

AMENDED



(a) Convention

AUSTRALIA

Patents Act

6

(b) Delete one

APPLICATION FOR A (b) STANDARD/~~PETTY~~ PATENT

(c) Insert FULL name(s) of applicant(s)

~~+/~~We (c) Rexene Products Company

603111

(d) Insert FULL address(es) of applicant(s)

of (d) 2400 South Grandview,
Odessa,
Texas 79766,
United States of America,

(e) Delete one

hereby apply for the grant of a (e) Standard/~~Petty~~ Patent for an invention entitled

(f) Insert TITLE of invention

(f) Novel Propylene Polymerization Process

(g) Insert "complete" or "provisional" or "petty patent"

which is described in the accompanying (g) complete specification.

(Note: The following applies only to Convention applications)

Details of basic application(s)

(h) Insert number, country and filing date for the/or each basic application

	Application No.	Country	Filing Date
(h)	880,456	United States of America	30 June 1986

DECLARATION AND AMENDMENTS

DECLARED 14-8-90

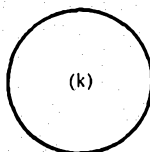
Address for Service:

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia 3000

(i) Insert date of signing

Dated (i) 2 May, 1989.

(j) Signature of applicant(s)
(For body corporate see headnote*)



(k) Corporate seal if any

(j) PHILLIPS ORMONDE & FITZPATRICK
ATTORNEYS FOR:
REXENE PRODUCTS COMPANY

Note: No legalization or other witness required

David B. Fitzpatrick

PHILLIPS ORMONDE AND FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne, Australia

AUSTRALIA

Patents Act

DECLARATION FOR A PATENT APPLICATION

INSTRUCTIONS

(a) Insert "Convention" if applicable

(b) Insert FULL name(s) of applicant(s)

(c) Insert "of addition" if applicable

(d) Insert TITLE of invention

(e) Insert FULL name(s) AND address(es) of declarant(s) (See headnote*)

(f) Insert FULL name(s) AND address(es) of actual inventor(s)

(g) Recite how applicant(s) derive(s) title from actual inventor(s) (See headnote**)

(h) Insert country, filing date, and basic applicant(s) for the/or EACH basic application

(k) Insert PLACE of signing

(l) Insert DATE of signing

(m) Signature(s) of declarant(s)

Note: No legalization or other witness required

In support of the (a) convention application made by

(b) EL PASO PRODUCTS COMPANY

(hereinafter called "applicant(s)" for a patent (c) invention entitled (d)

for an

NOVEL PROPYLENE POLYMERIZATION PROCESS

I/We (e) Fred S. Valles, Vice President and Assistant Secretary
 El Paso Products Company
 2400 South Grandview Avenue
 Odessa, Texas 79766, United States of America

do solemnly and sincerely declare as follows:

~~1. I am/We are the applicant(s).~~

(or, in the case of an application by a body corporate)

1. I am/We are authorized to make this declaration on behalf of the applicant(s).

~~2. I am/We are the actual inventor(s) of the invention.~~

(or, where the applicant(s) is/are not the actual inventor(s))

2. (f) George Cyrus Allen Brian Jay Pellon Michael Peyton Hughes
 16 Tanglewood 3942 Lyndale Drive 2800 Teakwood
 Odessa, Texas 79761 Odessa, Texas 79762 Odessa, Texas 79761
 (all of the United States of America, respectively)

is/are the actual inventor(s) of the invention and the facts upon which the applicant(s) is/are entitled to make the application are as follows:

(g) Applicant is the Assignee of the actual inventors.

(Note: Paragraphs 3 and 4 apply only to Convention applications)

3. The basic application(s) for patent or similar protection on which the application is based is/are identified by country, filing date, and basic applicant(s) as follows:

(h) USSN 880,456 June 30, 1986 George Cyrus Allen
 Brian Jay Pellon
 Michael Peyton Hughes

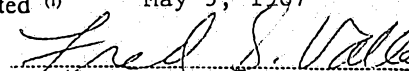
in the United States of America.

4. The basic application(s) referred to in paragraph 3 hereof was/were the first application(s) made in a Convention country in respect of the invention the subject of the application.

Declared at (k) Odessa, Texas

Dated (l) May 5, 1987

(m)



Fred S. Valles
 Vice President & Assistant Secretary

To: The Commissioner of Patents

P18/7/81

PHILLIPS ORMONDE & FITZPATRICK
 Patent and Trade Mark Attorneys
 367 Collins Street
 Melbourne, Australia

(12) PATENT ABRIDGMENT (11) Document No. AU-B-74665/87
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 603111

(54) Title
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(71) Applicant(s)
REXENE PRODUCTS COMPANY

(72) Inventor(s)
GEORGE CYRUS ALLEN; BRIAN JAY PELLON; MICHAEL PEYTON HUGHES

(74) Attorney or Agent
PHILLIPS ORMONDE & FITZPATRICK, 367 Collins Street, MELBOURNE VIC 3000

