenanthryl)phosphite, tris(3-cyclobutylphenyl)phosphite, tris(6-cycloheptyl-2-naphthyl)phosphite, tris 4-(2-naphthyl)phenyl phosphite and tris(7-phenyl-1-phenanthryl)phosphite.

d) diphenylphosphorochloridate, di-1-naphthylphosphorobromidate, di-o-tolylphosphoroiodidate, phenylphosphorodichloridite, 1-anthryl-phosphorodibromidite, catechyl

phosphotrichloride (o-phenylenephosphorotrichloridite), o-phenylenephosphochloridate and o-phenylenephosphorochloridite.

Preferred features of the invention will now be described.

The molar ratios of magnesium halide or manganous halide to catalyst adjuvant additive used in forming catalyst component A can range from 4:1 to 100:1. The magnesium halide or manganous halide support and the catalyst adjuvant materials for catalyst component A are generally admixed in a suitable milling means under intensive milling conditions. The milling employed is to be distinguished from ordinary admixing, shaking, or tumbling or the like. The milling referred to is the strong and thorough mixing of the solid ingredients together, and milling under milling conditions, in such a manner as to afford significant reduction in the particle size. Milling can be by means of a ball mill, vibrating ball mill, tower mill, or the like. A typical, specific mill employable is a vibratory mill, such as a Vibratom, manufactured by Siebtechnik G.M.B.H.

Milling can employ ambient, vacuum or other subatmospheric or superatmospheric, pressure, in an inert, dry atmosphere such as nitrogen, argon, or the like. Milling can result in heat being produced and where needed cooling means can be employed to avoid excessive temperatures, e.g. over 65°C which would adversely affect catalytic performance. Milling times can range widely, such as from 5 to 200 hours, though presently preferred times are from 10 to 175 hours because the catalysts are sufficiently activated after such milling times. No advantage in activity is gained by exceeding the specified times. Vibratory milling typically takes a shorter time than rotary ball milling.

Magnesium halide, manganous halide, preferably the chlorides, one or both, are employed substantially anhydrous, and in the form of a finely divided powder. The magnesium or manganous halide can be preactivated by a grinding operation prior to the milling step used to form component A though this preactivation is not considered generally necessary.

Usually, the anhydrous magnesium chloride or manganous chloride is added to the milling means prior to addition of the catalyst adjuvant material or additive of component A but the order of addition is not critical.

The milled product of magnesium halide or manganous halide and the catalyst adjuvant materials which forms catalyst component A is reacted, neat or in solution, with a titanium tetrahalide, usually the tetrachloride for convenience, at a temperature in the range from 0°C to 200°C for a time sufficient to incorporate TiCl_4 on at least a portion of the surface thereof, excess TiCl_4 is washed out with an inert solvent, such as n-heptane, and the resulting composite dried. To improve distribution of the Ti compound the reaction can be carried out in a hydrocarbon diluent which is inert in the process as, for example, isobutane, n-heptane, cyclohexane, benzene or gasoline, for a period of time in the range from 10 minutes to 5 hours. Suitably, if an alkane such as n-heptane is used as the diluent, the reaction can be conducted by refluxing the mixture for about 1 hour, for example. The reaction is conducted in the absence of water, and oxygen is excluded by operating with a dry gas purge, i.e., nitrogen, argon, etc.

The treated product is cooled to room temperature, the liquid decanted, and the slurry is washed with several portions of dry alkane, for example, and dried.

The Ti content of the finished catalyst is generally from 0.1 to 10 wt. % based on the dry composite. This corresponds to 0.5 to 70 mmoles titanium tetrahalide per mole of magnesium or manganous halide present.

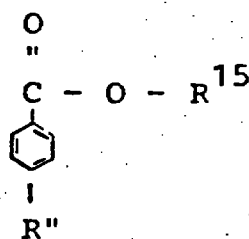
The weight ratio of the $MgCl_2$ -additive (adjuvant) composite to the
5 titanium tetrahalide applied thereto can range from 0.1:1 to 10:1.

It is within the scope of the invention to utilize more than one of the defined additives in preparing catalyst component A. In addition, catalyst component A can be admixed with a diluent in particulate form which is inert to the catalyst components, such as polyethylene, poly-
10 propylene, poly(methyl methacrylate), polyvinyltoluene, polycarbonate, polystyrene, silica, alumina and calcium carbonate. If a polymer is employed, its melting or softening temperature should be higher than the reaction temperature. Suitably, the diluent is admixed with the $MgCl_2$ and the additive or additives during the milling operation. The weight ratio of
15 $MgCl_2$ -additive mixture to diluent can range from 0.1:1 to 50:1.

