



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

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<b>(54) Title:</b> CATALYSTS FOR THE PREPARATION OF AMORPHOUS COPOLYMERS OF PROPYLENE AND OLEFINS		
<b>(57) Abstract</b>  Disclosed is a catalyst mixture comprising TiCl <sub>3</sub> , TiCl <sub>4</sub> , and an aluminum-alkyl cocatalyst. The catalyst mixture is particularly advantageous for the synthesis of pressure-sensitive amorphous adhesives that are copolymeres of propylene and 1-olefin, such as 1-hexene, in a high temperature solution process.		

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CATALYSTS FOR THE PREPARATION OF  
AMORPHOUS COPOLYMERS OF PROPYLENE AND OLEFINS

Field of Invention

5        This invention relates to a novel titanium-based catalyst mixture for the synthesis of pressure-sensitive adhesives that are amorphous copolymers of propylene and 1-olefins in a high temperature solution process.

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Background of the Invention

      Commerical catalysts based on  $TiCl_3$  or  $TiCl_4$  produce either amorphous polyolefins with good strength and poor tack or produce amorphous polyolefins with good tack and poor strength. Amorphous polyolefins, particularly propylene/hexene copolymers, are generally useful as pressure-sensitive adhesives. Pressure-sensitive adhesives for medical tape applications require a balance of high viscosity, good strength and good tack.

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      U.S. Patent 3,954,697 discloses single component, hot-melt, pressure-sensitive adhesives that are propylene copolymers containing 40 to 25 60 mole percent hexene and having a 130°C to 148°C softening point. While the copolymers of this patent are useful, they are limited in their utility to substrates with a higher melting point than the copolymer. Application of amorphous propylene-hexene 30 copolymers disclosed in this patent to substrates such as polyethylene is difficult without melting the substrate which results in undesirable holes and puckers in the substrate.

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The amorphous propylene/hexene copolymers disclosed in the prior art are made by use of single catalysts with an aluminum-alkyl cocatalyst. It has been discovered that a mixture of certain catalysts hereinafter described provide amorphous propylene-hexene copolymers with an unexpected balance of properties ideally suited for use as pressure-sensitive adhesives for medical tape applications.

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#### Summary of the Invention

The present invention is directed to a catalyst mixture comprising:

- 15 (a) About 5 to about 50 weight percent (based on the weight of (a) plus (b)) of a supported catalyst comprising  $TiCl_4$  supported on an inorganic halide salt,
- 20 (b) About 95 to about 50 weight percent (based on the weight of (a) plus (b)) of a preactivated catalyst comprising preactivated  $TiCl_3$ , and
- 25 (c) An aluminum-alkyl cocatalyst at a molar ratio of aluminum-alkyl:Ti-chloride at about 0.25:1 to about 2:1.

The present invention is also directed to a process for preparing an amorphous propylene/higher 1-olefin copolymer comprising contacting propylene and a higher 1-olefin with the above-described catalyst mixture for a sufficient reaction period and under conditions such that the desired copolymer is formed.

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The present invention is further directed to a copolymer that is prepared from the process of the invention. The copolymer of the present invention is a hot-melt, pressure-sensitive adhesive comprising an amorphous propylene/hexene copolymer containing about 40 to about 75 weight percent 1-hexene, said copolymer having a melt viscosity of about 5,000 to about 50,000 centipoises (cp) at 190°C, a softening point of about 90°C to about 125°C, a probe tack of at least about 500 grams, a quick stick of at least 1.5 pounds per inch, and a static shear of at least about 10 hours.

#### Detailed Description of the Invention

The teachings of U.S. Patent 3,954,697 link copolymer composition with its softening point. It is taught that as the weight percent polymerized hexene in the copolymer increases, the softening point decreases. Thus, as in most prior art copolymer systems, the softening point varies with comonomer concentration in the copolymer in a regular manner from the value of the softening point of the homopolymer of one monomer to the value of the homopolymer of the second monomer. In this case the softening point of the amorphous propylene-hexene copolymer ranges from the value for polyhexene (80°C) to the value for polypropylene (151°C).

However, it has been surprisingly discovered in the present invention that at a given hexene incorporation level in the copolymer it is possible to vary the softening point by making an appropriate choice of catalyst mixture and cocatalyst.