(56) Prior Art Documents
AU 74167/87 C08F 210/06; 210/16

(57) Claim

1. A process for the production of substantially amorphous interpolymers which comprise polymerizing from ~~about~~ 65 to ~~about~~ 90 wt % propylene, from ~~about~~ 10 to ~~about~~ 30 wt % ethylene and from ~~about~~ 0 to ~~about~~ 15 wt % of a C₄ - C₈ alpha-olefin at a temperature between ~~about~~ 130°F and ~~about~~ 175°F and at a reactor pressure sufficient to maintain propylene in the liquid phase, in the presence of from ~~about~~ 0.7 to ~~about~~ 3.0 mol % hydrogen based on the monomer feed to the process and employing as catalyst a composition comprised of:

(a) a solid catalyst component produced by the method comprising (i) co-comminuting magnesium halide support base and aluminum trihalide in the absence of added electron donor and (ii) then co-comminuting the product of step (i) with titanium tetrahalide in the absence of added electron donor; and

(b) a co-catalyst component comprised of a mixture of from ~~about~~ 15 to ~~about~~ 90 mol % of trialkylaluminum having from 1 to 9 carbon atoms in each alkyl group

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(11) AU-B-74665/87
(10) 603111

-2-

and ~~about~~ 85 to ~~about~~ 10 mol % of an alkylaluminum halide having at least one halide group per molecule in a sufficient quantity to provide an Al/Ti ratio in the range from ~~about~~ 50:1 to ~~about~~ 600:1; and recovering a substantially amorphous, random interpolymer having a tacticity index m/r ranging between ~~about~~ 3 and ~~about~~ 5 as determined by ¹³C NMR spectra.

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603111

COMPLETE SPECIFICATION
(ORIGINAL)

Application Number:
Lodged:

Class

Int. Class

Complete Specification Lodged:
Accepted:
Published:

Priority

Related Art:

This document contains the
amendments made under
Section 49 and is correct for
printing.

APPLICANT'S REFERENCE: EP-4076

Name(s) of Applicant(s):

Rexene Products Company
~~El Paso Products Company~~

Address(es) of Applicant(s):

2400 South Grandview Avenue,
Odessa,
Texas,
UNITED STATES OF AMERICA.

Address for Service is:



PHILLIPS ORMONDE & FITZPATRICK
Patent and Trade Mark Attorneys
367 Collins Street
Melbourne 3000 AUSTRALIA

Complete Specification for the invention entitled:

NOVEL PROPYLENE POLYMERIZATION PROCESS

Our Ref : 57497
POF Code: 734/734

The following statement is a full description of this invention, including
the best method of performing it known to applicant(s):

NOVEL PROPYLENE POLYMERIZATION PROCESS

This application is related to copending application ~~S.N. 61-00~~ AU 74167/87 1986, which pertains to the novel polymer obtained by the process of this invention.

BACKGROUND OF THE INVENTION

10 In the manufacture of propylene homopolymers and copolymers, conventional polymerization techniques using unsupported catalyst result in the simultaneous production of substantial quantities of atactic polymer in addition to the desired product of high crystallinity and isotacticity. Various methods have been employed for the purification and separation of these two polymers. The by-product, i.e. the atactic polymer of low crystallinity is being utilized commercially as a component in various adhesive compositions, roofing materials, caulking compounds, etc.

20 Recently, developments have been made of new catalysts which are highly active and more stereospecific than the afore-mentioned conventional catalysts. The proportions of atactic polymer in the polymers produced employing these catalysts are substantially reduced and therefore the polymer product generally does not require any purification for removal of the atactic or low crystalline polymer. Because of the rapid adaptation of existing polymer facilities to the use of these new catalysts, there has been generated a serious shortage of low-crystalline, atactic polymers.

It is therefore an object of the present invention to provide novel process for the production of substantially amorphous polymers of propylene and ethylene.

30 It is another object of the present invention to provide a process for the production of a novel amorphous polymer of propylene and ethylene and optionally a third alpha-olefin comonomer having improved physical properties.

THE FIGURES

40 Figures 1A and 1B are comparative hot stage micrographs of two different polymers and Figures 2A and 2B are films of the same samples exposed to wide angle x-ray diffraction.

THE INVENTION

In accordance with the present invention there is



provided a process for the production of substantially amorphous interpolymers which comprises polymerizing from about 65 to about 90 wt.% propylene, from about 10 to about 30 wt.% ethylene and from about 0 to about 15 wt.% of a C₄ - C₈ alpha-olefin at a temperature between about 130 and about 175°F and a reactor pressure sufficient to maintain propylene in the liquid phase, in the presence of from about 0.7 mol % to about 3.0 mol% hydrogen based on the monomer feed to the process and employing as catalyst a composition comprised of:

- (a) a solid catalyst component produced by the method comprising (i) co-comminuting magnesium halide support base and aluminum trihalide in the absence of added electron donor and (ii) then co-comminuting the product of step (i) with titanium tetrahalide in the absence of added electron donor; and
- (b) a co-catalyst component comprises of a mixture of from about 15 to about 90 mol % of trialkylaluminum having from 1 to 9 carbon atoms in each alkyl group and about 85 to about 10 mol % of an alkyl-aluminum halide having at least one halide group per molecule in a sufficient quantity to provide an Al/Ti ratio in the range from about 50:1 to about 600:1;

and recovering a substantially amorphous, random interpolymer having a tacticity index m/r ranging between about 3 and about 5 as determined by ¹³C NMR spectra. In the absence of the third C₄ - C₈ alpha-olefin comonomer, the m/r ratio will range between about 3 and about 4. When a third monomer is used the preferred amount is between about 5 and about 15 wt.% based on the total polymer weight. Preferably, the halides are chloride, the alkyls are ethyl groups and the alkylaluminum halide contains one halide group. The invention will be described hereinafter in connection with the preferred embodiments of the catalyst system.