Catalyst component B comprises one or more organometal compounds selected from trihydrocarbylaluminum compounds and dialkylaluminum halides. The compounds are defined by the generic formula $Al R_3$ where the R is as previously defined and $(R')_2Al X$ wherein R' is an
20 alkyl group containing from 1 to about 20 carbon atoms, and X is bromine, chlorine or iodine. Exemplary compounds include trimethylaluminum triethylaluminum, triicosylaluminum, triphenylaluminum, tribenzylaluminum, tricyclohexylaluminum, dimethylaluminum bromide, diethylaluminum chloride, dibutylaluminum iodide and dieicosylaluminum chloride.

Generally, when ethylene is to be polymerized, a single organoaluminum such as triethylaluminum or triisobutylaluminum is employed. When a branched chain 1-olefin such as propylene is to be polymerized, the catalyst system consists of a trihydrocarbylaluminum compound and preferably an aromatic ester, e.g. ethyl anisate or ethyl benzoate, to improve stereospecificity and optionally a dialkylaluminum halide compound to increase polymer yields.

Particularly applicable compounds for improving stereospecificity are esters represented by the formula:



- 10 wherein R^{15} represents alkyl groups having from 1 to 4 carbon atoms and wherein R'' represents monovalent radicals selected from -F, -Cl, -Br, -I, -OH, -OR', -OOCR', -SH, -NH₂, -NR'₂, NO₂, -CN, -CHO, -COR', -COOR', -CONH₂, CONR₂, -SO₂R', -CF₃, -NHCOR', and hydrogen; wherein R' is a C₁₋₂₀ alkyl group. Some examples of such compounds are ethyl benzoate, ethyl anisate (p-methoxybenzoate), ethyl p-dimethylaminobenzoate, ethyl p-fluorobenzoate, ethyl p-cyanobenzoate, methyl benzoate, isopropyl p-diethylaminobenzoate, butyl p-fluorobenzoate, n-propyl p-cyanobenzoate, ethyl p-trifluoromethylbenzoate, methyl p-hydroxybenzoate, ethyl p-methoxycarbonylbenzoate, methyl p-acetylbenzoate, isopropyl p-formyl
- 15

benzoate, methyl p-nitrobenzoate, ethyl p-carbamoylbenzoate, methyl p-mercaptobenzoate and mixtures thereof.

The molar ratio of AlR_3 to titanium compound can be from 1:1 to 2000:1. The molar ratio of $(R')_2Al X$ to titanium compound can be from 0.5:1 to 2000:1. The molar ratio of AlR_3 to $(R')_2Al X$ can be from 0.1 to 100:1. The molar ratio of AlR_3 to aromatic ester can be from 1:1 to 8:1. Desirably, when polymerizing propylene, a molar ratio of AlR_3 to $(R')_2Al X$ of 0.7:1 to 50:1 is employed.

The catalyst components can be individually introduced into the polymerization reaction zone. The desired amounts can be added directly, or flushed in with portions of diluent, as may be convenient. The particular order of addition to the polymerization reactor means does not appear to be critical. Components A and B are usually not premixed before charging to the reactor. Any order of charging can be employed.

In the following description of the preferred embodiments the reference numerals refer to the definition of the invention set out above.

In one preferred embodiment, in component A of the catalyst (1) is $MgCl_2$, (2) is diphenyl phosphite, (3) is $TiCl_4$ and component B comprises triethylaluminum and ethyl anisate.

In a further preferred embodiment, in component A of the catalyst (1) is $MgCl_2$, (2) is triphenylphosphine oxide (3) is $TiCl_4$ and component B comprises triethylaluminum and ethyl anisate.

In a further preferred embodiment, in component A of the catalyst (1) is $MgCl_2$, (2) is triphenyl phosphite, and component B comprises triethylaluminum, ethyl anisate and diethylaluminum chloride.

In yet a further preferred embodiment, in component A of the catalyst (1) is MgCl_2 , (2) is catechylphosphotrichloride, diphenylphosphorochloridate, phenylphosphorodichloridite, or o-phenylenephosphorochloridate, (3) is TiCl_4 and component B comprises triethylaluminum and ethyl anisate.