In the catalyst mixture of the present invention it is preferred that the weight percent of supported catalyst (a) is about 15 to about 45 (based on the weight of (a) plus (b)), more preferably about 25;

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that the weight percent of preactivated catalyst (b) is about 85 to about 55 (based on the weight of (a) plus (b)), more preferably about 75; and that the molar ratio of aluminum-alkyl:Ti-chloride is about  
5 1:1 to about 1.5:1, more preferably about 1.25:1.

The supported catalyst useful in the present invention preferably comprises  $TiCl_4$  supported on  $MgCl_2$ . The amount of  $TiCl_4$  on the support is preferably about 1 to about 15 weight percent; more  
10 preferably about 1 to about 10 weight percent; and most preferably about 10 weight percent. The supported catalyst can optionally contain up to about 25 weight percent organic esters and ethers. Such organic esters and ethers are typically present in  
15 commercial supported catalyst preparations and can include, for example, anisole, ethyl benzoate, methyl benzoate, and the like. A commercially available supported catalyst suitable for use in the present invention is Lynx 705, available from Catalyst  
20 Resources, Inc., Houston, Texas.

The preactivated catalyst useful in the present invention is preactivated  $TiCl_3$ . The  $TiCl_3$  used to prepare the preactivated  $TiCl_3$  can be any of the commonly available forms of  $TiCl_3$  such as aluminum  
25 reduced and activated  $TiCl_3$  (AA- $TiCl_3$ ), hydrogen reduced and activated  $TiCl_3$ , or chemically reduced  $TiCl_3$ . In the case of AA- $TiCl_3$ , the  $TiCl_3$  is complexed with  $AlCl_3$ . The  $TiCl_3$  can be preactivated by any suitable means known in the  
30 catalyst art. It is preferred to preactivate  $TiCl_3$  by prepolymerizing propylene to about the 10 to 50 percent polypropylene level to obtain a preactivated catalyst comprising about 10 to 50 weight percent polypropylene and about 90 to 50  
35 weight percent  $TiCl_3$ . A preferred weight ratio of  $TiCl_3$  to polypropylene is about 50 to 50. The

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preactivated catalyst prepared from chemically reduced  $\text{TiCl}_3$  may also contain traces of other inorganic substances such as  $\text{AlCl}_3$ . A commercially available preactivated catalyst for use in the present invention is Lynx 900 (prepared from chemically reduced  $\text{TiCl}_3$ ), available from Catalyst Resources, Inc., Houston, Texas.

The aluminum-alkyl cocatalyst useful in the present invention complexes with the Ti-chloride (i.e., both  $\text{TiCl}_3$  and  $\text{TiCl}_4$ ). As used herein "alkyl" refers to  $\text{C}_2$  to  $\text{C}_6$  alkyls. Preferred aluminum-alkyls are triethyl aluminum, tributyl aluminum, and triisobutyl aluminum. The most preferred catalyst is triethyl aluminum.

Although the preferred process of the present invention produces a copolymer of propylene/hexene-1, the process is not so limited and is applicable for production of copolymers of propylene and other higher 1-olefins. Higher 1-olefins suitable for use in the present invention include, for example, heptene-1, octene-1, nonene-1, decene-1, dodecene-1, octadecene-1, and the like.

The process of the present invention can be characterized as a high temperature solution polymerization process.

Preferred conditions for the process of the present invention include a temperature at about  $140^\circ\text{C}$  to about  $200^\circ\text{C}$ , and a pressure of about 400 to about 2000 pounds per square inch gauge (psig); more preferred is a temperature of from about  $150^\circ\text{C}$  to about  $180^\circ\text{C}$  and a pressure of about 1000 to about 1500 psig. The process preferably takes place under an inert atmosphere, such as nitrogen or argon, for a time sufficient to form the desired product, for example, about 1/2 to about 10 hours, with about 2 to

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about 4 hours being preferred. The process generally is preferably carried out with agitation, e.g., stirring.

It is also preferred that a solvent or diluent is used for the process of the present invention, particularly as a diluent for the catalyst mixture. Organic solvents which can be used for the addition of catalyst mixtures and diluent include, for example, aliphatic alkanes or cycloalkanes such as propane, pentane, hexane, heptane, cyclohexane, and the like, or hydrogenated aromatic compounds such as decahydronaphthalene, or aromatic hydrocarbons such as benzene, toluene, xylene, and the like. The nature of the solvent is subject to considerable variation but should be a liquid form at the reaction conditions and essentially inert to the reactants and reaction products. A petroleum fraction of suitable boiling range such as mineral spirits (a sulfuric acid washed paraffinic hydrocarbon boiling at 180°C to 220°C) is a particularly good and preferred solvent or diluent.