Although the polymerization can be carried out in a batch reactor, it is preferred to utilize a continuous process to achieve the most random incorporation of the comonomer(s). Usually, pressures in the range between about 400 psig and about 550 psig are suitable for maintaining propylene in

liquid phase, the preferred temperature is between about 150°F and about 160°F.

The hydrogen is added to the polymerization reactor for control of polymer molecular weight and other properties at concentrations generally about 7 to 10 times the amount conventionally used in the manufacture of isotactic polymer. Moreover, as the ethylene content of the interpolmer is increased it is necessary to increase the hydrogen concentration in the reactor to maintain a constant melt viscosity. As an example, for a 100% increase in ethylene content about a 50 to 150% increase in hydrogen is required. The concentration of hydrogen in the total feed to the reaction zone preferably ranges between about 1.2 and about 2.5 mol %.

The solid, supported catalyst component should have a molar ratio of magnesium chloride to aluminum ^{trichloride} ~~chloride~~ of about 8:0.5 - 3.0 and preferably about 8:1.0 - 1.5.

The molar ratio of magnesium chloride to titanium tetrachloride is between about 8:1.0 - 1.0 and preferably about 8:0.4 - 0.6. A critical feature of the solid supported catalyst component is that no electron donor compounds should be used in any of the catalyst manufacturing steps. Also, the polymerization process using the catalyst should be carried out in the absence of added electron donors.

Any of the general methods described in U.S. Patents No. 4,347,159 and 4,555,496 (hereby incorporated by reference in this application) can be used in preparing the solid supported catalyst component except that these methods must be modified to exclude the use of electron donor compounds.

Briefly, the modified method involves co-comminuting magnesium chloride and aluminum trichloride in the absence of an electron donor and then co-comminuting the catalyst support so formed with titanium tetrachloride, also in the absence of an electron donor.

The solid catalyst component is used in conjunction with an organoaluminum co-catalyst, which, as stated above, is a mixture of triethylaluminum and diethylaluminum chloride, the triethylaluminum content ranging between about 15 and about 90 mol percent in the total organoaluminum component.



At lower than 15% triethylaluminum concentrations, the polymer productivity is drastically reduced and diethylaluminum chloride alone fails completely to promote polymerization. At higher than 90 mol % triethylaluminum some of the physical properties of this polymer are affected in an undesirable manner. The use of diethylaluminum chloride is not for the purpose of promoting polymerization but very importantly, to impart to the catalyst system the ability to produce polymer with desirable properties. The preferred co-catalyst is a mixture containing from about 40 to 60 mol % triethylaluminum. The molar ratio of total organoaluminum co-catalyst to titanium-containing catalyst component, i.e. Al/Ti ratio should range between about 50:1 and about 600:1, preferably between about 90:1 and about 300:1.

The polymerization is carried out in a stirred reactor at average residence times between about 1 hour and about 3 hours. Sufficient catalyst quantities are fed to the reactor to result in a polymer content in the reactor slurry of from about 30 wt % to about 60 wt %. The reactor effluent is withdrawn from the reactor, and unreacted monomer and hydrogen is flashed from the product polymer.

The specific catalyst used in the process of this invention has the ability to produce propylene units in the polymer with little or no control of the stereochemistry, and also to incorporate ethylene as randomly as possible to provide maximum disorder in the polymer chain.

The products of the process of this invention have a tacticity index m/r between about 3 and 5. This is determined directly by ¹³C Nuclear Magnetic Resonance (NMR). the "m" and "r" describe the stereochemistries of pairs of contiguous propylene groups bonded to one or more ethylene groups, "m" referring to meso and "r" to racemic. An m/r ratio of 1.0 describes a syndiotactic polymer and an m/r ratio of 2.0 a truly atactic material. An isotactic material theroretically will have a ratio approaching infinity and many by-product atactic polymers have sufficient isotactic content to result in ratios of 50 and above. It has been found that the m/r ratio substantially agrees with the number average sequence length n of like groups i.e. meso and racemic groups in case

of propylene homopolymer produced under the same conditions as the random copolymer, except for the absence of ethylene in the feed. Thus, it was established that the tacticity is independent of comonomer content in the polymer. Also, the comonomer such as the ethylene is distributed throughout the polymer molecule in the most random fashion. The method used in calculating n for homopolymer is disclosed in J.C. C. Randall, J. POLYM. SCI., POLYM. PHYS. ED., 14, 2083 (1976). The tacticity index m/r is obtained by inverting the r'/m' ratio calculated according to the method devised by H. N. Cheng, MACROMOLECULES, 17, 1950 (1984).