5 Polymerization can be carried out under conditions known in the art, such as in a liquid phase in the presence or absence of a diluent substantially inert under the reaction conditions employed, or the reaction can be carried out in the vapor phase.

It presently is preferred to polymerize propylene in liquid propylene
10 in the absence of an inert diluent because separation of components is simplified and good results are obtained.

Ethylene presently is preferably polymerized in a diluent, though other alpha monoolefins conveniently need not be.

Typical suitable diluents include n-butane, isobutane, pentane, n-
15 hexane, n-heptane, n-octane, cyclohexane, methylcyclohexane, and the like or other saturated aliphatic hydrocarbons, alone, or in admixture.

Polymerization temperatures employed can range widely, as convenient and desirable for the equipment, monomer, and the like.

Exemplary temperatures of polymerization lie in the range -80°C to 150°C ,

20 preferably 15°C to 120°C . Polymerization temperatures can vary somewhat depending on the particular monomer, employment of diluent and the like.

For example, the polymerization of propylene using liquid propylene phase conveniently is carried out in the range 24°C to 80°C , preferably 49°C to 75°C , because of better results with regard to productivity and solubles.

Polymerization pressures can range widely, as convenient, depending on whether vapor phase or liquid phase conditions are employed, whether diluent is employed, and the like. Where liquid phase operation is desired, with or without diluent, the pressure employed should be sufficient to
5 maintain reactants and diluent substantially in the liquid phase.

Control of the molecular weight of the polymeric product can be exerted by including small amounts of hydrogen during polymerization, and this normally is considered advantageous. The presence of hydrogen tends to decrease the molecular weight of the polymeric products.

10 The polymerization process can be conducted either continuously or batchwise, as may be convenient depending on desired output, equipment, and the like.

Of course, the catalyst components employed are, to some extent, sensitive to poisons, such as water, air, and the like. Equipment, diluent,
15 alpha-monoolefin, and the like all should be maintained in substantially anhydrous conditions or dried prior to employment. An atmosphere inert to the components should be maintained in substantially anhydrous conditions or dried prior to employment. An atmosphere inert to the components should be employed, such as nitrogen, argon, helium, n-hexane, and the like.
20 Polymerization starts almost immediately on combination of the catalyst components with the monomer and is generally terminated within about two hours.

After completion of the polymerization reaction, or after suitable residence time in the reaction zone to obtain the desired conversion, the

contents of the reactor means then are discharged. The catalyst can be inactivated by treatment with an agent such as a lower alcohol such as ethanol or methanol, the mixture then separated, and the polymer isolated. The polymer recovered can be purified as desired by such as drying under vacuum, and the like. The polymeric product can be treated for removal of solubles by contacting with n-hexane, n-heptane, etc., which dissolves the soluble amorphous material and leaves a white, solid, predominantly crystalline polymer as the final product.

Example I

Two series of catalyst component A were prepared by intensive ball milling of anhydrous magnesium chloride with the specified additive. After recovery, each composite was individually treated with titanium tetrachloride, washed and recovered. The additive employed was triphenyl phosphite. Each sample was prepared by charging a one-liter stainless steel vessel with 108 g magnesium chloride, 2000 g of 1.3 cm steel balls, and a specified quantity of additive. Each sample was subjected to milling for 24 hours with a cooling tap water spray on the outside of the vessel by employing a Vibratom vibratory mill, Model 6L-b, a product of Siebtechnik GMBH, Mulheim, West Germany, which operated at a frequency of 1,760 cycles per minute at an amplitude of about 9mm.

Of the eight samples prepared with triphenyl phosphite, one was milled with 16.5 g of the phosphite and the remainder with 18.9 g of the phosphite. Thus, the calculated mole ratio of $MgCl_2$ to phosphite was 21:1 for the one sample and 18.6:1 for the remainder. The calculated $MgCl_2$ to phosphite mole ratio of the combined samples was 19:1.

While under a dry nitrogen purge, each milled sample was charged to a vessel equipped for stirring and refluxing, to which was added 40 ml (69.04 g) of titanium tetrachloride and 250 ml of dry n-heptane. The stirred mixture was refluxed for one hour (about 100° C). After the reaction period, stirring was discontinued, the mixture was cooled to about room temperature, and the supernatant liquid removed by decanting. The product (slurry) was washed to remove unreacted titanium tetrachloride by contact with a 250 ml portion of dry n-hexane while being stirred. Stirring was discontinued, the solids left to settle, and the supernatant liquid removed by decanting. The washing process was repeated using a 250 ml portion of dry n-pentane as the contacting liquid. After decanting the supernatant liquid, the product was dried over a warm water bath, 50°C, in a current of dry nitrogen. Each catalyst component thus prepared was tested for propylene polymerization by charging a portion thereof to a reactor as detailed below with triethylaluminum (TEA) and ethyl anisate (EA) as the cocatalyst system. The unused portions of the catalyst samples were combined and mixed to form a composite sample for later use.