The process of the present invention can be performed either continuously or batchwise; preferred is continuously. In a continuous process, generally the catalyst mixture in solvent and monomer mixture are fed into a suitable reactor and polymerization is allowed to occur under polymerization conditions. Preferably, the catalyst mixture is charged into the reactor first. After polymerization it is typically desired to remove unreacted monomer, deactivate the catalyst and further purify the copolymer, for example, by passing through an alumina bed and/or filtration and subsequent solvent removal.

The propylene/hexene-1 copolymer produced by the process of the present invention has a unique balance of adhesive properties. The copolymer contains about



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40 to 75 weight percent hexene-1, preferably 55 to 65 weight percent hexene-1. Hexene content can be determined by either C<sup>13</sup> nuclear magnetic resonance or by Fourier transfer infrared spectroscopy. The copolymer has a melt viscosity of about 5,000 to about 50,000 cp at 190°C, preferably about 15,000 to about 25,000 cp at 190°C.

The melt viscosity of the polymer can be determined by using a Brookfield Thermosel Viscometer according to the methodology described in American Society for Testing and Materials (ASTM) Method D-1824-66.

The softening point of the copolymer of the present invention is between about 90°C and about 125°C, preferably between about 95°C and about 120°C. The softening point can be determined using the Ring and Ball method described in ASTM Method E-28.

The copolymer of the present invention has a probe tack of at least about 500 grams, preferably between about 500 grams and about 650 grams. Probe tack can be measured on a Polyken Probe Tack tester at a dwell time of 2 seconds and a carrier speed of 2 centimeters (cm)/second (sec).

The copolymer of the present invention has a quick stick of at least about 1.5 pounds per inch, preferably about 1.7. Quick stick can be determined by Pressure-Sensitive Tape Council (PSTC) Procedure PSTC-5.

The copolymer of the present invention has a 180° peel adhesion of at least about 2.5 pounds per inch; preferably about 3.0. Peel adhesion can be determined using Procedure PSTC-1.

The copolymer of the present invention has a static shear of at least about 10 hours, preferably about 15 hours. Static shear can be determined using

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Procedure PSTC-7 with 1 kilogram (kg) weight. The time taken for coated tape to completely separate from the test panel is reported as the static shear value.

5 The following examples are to illustrate the invention but should not be interpreted as a limitation thereon. All percentages are by weight unless specified otherwise. For the following examples, the following general conditions were used:

10 A 6.7-gallon stirred loop reactor was fed continuously with the monomer mixture and a catalyst slurry using mineral spirits as diluent. The polymerization was controlled at a pressure of 1,000 psi and a temperature of 150°C to 180°C  
15 depending on the amorphous propylene/hexene (APH) viscosity target. The APH product containing unreacted monomers, catalyst, and some solvent was transferred continuously to a letdown tank where the monomers were flashed overhead. The product was then  
20 subjected to a steam/air catalyst deactivation process in the solvent stripper and finally pumped through an alumina bed. The finished product was characterized by viscosity, ring and ball softening point (RBSP), weight percent hexene by infrared, and  
25 adhesive property determination.

In general the following reaction conditions were maintained.

	Reactor Temp, °C	162
	Reactor Glycol Jacket Temp, °C	154
30	Reactor Pressure, psig	1000
	Stirrer Speed,	750
	Revolutions per Minute (RPM)	
	Propylene Charge,	3.07
	pound (lb)/hour (hr)	
35	Hexene Charge, lb/hr	6.17

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Catalyst Charge, grams (g)/hr	1.2
Residence Time, hr	3.3
Polymer Produced, lb/hr	7.5

Table I shows how the changes in catalyst, catalyst mole ratio, and reaction conditions affect the polymer yield, monomer conversions, and the viscosity, RBSP, and hexene content of the APH product. Table II shows the effect of catalyst and catalyst mole ratio on the adhesive properties of the APH products.