The interpolymers are unique in that although they exhibit a birefringent granular spherulitic structure when examined by hot stage microscopy, they are substantially amorphous. Usually, truly amorphous materials will show no structure by this method. The formation of these granules upon cooling implies that there is enough tacticity for short portions of the chain, i.e. ordered arrays of monomer without long range order, which would tend to form crystallites. The average length of the granules range between about 15 and about 50 microns, although occasionally larger grain sizes might be obtained. The hot state microscopy method is described in "The Light Microscopy of Synthetic Polymers" D.C. Helmsley in Oxford University Press, Oxford, England 1984. The determinations are made by heating the samples on glass slides in a hot stage to 170°C and then slowly cooling them by turning off the heaters, while viewing the samples through a crossed polarizer. Photomicrographs (400X) are made of the cooled samples, and measurements are made of the largest dimension (=the length) of the granules. Figure 1A shows a hot stage photomicrograph of a typical interpolymers of this invention (Example 3 of Table 1), Figure 1B shows that of commercially available product (Commercial Sample C of Table 2) believed to be a purified atactic by-product polymer.

The interpolymers exhibit no significant crystallinity under wide angle x-ray diffraction (X-ray Diffraction Methods In Polymer Science" L. E. Alexander, Krieger Publishing Company, Huntington, New York, 1979). In these tests the samples are placed between two thin films of

Mylar^R and placed at the exit collimator of the x-ray tube. A beam stop is used to block out the primary beam and flat films record the scattered radiation with a sample-to-film distance of 30mm. The presence of no more than 2 discrete concentric rings superimposed on the diffuse halos on the exposed film indicates the presence of no significant polymer crystallinity.

Figure 2A shows an exposed film using the same interpolymer as in Figure 1A, while Figure 2B is an exposed film of the same samples as of Figure 1B. As seen in Figure 2A, where are no rings present indicating an amorphous nature of the polymer sample, while in Figure 2B there are 4 clearly defined rings, which indicate a high degree of crystalline der of the sample.

The novel polymer has a very low heat of fusion, typically less than about 0.6 cal/g, as determined by Differential Scanning Calorimetry techniques (DSC), a further indication of the amorphous nature of the polymer and the lack of significant crystallinity in the polymer structure.

Various additives can be incorporated into the polymer, such as antioxidants, U.V. stabilizers, pigments, etcetera.

The polymer products of the process of this invention have excellent properties making them useful in a variety of applications, such as for adhesives, caulking and sealing compounds, roofing compositions and others. By varying the comonomer content in the polymer and hydrogen addition to the reactor, it is possible to tailor the properties for any desired application. The important product properties include melt viscosity, ring and ball softening point, needle penetration and open time.

The melt viscosity of 375°F is determined by ASTM test method D-3236 using a Brookfield RVT Viscometer and a #27 spindle. Hydrogen is used to control molecular weight and thus melt viscosity. It has been found that at increased ethylene content more hydrogen is required to maintain a certain viscosity level. For hot melt adhesives the desired viscosity range is between about 1000 and about 5000 cps at 375°F, while for other applications such as bitumen-modified

product, the polymer component should have a viscosity above 5000 cps, preferably in the range between about 10,000 and about 25,000 cps.

The ring and ball softening point determinations are carried out using ASTM E-28 test method. The variables affecting the softening point are ethylene content of the polymer and the triethylaluminum concentration in the organoaluminum co-catalyst used in the polymerization process. A decrease in the ethylene content as well as in diethylaluminum chloride concentration in the co-catalyst both cause an increase in the ring and ball softening point. The preferred range for this property is between about 235°F and about 270°F for the hot melt adhesive applications.

Needle penetration is another test which measures the softness of the material, in this case by the resistance to penetration according to ASTM test method D-1321. Typically, the penetration values of the interpolymers of this invention range between 25 and about 75 dmm (1 dmm=0.1mm). The same process variables affect this property as in the case of ring and ball softening point.

Perhaps the most important test of a hot melt adhesive is the open time. This test is an indication of the elapsed time available between adhesive application to kraft paper and bonding of a kraft paper laminate. This is a very important property for the user, as he must know how soon after applying the adhesive he must add the second sheet of paper. In this test, an 8 1/2" x 11" sheet of kraft paper, rough side-up is taped to a drawdown plate. A polymer sample is heated to 375°F along with a Bird drawdown applicator.

When at temperature, the applicator is placed at the top of the kraft paper and a small puddle of molten polymer is poured near the edge. The polymer is drawn into a smooth film, and as soon as the bottom of the paper is reached, a stopwatch is started. At 10 second intervals, precut strips of kraft paper (rough side down transverse machine direction) are placed across the film and pressed into place with a rubber roller. After the last strip is applied, and a subsequent waiting period of 5 minutes, the strips are removed in a smooth, brisk motion. The open time is defined as the longest time when 90%

or more of the fiber remains. The open times should preferably range between 10 and 60 seconds.

An additional benefit of the polymers of this invention is that they contain extremely small quantities of catalyst residues because of the very large productivity rates of the specific catalyst used in the polymerization. There is no need to remove these small amounts of catalysts from the polymer.

The following examples illustrate the invention.