To a dry, stirred, stainless steel reactor of 3.8 liter (one gallon) capacity at 70°C was charged in order under a gaseous propylene purge 5.4 mmoles TEA as a 15 weight percent solution in dry n-heptane, 1.6 mmoles EA, and catalyst component A. The reactor was sealed hydrogen added from a 360 ml bomb (delta pressure of 276 kPa (40 psig) on the bomb) and about 1.9 liters of liquid propylene was charged. The reactor temperature was adjusted to 70°C, and the reactor filled liquid full with additional liquid

propylene. The liquid full condition was maintained during each one-hour polymerization run by adding more propylene as required.

Each run was terminated by injecting a 10 ml portion of methanol to the reactor, and the reactor and contents cooled to about room
5 temperature. The reactor was drained, and the solid polymer recovered, dried, and weighed. Soluble polymer in the liquid propylene effluent was determined by flashing off the propylene and weighing the dried residue. The xylene-soluble polymer content of the solid polymer was determined by
10 adding a weighed amount of the polymer to heated xylene at approximately 52°C (125°F) and determining the amount of polymer precipitated from solution after cooling the mixture to room temperature. The difference represents the xylene-soluble polymer.

Several runs (2-7) were conducted in a stirred, stainless steel reactor of 1-liter capacity following the same procedure enumerated for the
15 3.8 liter reactor except for charging the reactor at room temperature (23°C) and a reduction in the quantities charged to the reactor. However, the polymer produced was isolated by venting unreacted propylene. Thus the recovered polymer contained propylene-soluble polymer, as well as propylene-insoluble polymer. Resulting determination of soluble polymer by
20 xylene in this instance yields a value which includes xylene-soluble material, as well as propylene-soluble material.

Analysis of the combined MgCl_2 -triphenyl phosphite milled samples showed it contained 1.65 weight percent titanium (equivalent to 6.53 weight percent TiCl_4 , the basis used for calculations involving TiCl_4 and TEA) and
25 19.9 weight percent magnesium.

The amount of catalyst component A employed in each run, calculated amount of TiCl_4 present, calculated TiCl_4 : TEA mole ratio, polymer yields, and calculated productivities based on grams polymer obtained per g catalyst component A are given in Table 1. Calculated
5 productivity for "solid" polymer represents that insoluble polymer recovered from the 3.8 liter reactor. Calculated productivity for total polymer includes the solid recovered polymer plus recovered propylene-soluble polymer.

Table 1 - Propylene Polymerization

Run No.	Additives	Cat. Component A		Calculated TEA/TiCl ₄ mole ratio	Polymer yield, g		Calculated Productivity solid total	Soluble Polymer, wt %			
		mg.	calc. mg.		solid	propylene soluble		xylene propylene combined			
1	triphenyl- phosphite	49.8	3.25	0.017	346	13	6950	7210	5.2	3.6	8.3
2	"	9.7	0.63	0.003	85.4	--	--	8800	--	--	10.0
3	"	7.2	0.47	0.002	65.7	--	--	9120	--	--	11.1
4	"	8.8	0.57	0.003	91.5	--	--	10400	--	--	14.2
5	"	10.2	0.67	0.004	95.4	--	--	9350	--	--	14.0
6	"	10.9	0.71	0.004	103.6	--	--	9500	--	--	10.3
7	"	9.7	0.63	0.003	94.1	--	--	9700	--	--	3.2
8	"	29.5	1.93	0.010	201.	8	6820	7080	5.3	3.8	9.1
Average					na	na	na	8890	na	na	12.2

Notes: Runs 2-7, TEA was 3 mmoles, EA was 0.8 mmoles. Reactor capacity was 1.1 liter.

Polymer recovered included propylene solubles.

Xylene soluble polymer included all soluble polymers.

The dashes indicate that individual determination of propylene soluble polymer, calculated productivity for solid polymer, xylene soluble polymer, and propylene soluble polymer is not made with this reactor product.

na means not applicable because of process differences with two reactors employed.