#### Examples 1 through 8 (Comparative)

In Examples 1 through 8 the triethyl aluminum ( $\text{AlEt}_3$ )/Lynx 900 catalyst was evaluated for production of pressure-sensitive APH. The catalyst mole ratio, temperature, and propylene and hexene feeds were varied in an effort to produce a 20,000 cp viscosity APH with a good balance of adhesive properties. This catalyst at a  $\text{AlEt}_3$ /Ti-halide mole ratio of 0.5/1 gave the best results considering polymer yield and APH adhesive properties. Raising the catalyst mole ratio from 0.5/1 to 1/1 increases the polymer yield somewhat but also increases the APH viscosity considerably at a reactor temperature of 162°C. Increasing the reactor temperature from 162°C to 171°C decreased the viscosity from 42,000 cp to the desired 20,000 cp but had a very detrimental effect on polymer yield, decreasing it from 5,758 to 1,400 pounds APH per pound of catalyst. APH produced with  $\text{AlEt}_3$ /Lynx 900 catalyst at a mole ratio of 1/1 had also very poor quick stick, 0.7 to 0.8 pounds per inch. Decreasing the  $\text{AlEt}_3$ /Ti-halide mole ratio from 0.5/1 to 0.25/1 decreased the APH yield from about 4,000 to 2,000 pounds per pound and decreased the viscosity from 20,000 cp to 8,500 cp. To bring the viscosity up into specification range

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the reactor temperature had to be lowered from 161°C to 156°C and the propylene feed had to be raised from 3.1 to 3.4 pounds per hour. These changes resulted in APH having a viscosity of 15,500 cp and a hexene content of 59%. The adhesive properties of this product are inferior to those of the best APH produced with the AlEt<sub>3</sub>/Lynx 900 catalyst at a mole ratio of 0.5/1, especially in probe tack and static shear. Compare Example 4 with Example 8 in Tables I and II.

To meet the specifications of pressure-sensitive adhesives for medical tape applications, products should exhibit a viscosity of about 20,000 cp, a probe tack of 650 to 700 grams, a quick stick of 1.5 to 2.0 pounds per inch, a 180° peel adhesion of 2.5 to 3.0 pounds per inch, and a static shear adhesion of 15 to 20 hours. In an effort to produce such a product propylene and hexene was copolymerized using the AlEt<sub>3</sub>/Lynx 900 catalyst system. The effect of catalyst mole ratio, reactor temperature, and product composition on the polymer yield and APH adhesive properties was studied. The best APH product for the medical tape application contained 62% hexene and was produced at 163°C using the AlEt<sub>3</sub>/Lynx 900 catalyst at a AlEt<sub>3</sub>/TiCl<sub>3</sub> mole ratio of 0.5/1. See Example 4.

#### Example 9 (Comparative)

APH was produced in a batch polymerization process using a 2-liter stainless steel stirred autoclave. The catalyst (0.7 gram) AlEt<sub>3</sub>/Lynx 705 at a AlEt<sub>3</sub>/TiCl<sub>4</sub> mole ratio of 4/1 was charged to a preheated autoclave containing 100 mL mineral spirits, 800 mL hexene, and 500 psi C<sub>3</sub>H<sub>6</sub>. The polymerization was conducted at 140°C, a pressure of 400 psi and a reaction time of 180 minutes. The

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discharged polymer was recovered by vacuum stripping at 230°C for 3 hours. The final product (200 grams) contained 51% hexene, and had a viscosity of 8.125 cp and a RBSP of 98°C. Its adhesive properties showed  
5 good probe tack (780 grams), good 180° peel adhesion (3.0 pounds per inch), fair quick stick (1.3 pounds per inch) and very poor static shear adhesion (1.1 hours).

10 Examples 10 through 18

In Examples 10 through 18 a mixed catalyst consisting of Lynx 900 and Lynx 705 was evaluated for the production of pressure-sensitive APH. The catalyst composition, catalyst mole ratio,  
15 temperature, and propylene and hexene feeds were varied in an effort to optimize the balance of adhesive properties of APH. Best results were obtained with a catalyst consisting of 75% Lynx 900 and 25% Lynx 705 cocatalyzed with AlEt<sub>3</sub> at a  
20 AlEt<sub>3</sub> to Ti-halide mole ratio of 1/1 to 1.25/1. APH containing 59% to 60% hexane and having the desired viscosity of about 20,000 cp and a RBSP of 118°C to 119°C showed a very good balance of adhesive properties. See Examples 12 and 15. The APH  
25 products combined good probe tack (659 to 693 grams), good quick stick (1.5 to 1.7 pounds per inch), and good 180° peel adhesion (2.5 to 2.8 pounds per inch) with good static shear adhesion 19 to 22 hours). They also proved to be nonirritants to the human  
30 skin. This combination of properties makes them particularly well-suited for medical tape application.