10

EXAMPLES 1 - 8

Polymers were prepared in large scale continuous pilot plant operations, wherein monomers, hydrogen and catalyst components were separately and continuously charged to a stirred reactor, the total monomer feed rate corresponding to about a 2 hour residence time in the reactor. The organoaluminum compound of the catalyst system was a heptane solution of an equimolar mixture of triethylaluminum (TEA) and diethylaluminum chloride (DEAC). The solid supported titanium tetrachloride catalyst component had a titanium content of about 2.5 wt.% and was prepared by a modification of the preferred technique disclosed in U.S. Patent No. 4,347,158 i.e., modified only in that all process steps were carried out in the absence of any electron donor compounds. The solid catalyst component was pumped into the reactor as a 10 wt.% mixture in a blend of petrolatum and mineral oil in a 50/50 weight ratio. The two catalyst components were added at rates directly proportioned to the polymer production rates and in the amounts sufficient to maintain the polymer solids concentration in the reactor slurry at values usually in the range between about 40% and about 60%. The catalyst productivity (lb polymer/lb of Ti-catalyst component) was calculated in each case from the polymer slurry withdrawal rate,

9 07 7488

T A B L E 1

EXAMPLE NO.	1	2	3	4	5	6	COMP 7	COMP 8
Reactor Temp. - °F	157	150	154	154	157	142	155	155
Reactor Press. - psig	456	434	466	484	491	495	448	442
Propylene - lbs/hr	111	111	111	111	102	111	112	124
Ethylene - lbs/hr	8.8	9.0	12.0	12.0	8.5	12.9	5.0	---
Hydrogen - lbs/hr	0.14	0.05	0.06	0.10	0.06	0.14	0.10	0.07
Al/Ti mol ratio	311	289	301	299	263	291	299	533
Reactor Solids - wt %	60.5	47.7	51	51	32	38	61	59
Productivity - lbs/lb Catalyst	55,420	34,390	33,520	35,500	23,950	30,260	37,440	20,680
Ethylene Content - wt %	12.2	13.5	14.3	15.5	17.5	25.7	4.0	0
m.r Ratio (or n)	3.1	3.3	3.8	3.7	3.5	3.5	3.2	3.3
Average Granule Length - Microns	15	20	12	18	25	15	38	50
No. of Rings (Wide angle X-ray)	0	2	0	2	0	0	1	4
ΔH_F - cal/g (DSC)	0.50	0.50	0.27	0.33	0.16	0.00	1.79	4.37
Melt Viscosity @ 375°F - cps	3,000	15,000	7,750	3,780	9,210	7,900	2,100	2,800
Open Time - secs	10	20	20	30	20	> 60	< 10	0
Ring & Ball Softening Point - °F	266	257	252	251	253	237	279	304
Needle Penetration - 0.1 mm	37	28	43	45	41	71	17	8

0 0 0 7 7 4 8 8 8

T A B L E 2

PRODUCT PROPERTY	Ethylene wt%	m/r or $\bar{n}$	Granule Length	No of Rings X-ray	ΔH_f - cal/g	Melt Visc. @375°F cps	Open Time Secs	Soft Pt. °F	Needle Pen 0.1 mm
Example 1	12.2	3.1	15	0	0.50	3,000	10	266	37
2	13.5	3.3	20	2	0.50	15,000	20	257	28
3	14.3	3.8	12	0	0.27	7,750	20	252	43
4	15.5	3.7	18	2	0.33	3,780	30	251	45
5	17.5	3.7	25	0	0.16	9,210	20	253	41
6	25.7	3.5	15	0	0.00	7,900	>60	237	71
Comp. 7	4.0	3.2	38	1	1.79	2,100	<10	279	17
Comp. 8	0	3.3	50	4	4.37	2,800	0	304	8
Commercial Sample A*	5.0	---	0	4	0.10	22,000	60	176	13
B	8.6	2.1	33	2	0.10	11,000	40	284	29
C	3	2.1	45	4	1.04	1,300	>60	287	43
D	8.0	1.6	0	5	0.00	250	---	---	---
E	22.1	49.0	5	2	0.93	>500,000	---	---	---
F	17.1	99.0	18	4	0.75	56,000	---	---	---
G	0	2.7	90	2	3.81	2,000	5	314	10
H	0	2.9	130	2	---	2,400	0	295	12
I	0	2.1	98	3	0.44	500	0	---	---
J	0	2.0	18	4	0.00	100	---	---	---
K	0	2.1	92	2	1.38	3,200	---	---	---
L	0	2.5	148	3	1.12	900	---	---	---
M	0	2.7	170	7	4.21	4,300	---	---	---
N	0	2.5	75	7	0.50	250	---	---	---
O	0	1.9	40	4	0.25	350	---	---	---

* Terpolymer ethylene/propylene/butene - 1

solids content in the slurry and the titanium catalyst addition rate. The product polymer was separated from unreacted monomer, stabilized with Isonox^R 129 and then subjected to testing. Table 1 summarizes the pertinent operating conditions and the results of physical testing. The product characteristics of Example 1-6 all are the results of operating the process within the claimed limits of this invention, while those of Comparative Examples 7 and 8 reflect the insufficient amount of ethylene in the process i.e. high softening points, low needle penetration, high heat of fusion.