Inspection of the data indicates that the invention catalysts employing triphenyl phosphite in catalyst component A were very active for propylene polymerization and that soluble polymer formation was relatively low. Replicate run data are presented to show that, generally, reproducibility of polymerization results with catalyst component A present are very good.

Example II

A series of comparison catalysts was prepared to show that milling together MgCl_2 and triphenyl phosphite and treating the product with TiCl_4 is required in order to obtain very active propylene polymerization catalyst components.

Catalyst A: 9.4 g of milled MgCl_2 was added to a dry flask equipped for stirring and refluxing under a dry nitrogen purge. To the flask was added 250 ml of dry n-heptane and 3 ml (3.5 g) of triphenyl phosphite. The stirred mixture was heated to refluxing temperature for one hour and the mixture then cooled in the absence of stirring. The supernatant liquid was decanted and about an equal quantity of dry n-hexane was added, mixed with the slurry and the solids allowed to settle. The supernatant liquid was removed by decanting and about an equal portion of dry n-hexane added back along with 20 ml (34.5 g) of titanium tetrachloride. The mixture was refluxed for one hour, then washed and isolated as described in Example I.

Catalyst B: A mixture was obtained by ball milling 15 g dry MgCl_2 (250 ml stainless steel vessel with 400 g of 0.95 cm (3/8") steel balls) and

0.6 ml (1.04 g) TiCl_4 in the manner previously described for 24 hours. The calculated mole ratio of $\text{MgCl}_2:\text{TiCl}_4$ was 28.7. 13.4 g of the product was added to a dry flask as in the manner used for Catalyst A. To the flask was added 250 ml of dry *n*-heptane and 2.0 ml (2.4 g) of triphenyl phosphite. The mixture was heated to refluxing temperature for one hour, then cooled, washed, and recovered as before.

Catalyst C: A mixture was obtained by ball milling 15 g dry MgCl_2 and 2 g triphenyl phosphine oxide for 24 hours as previously described. 16.0 g of the product was charged to a flask along with 250 ml dry *n*-heptane and 20 ml titanium tetrachloride. After refluxing one hour the mixture was washed and the product recovered as in Example I. The calculated MgCl_2 :triphenyl phosphine mole ratio was 20.7:1.

Catalyst D: A mixture was obtained by ball milling 15 g dry MgCl_2 , 2.4 g of triphenyl phosphite, and 0.5 g TiCl_4 for 24 hours. The calculated MgCl_2 :triphenyl phosphite mole ratio was 20.8.

Catalyst E: 15 g of milled MgCl_2 was added to a dry flask equipped for stirring and refluxing under a dry nitrogen purge. To the flask was added 250 ml of dry *n*-heptane and 20 ml (34.5g) of titanium tetrachloride. The stirred mixture was heated to refluxing temperature for one hour and then cooled to room temperature in the absence of stirring. The solids that settled were recovered by washing with a 250 ml portion of dry *n*-hexane and two 250 ml portions of dry *n*-pentane, evaporating away the wash solutions and finally drying the solid product over a warm water bath.

Each catalyst was used to polymerize propylene in the manner described in the first example using the same quantities of TEA, EA, and hydrogen as in Example I.

The amounts of catalysts charged, mole ratios employed, and results obtained are given in Table 2.

30

Table 2
Propylene Polymerization With Comparison Catalysts

Run No.	Catalyst Component A		Cocatalyst, mmoles		Polymer yield, g		Calculated Productivities		Soluble Polymer		
	Catalyst	Charged mg	TEA	EA	solid	propylene soluble	solid	total	wt % xylene	propylene	combined
1	A(c)	38.6	5.4	1.6	24	0	622	622	7.2	0	7.2
2	B(c)	39.0	"	"	58	6	1490	1640	4.0	9.4	13.4
3	C(d)	39.5	"	"	115	10	2910	3160	5.7	8.0	13.7
4(a)	D(d)	49.8	"	"	318	13	6950	7210	5.2	3.6	8.8
5	D(c)	45.8	"	"	110	5	2400	2500	3.6	4.4	8.0
6	E(f)	44.0	"	"	18	2.3	410	460	7.6	11.3	18.9

Notes: (a) Run 4 is the same as run 1 of Example I, triphenyl phosphite additive.
(c) Comparison
(d) Invention
(f) Control

The results given in Table 2 indicate in run 6 that treating $MgCl_2$ with $TiCl_4$ yields a catalyst that has low activity for propylene polymerization, and moreover produced much soluble polymer (about 19 wt.%).

Run 1 shows that merely contacting $MgCl_2$ with triphenyl phosphite, isolating the product, and treating it with $TiCl_4$ is not equivalent to intensively ball milling $MgCl_2$ and triphenyl phosphite before the $TiCl_4$ treatment. Thus, calculated productivity for solid polymer recovered from the reactor in control run was 622 g polymer per g catalyst component A versus 6950 g polymer per g catalyst for the invention catalyst of run 6.

Run 2 shows that refluxing a milled mixture of $MgCl_2$ and $TiCl_4$ with triphenyl phosphite, and recovering the product yields a catalyst which is somewhat more active for propylene polymerization than shown in run 1 (calculated productivity of about 1500 g solid polymer per g catalyst component A) but still far below the 6950 g figure of the invention catalyst.

The results shown in run 3 show that ball milling $MgCl_2$ and triphenyl phosphine oxide yields a catalyst after $TiCl_4$ treatment that is active; that is, calculated solid polymer per g catalyst component A is about 2900 g and about 14 wt % soluble polymer. Although a good catalyst is made in the fashion of this invention with triphenyl phosphine oxide, the results shown in run 4 with triphenyl phosphite indicate that the triaryl phosphites are more preferred than the triaryl phosphine oxides in preparing catalyst component A of this invention.

The results obtained in run 5 demonstrate that catalyst component

A which is obtained by ball milling MgCl_2 , triphenyl phosphite, and TiCl_4 forms a relatively good catalyst. However, catalyst productivity is calculated at 2400 g solid polymer per g catalyst component A compared to the invention catalyst component A containing triphenyl phosphite and MgCl_2 followed by a TiCl_4 treatment which produced 7200 g polymer per g catalyst component A (run 4).

Example III

A series of invention catalyst component A's were prepared by ball milling dry MgCl_2 with a specified additive for 24 hours as described before. Unless otherwise specified, the compositions were prepared by ball milling 15 g dry MgCl_2 with 2 g or 2 ml of the additive. Each recovered product was then refluxed with TiCl_4 in the presence of n-heptane (unless otherwise indicated) for 1 hour, and the final product washed and recovered as previously described.

Each catalyst component A was used in propylene polymerization using a 3.8 liter reactor in the manner previously described in conjunction with 5.4 mmoles TEA and 1.6 mmoles EA.

The mole ratio of each MgCl_2 : additive prepared, amounts of catalyst component A charged, and results obtained are presented in Table

3.

Table 3

Propylene Polymerization

Catalyst Component A

Run No.	Additive used	mole ratio		wt ratio
		MgCl ₂ : additive	MgCl ₂ / additive	
1	triphenyl phosphite	19	1.7	
2	diphenyl phosphite	15	0.46	
3	triphenylphosphine oxide	14	0.39	
4	catechylphosphotri-chloride	18	0.46	
5	diphenylphosphorochloridate	12	0.47	
6	phenylphosphorodichloridite	10	0.50	
7	o-phenylenephosphorochloridate	14	0.45	

Component A charged	Polymer yield, g		Calculated productivity	Soluble Polymer, wt %	
	mg.	solid	solid	propylene	xylylene propylene
34.9	377	15	10380	7.0	3.8
44.0	344	13	7820	5.9	3.6
44.4	207	9	4660	5.5	4.2
42.6	205	10.4	4810	5.5	4.8
39.1	226	9	5780	4.8	3.8
43.7	287	9.8	6510	6.3	3.3
38.6	178	10.3	4610	5.3	5.8

The additives used in preparing catalyst component A are presented in Table 3. in the general order given in the preliminary discussion. The results obtained, based on an arbitrary calculated productivity of the solid polymer obtained of at least about 4,500 g polymer per g catalyst component A disclose that triphenyl phosphite, Run 1 (repeated for emphasis), diphenyl phosphite in Run 2, triphenylphosphine oxide of Run 3, and the organic phosphorus and chlorine-phosphorus compounds of Runs 4-7, all yield superior catalysts when prepared in the manner of this invention.

Example IV

10 As described in Example I, catalyst component A was prepared by ball milling 15 g anhydrous MgCl_2 with 2.4 g triphenyl phosphite for 24 hours. Thus, the mole ratio of MgCl_2 to the phosphite was 20.8. As before, the recovered product was refluxed with 34.5 g of TiCl_4 and 250 ml of dry n-heptane for one hour. The reaction product after washing and drying as
15 before was found by analysis to contain 1.91 weight percent titanium. This is equivalent to a calculated TiCl_4 content of 7.6 weight percent.