Table 2 lists the physical properties of Examples 1-8 and also of fifteen atactic polymers (Commercial Examples (A-O) obtained from various manufacturers in the United States, Europe and Asia. Commercial Sample A is a terpolymer of ethylene, propylene and a major proportion of butene-1, while the remaining samples are either propylene homopolymers or ethylene-propylene copolymers. Samples B, C, G and H are believed to have been produced in processes under conditions deliberately selected to yield relatively large concentrations of atactic polymer in the total polymer product. It is further believed that the atactic portions have subsequently been removed from the isotactic by-product by solvent treatment. Samples D-F and I-O are believed to be atactic polypropylene by-products. None of these commercial samples have the physical properties required of the polymer products of this invention.

EXAMPLES 9 and 10

Both experiments were performed in a 1-liter, jacketed autoclave equipped with a magnetically coupled stirrer. The temperature of the autoclave was controlled by the use of a mixture of equal weights of glycol and water as the heat transfer fluid flowing through the jacket. The temperature of this fluid was controlled by a microprocessor whose temperature indicator was an iron/constantin thermocouple inside the autoclave. With this system, set point temperature could be maintained $\pm 0.2^{\circ}\text{C}$. All monomers were polymerization grade, 99.9% pure, and were also passed through molecular sieve beds, as well as beds of copper catalyst for oxygen removal, prior to use. Hydrogen was

ultra-high purity, 99.99% and used as is. Aluminum alkyl solutions were purchased as 25% W/W in normal heptane and were used as is. One wt % catalyst slurries were prepared in degassed mineral oil using catalysts of the same type as that of in Examples 1-8. Prior to each use, the autoclaves were heated to 90°C with a slow nitrogen purge for 30 minutes. After cooling to 30°C, the nitrogen atmosphere was replaced with a propylene purge. Alkyl solutions and catalyst slurries were prepared in septum vials in dry boxes (nitrogen atmosphere), purged with nitrogen upon removal, and pressurized slightly to avoid contamination. Alkyl solutions and catalyst slurries were introduced into the reactors using hypodermic syringes, previously cleaned with de-ionized water, dried at 120°C, and purged with nitrogen prior to use. In Example 9, 0.34 ml TEA, 0.34 ml DEAC (Al - 1.77×10^{-3} mole/l), and 0.58 ml of 1% W/W catalyst slurry (2.5% W/W titanium content) were added to the autoclave. Hydrogen was added to equal a partial pressure of 70 psig. 0.6 liters of propylene was introduced using a sight guage and nitrogen pressure. The reactor content was heated to 60°C and maintained while stirring at 500 rpm. As soon as the temperature stabilized at 60°C (5-10 minutes), ethylene was added to the reactor to maintain a constant overpressure of 50 psig greater than the reactor pressure. After 1 hour, the temperature was lowered and excess propylene vented. The ethylene-propylene copolymer was dried under vacuum at 40°C overnight. Example 10 was carried under the conditions of the previous example except that 0.1 liter of butene-1 and 0.5 liter of propylene was charged to the autoclave instead of the 0.6 liters of propylene of Example 9. The resulting terpolymer was dried as before.

Table 3 lists the pertinent physical properties of the products of Examples 9 and 10.

TABLE 3

EXAMPLE NO	9	10
Ethylene - wt %	21.1	23.3
Butylene - wt %	----	9.2
m/r	3.3	4.8
Average Granule Length-microns	22	20

No. of Rings - X-ray	0	0
H _F -cal/g	0.03	0.00
Melt Viscosity @ 375°F cps	2810	3250
Open Time - secs	60	60
Softening Point - °F	260	237
Needle Penetration - 0.1 mm	71	72
Catalyst Efficiency Kg/g	41.2	34.6

COMPARATIVE EXAMPLES 11 and 12

10 These examples were carried out using the procedure described in connection with Example 9 except for the alkyl co-catalyst addition. In Example 11 0.68 ml TEA was used exclusively while in Example 12 the same amount of DEAC only was added. Table 4 lists the pertinent data of these comparative examples.

TABLE 4

EXAMPLE NO.	COMP. 11	COMP. 12
Co-Catalyst		
TEA	100%	----
DEAC	----	100%
Catalyst Efficiency Kg/g	40.0	0.0
Ethylene - wt %	18.1	----
m/r	4.2	----
Melt Viscosity @ 375° cps	3700	----
Open Time - secs	60	----
Softening Point - °F	275	----
Needle Penetration - 0.1 mm	43	----

As seen from the above data, the use of 100% TEA instead of a mixture of TEA and DEAC (as in Example 9) resulted in a higher m/r ratio of the polymer product. Also, the softening point and needle penetration values were affected in a detrimental way. The use of 100% DEAC as co-catalyst resulted in no formation of polymer.

It is to be understood that many alterations and modifications can be made to the process of this invention. All such departures are considered within the scope of this invention as defined by the specifications and appended claims.