Propylene was polymerized as described in Example I, except that a cocatalyst system containing 5.4 mmoles triethylaluminum, 1.6 mmoles ethyl anisate, and 0.2 mmoles diethylaluminum chloride were employed. A
20 polymerization time of 2.5 hours was used. 20.4 mg of catalyst component A was charged to the reactor in this run.

Recovered solid polymer was found to weigh 346 g, and recovered propylene soluble polymer was found to weigh 10g. Calculated productivity

of solid polymer over the 2.5 hour run was found to be 16,960 g polymer per g catalyst component A. The xylene soluble polymer produced was 5.0 wt %, and propylene soluble polymer was 2.8 wt %.

5 This polymerization run represents a method in which catalyst productivity is high (based on catalyst component A), and soluble polymer formation is low. It is seen that the catalyst system employed retains good activity over the 2.5 hour polymerization run time used.

Example V

10 Catalyst components A in this Example was prepared as described in Example I, except that two additives were employed. One of the additives used was a diluent, i.e., polymethylacrylate, and the active additive was triphenylphosphite.

Propylene was polymerized as described in the first example using 5.4 mmoles of TEA and 1.6 mmoles EA as the cocatalyst system.

15 The additives and ratios employed in preparing catalyst component A and results obtained are given in Table 4.

Table 4

Propylene Polymerization

Component A		Wt. ratio additive to diluent	Wt. ratio additive to diluent	Com- ponent A charged, mg	Co- catalyst molecules TEA	EA	solid soluble	propy- lene-	Calculated Productivity	Soluble Polymer, wt. percent	xylene propylene comb.	
Wt. ratio MgCl ₂ + additive to diluent	Wt. ratio MgCl ₂ + additive + diluent to											
17	0.47	2.4	38.2	"	"	233	13	6100	6440	6.2	5.3	11.5

The results in Table 4 show that a polymeric diluent such as poly(methyl methacrylate) can be used to advantage in preparing catalyst component A to yield an active catalyst.

Example VI

5 Some of the catalyst component A samples used in propylene polymerization were also tested for ethylene polymerization. In these runs, a 3.8 liter reactor similar to that employed in propylene polymerization was employed.

10 The polymerization procedure consisted of heating the reactor containing about 3 liters of dry n-heptane to 175°C for about 30 minutes. The reactor was drained, residual n-heptane purged by means of a stream of dry nitrogen and the closed reactor cooled to room temperature while under nitrogen. The cooled reactor was purged with isobutane vapor, 2.7 mmoles of TEA as a 15 wt % solution in n-heptane added, and a catalyst component
15 A charged. The reactor was closed, 2 liters of isobutane were charged, the reactor and contents were heated to 80°C, and 0.69 MPa (100 psig) ethylene pressure admitted. Additional ethylene was charged as required during polymerization to maintain the pressure. Following each 1 hour run, the run was terminated by venting the ethylene and isobutane, and the polymer
20 recovered and weighed.

The additives employed, amount of catalyst component A charged to the reactor in each run, and results obtained are given in Table 5.

Table 5 - Ethylene Polymerization

Catalyst Component A Prior Description Table	Run	Present Run No.	Additive(s) employed	Catalyst Component A Charged to Reactor, mg		Reactor Pressure psi MPa		Polymer Yield g	Calculated Productivity, g solid polymer/g catalyst Component A
J	1	1	triphenylphosphite	10.5	275	1.90	163	15,500	
	2	2	diphenylphosphite	18.6	290	2.00	439	23,500	

The results demonstrate that the various catalyst component A's that were active in propylene polymerization are also active in ethylene polymerization.

CLAIMS

1. An olefin polymerization catalyst comprising the product which forms on mixing:

(A) a catalyst component A formed by milling

(1) magnesium halide or manganous halide with

5

(2) at least one catalyst adjuvant

to form a milled composite wherein the molar ratio of (1) to (2) is in the range from 4:1 to 100:1; and then treating the composite thus obtained from (1) and (2) with (3) a tetravalent titanium halide for a period of time sufficient to incorporate tetravalent titanium halide on at least a portion of the surface of said milled composite; and

10

(B) a cocatalyst component B comprising at least one of a trihydrocarbyl aluminum compound and an organoaluminum monohalide of the formula $(R')_2AlX$ in which R' is an alkyl group having 1-20 carbon atoms and X is bromine, chlorine or iodine, wherein the molar ratio of component B to titanium compound is in the range from 0.5:1 to 2000:1 and the amount of titanium present in the finished catalyst is in the range from 0.1 to 10 weight percent based on the dry composite,

15

wherein said adjuvant A(2) is an aromatic organophosphorus compound selected from

(a) aromatic organo phosphites of the formula $\begin{array}{c} R^2 \\ R^2 - O - P - H \\ R^2 - O - \end{array}$

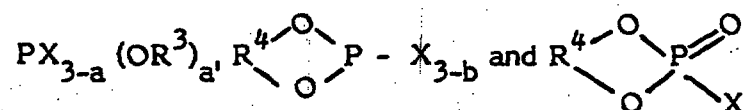
wherein each R^2 group is an aryl, aralkyl, alkaryl or haloaryl group having from 6 to 20 carbon atoms,

(b) triaryl phosphine oxides of the formula $R^{10} - P \begin{array}{c} R^9 \\ R^{11} \end{array} = O$

wherein R^9 , R^{10} and R^{11} are each aromatic hydrocarbyl groups containing up to 20 carbon atoms,

(c) triarylphosphites having from 6 to 24 carbon atoms in each aryl group, and

(d) halogen-containing aromatic organo phosphorus compounds of the formulae



wherein R^3 is an aryl group of 6-20 carbon atoms, R^4 is an arylene group of 6-20 carbon atoms, X is a halogen, a is 1 or 2, and b is 0 or 2.

2. A catalyst according to claim 1 which additionally contains an aromatic ester as part of cocatalyst component B.

3. A catalyst according to claim 1 wherein B comprises a trihydrocarbyl ^{aluminium} compound and additionally contains an aromatic ester such that the molar ratio of trihydrocarbyl ^{aluminium} compound to aromatic ester is from 1:1 to 8:1.

4. A catalyst according to claim 1 wherein the halide (1) is $MgCl_2$ and the titanium halide (3) is $TiCl_4$.



5. A catalyst according to claim 4 wherein B is triethylaluminum and the catalyst additionally contains ethyl anisate.

6. A catalyst according to claim 5 wherein the catalyst adjuvant is triphenyl phosphite.

5 7. A catalyst according to any one of claims 1 to 5 wherein the catalyst adjuvant is selected from diphenyl phosphite, triphenylphosphine oxide, catechylphosphotrichloride, diphenylphosphorochloridate, phenylphosphorodichloridite and o-phenylenephosphorochloridate.

8. A catalyst according to any one of claims 1 to 7 further including
10 a solid particulate material which is inert to the catalyst components.

9. A catalyst according to claim 8 wherein said solid particulate material is selected from silica, alumina, calcium carbonate, polyvinyltoluene, polycarbonate, polyethylene, polypropylene, polystyrene, polymethylmethacrylate, and mixtures thereof.

15 10. A catalyst according to claim 9 wherein said solid particulate material was milled with the halide (1) and adjuvant (2).

11. A catalyst according to any one of claims 1 to 10 wherein the catalyst composite obtained after treating the product of halide (1) and adjuvant (2) with titanium halide (3) was washed with an inert solvent to
20 remove excess titanium tetrahalide and the resulting composite was dried prior to combining with cocatalyst component B.

12. A process comprising polymerizing an alpha-olefin employing a catalyst according to any one of claims 1 to 11.

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13. A process according to claim 12 wherein the alpha-olefin is propylene, the halide (1) is $MgCl_2$, the titanium halide (3) is $TiCl_4$, and the cocatalyst component B is triethylaluminum, the cocatalyst additionally containing an aromatic ester.

5 14. A process according to claim 12 wherein the alpha-olefin is ethylene, the halide (1) is $MgCl_2$, the titanium halide (3) is $TiCl_4$, and the catalyst component B is triethylaluminum,

15. A process according to claim 12 wherein the alpha-olefin is propylene, the halide (1) is $MgCl_2$, the adjuvant (2) is triphenyl phosphite,
10 the titanium halide (3) is $TiCl_4$, and the cocatalyst component B is triethylaluminum, the cocatalyst additionally containing ethyl anisate.

16. An alpha-olefin polymer obtained by a process according to any one of claims 12-15.

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15

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