THE CLAIMS DEFINING THE INVENTION ARE AS FOLLOWS:

1. A process for the production of substantially amorphous interpolymers which comprise polymerizing from ~~about~~ 65 to ~~about~~ 90 wt % propylene, from ~~about~~ 10 to ~~about~~ 30 wt % ethylene and from ~~about~~ 0 to ~~about~~ 15 wt % of a C₄ - C₈ alpha-olefin at a temperature between ~~about~~ 130°F and ~~about~~ 175°F and at a reactor pressure sufficient to maintain propylene in the liquid phase, in the presence of from ~~about~~ 0.7 to ~~about~~ 3.0 mol % hydrogen based on the monomer feed to the process and employing as catalyst a composition comprised of:

- (a) a solid catalyst component produced by the method comprising (i) co-comminuting magnesium halide support base and aluminum trihalide in the absence of added electron donor and (ii) then co-comminuting the product of step (i) with titanium tetrahalide in the absence of added electron donor; and
- (b) a co-catalyst component comprised of a mixture of from ~~about~~ 15 to ~~about~~ 90 mol % of trialkylaluminum having from 1 to 9 carbon atoms in each alkyl group and ~~about~~ 85 to ~~about~~ 10 mol % of an alkylaluminum halide having at least one halide group per molecule in a sufficient quantity to provide an Al/Ti ratio in the range from ~~about~~ 50:1 to ~~about~~ 600:1;

and recovering a substantially amorphous, random interpolymer having a tacticity index m/r ranging between ~~about~~ 3 and ~~about~~ 5 as determined by ¹³C NMR spectra.

2. The process of claim 1 wherein each halide is a chloride, each alkyl is an ethyl group and the alkylaluminum halide is diethylaluminum chloride.

3. The process of claim 2 wherein the polymerization is conducted in the absence of a C₄ - C₈ alpha-olefin and the recovered interpolymer has a tacticity index between about 3 and about 4.

4. The process of claim 2 wherein said pressure is between about 400 psig and about 550 psig and the temperature is between about 150°F and 160°F.

5. The process of claim 2 wherein the molar ratio of magnesium chloride to aluminum ~~chloride~~ ^{tetrachloride} in the solid catalyst



component ranges from about 8:0.5 to about 8:3.0.

6. The process of claim 5 wherein said ratio ranges from about 8:1 to about 8:1.5.

7. The process of claim 2 wherein the molar ratio of magnesium chloride to titanium tetrachloride in the solid catalyst component ranges from about 8:0.4 to about 8:1.

8. The process of claim 7 wherein said molar ratio ranges from about 8:0.4 to about 8:0.6.

10 9. The process of claim 2 wherein the triethylaluminum content of the co-catalyst mixture ranges between about 40 and about 60 mol %.

10. The process of claim 1 wherein the Al/Ti ratio is maintained between about 90:1 and about 300:1.

11. The process of claim 2 wherein the hydrogen is maintained between about 1.2 and about 2.5 mol % based on the total monomer feed to the process.

12. The process of claim 2 carried out under continuous conditions at an average residence time between about 1 hour and about 3 hours.

20 13. The process of claim 2 wherein the solids content of the reactor slurry is maintained between about 30 wt % and about 60 wt %.

14. A process as in claim 2 wherein the hydrogen concentration is increased as the ethylene concentration is increased resulting in a constant viscosity product.

15. A process as in claim 11 wherein the hydrogen concentration is increased as the ethylene concentration is increased resulting in a constant viscosity product.

~~DATED: 24 June 1987~~

PHILLIPS ORMONDE & FITZPATRICK
Attorneys for:

~~EL PASO PRODUCTS COMPANY~~



16. A process as claimed in Claim 1 substantially as hereinbefore described with reference to any one of the examples.

DATED: 2 AUGUST 1990

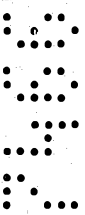
PHILLIPS ORMONDE & FITZPATRICK

Attorneys for:

~~EL PASO PRODUCTS COMPANY~~

Rexene Products Company

David B Fitzpatrick



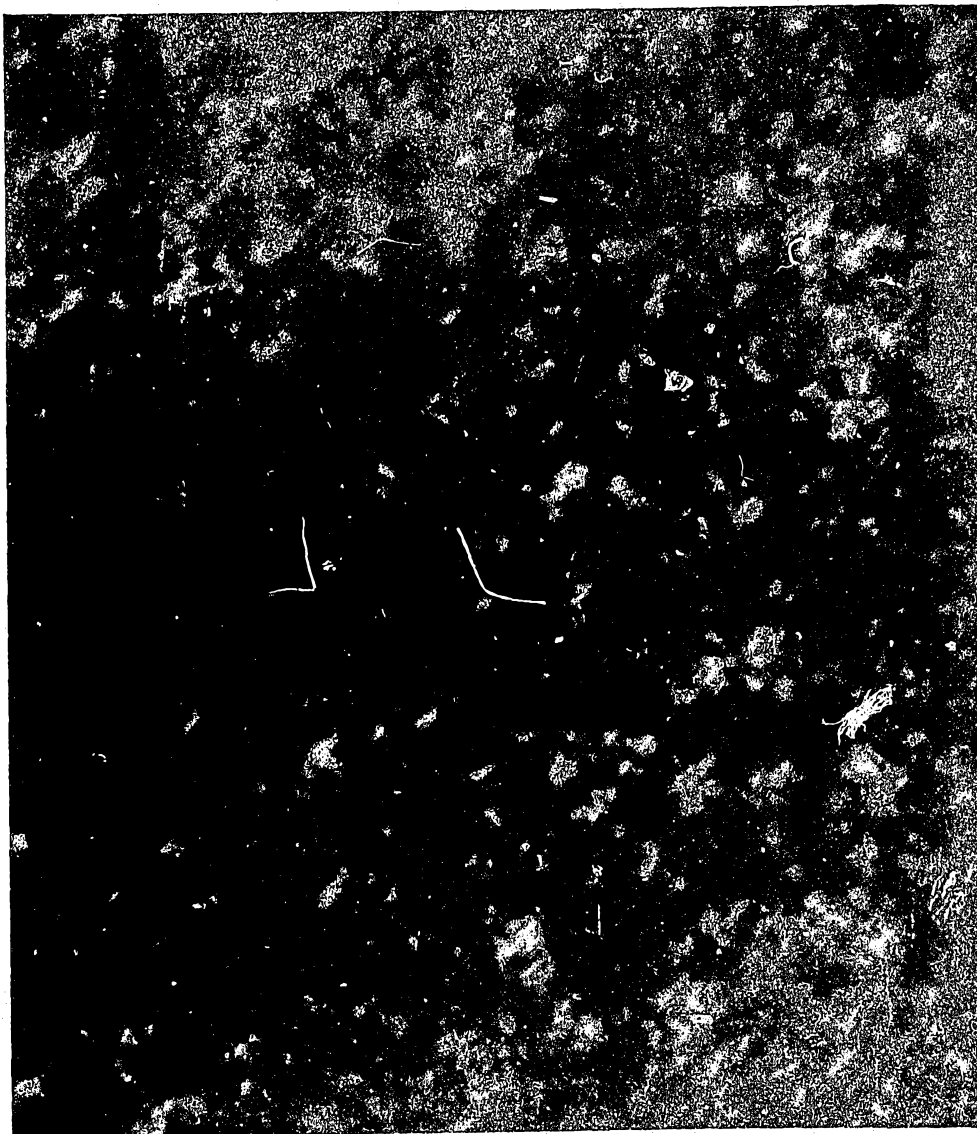


FIG.1A



FIG.1B

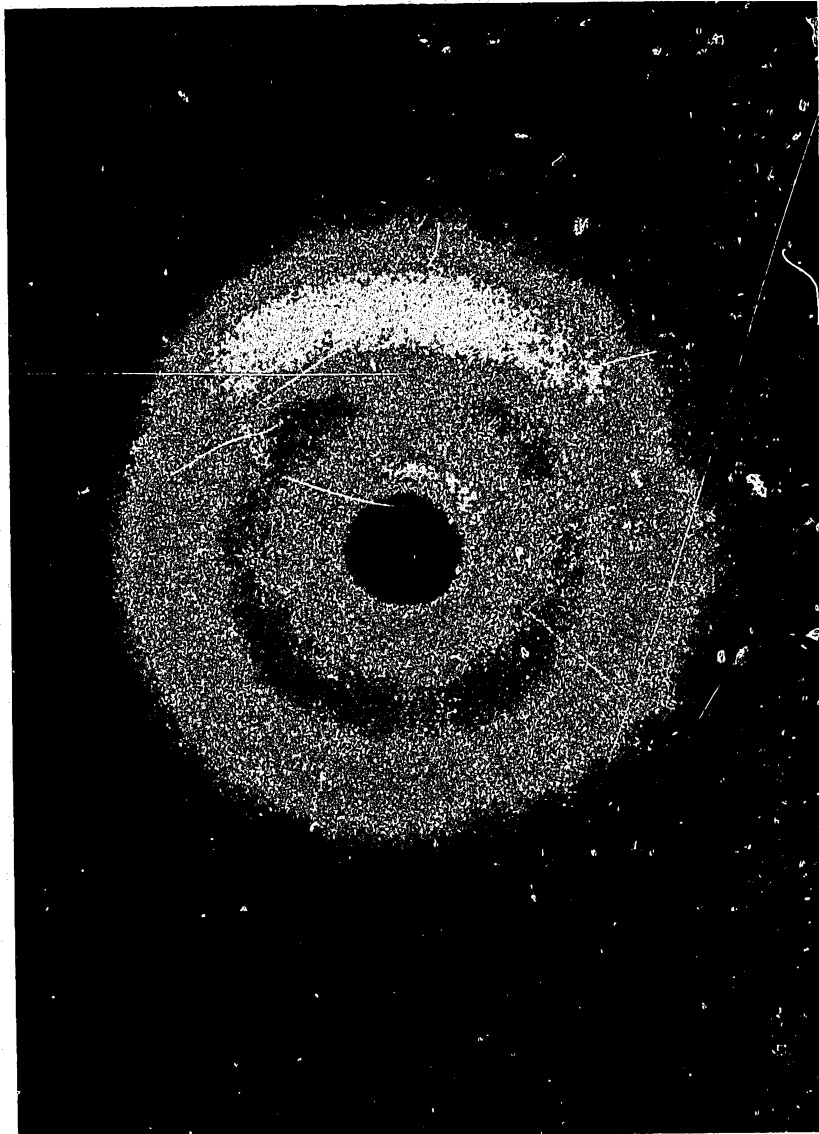


FIG.2A



FIG. 2B