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Examples 19 and 20 (Comparative)

In Examples 19 and 20 the  $\text{AlEt}_3/\text{AA-TiCl}_3$  catalyst was evaluated for the production of pressure-sensitive APH. This catalyst system was taught for APH synthesis in U.S. Patent 3,954,697. As can be seen in Table II APH varying from 59% to 64% in hexene content exhibits adhesive properties very much inferior to APH produced with the catalyst of this invention.

TABLE I  
SYNTHESIS OF PRESSURE-SENSITIVE AMORPHOUS PROPYLENE-HEXENE COPOLYMERS

Ex.	Catalyst System	Reactions Conditions			Feeds			Residence Time, Hr	APH Prodn, Lb/Hr	Cat. Yield, Lb/Lb	Conversion		APH Properties				
		Mole Ratio	Temp., °C	Press., PSI	Propylene, Lb/Hr	Hexene, Lb/Hr	Catalyst, G/Hr				Propylene, %	Hexene, %	Viscosity @ 190°C	RBS, %	Hexene, %	WT %	
																C	C
1	AlEt <sub>3</sub>	1/1	162	1,000	3.1	6.1	0.58	3.5	7.1	5,758	88	70	42,000	112	60.0		
LYNX 900																	
2	"	1/1	171	1,000	3.1	10.4	3.48	2.3	9.7	1,400	94	67	23,000	98	69.5		
3	"	1/1	168	1,000	2.7	6.1	2.71	3.3	7.5	1,459	95	77	25,000	111	64.0		
4	"	0.5/1	163	1,000	3.1	6.1	0.91	3.4	7.6	3,767	91	76	20,000	94	62.0		
5	"	0.5/1	162	1,000	3.6	6.1	0.70	3.2	7.8	5,400	88	71	26,500	105	57.0		
6	"	0.5/1	161	1,000	3.8	6.1	0.63	3.1	8.3	3,884	87	76	26,500	108	56.0		
7	"	0.25/1	161	1,000	3.1	6.1	2.02	3.2	7.8	1,480	91	81	8,500	80	64.0		
8	"	0.25/1	156	1,000	3.4	6.1	1.39	3.3	7.1	2,355	85	69	15,500	94	59.0		
9	AlEt <sub>3</sub>	4/1	140	1,000	BATCH PROCESS												
LYNX 705																	
10	AlEt <sub>3</sub>	1.5/1	154	1,000	3.1	6.1	1.11	3.3	7.3	2,014	91	71	8,475	121	60.5		
50% LYNX 900																	
50% LYNX 705																	

Table 1 (Continued)

Ex.	Catalyst System	Reactions Conditions		Feeds		Residence Time, Hr	APH Prodn, Lb/Hr	Cat. Yield, Lb/Lb	Conversion		APH Properties			
		Mole Ratio	Temp, °C	Propylene, Lb/Hr	Hexene, Lb/Hr				Propylene, %	Hexene, %	Viscosity @ 190°C	RBSP, C	Hexene, C	WL, %
11	AlEt <sub>3</sub> / 75% LYNX 900 25% LYNX 705	0.5/1	153	1,000	6.1	1.18	3.3	7.7	2,780	89	75	7,500	113	60.2
12	"	1/1	162	1,000	6.1	1.29	3.4	7.2	2,600	89	69	20,000	119	60.0
13	"	1/1	162	1,000	7.1	1.22	3.1	7.9	2,830	93	70	18,500	107	62.5
14	"	1/1	162	1,000	8.3	1.22	2.7	8.4	3,200	92	63	20,000	96	65.0
15	"	1.25/1	163	1,000	6.1	0.94	3.4	7.4	3,500	90	70	19,000	118	59.0
16	AlEt <sub>3</sub> / 90% LYNX 900 10% LYNX 705	0.5/1	155	1,000	6.1	1.18	3.3	7.6	2,780	89	75	10,500	96	
17	"	0.75/1	161	1,000	7.0	0.66	3.1	7.9	5,000	86	68	18,000	106	60.0
18	"	0.75/1	158	1,000	6.1	0.70	3.3	7.8	5,000	88	73	20,000	111	57.0
19	AlEt <sub>3</sub> / AA-TiCl <sub>3</sub>	0.5/1	165	1,000	6.1	1.22	3.3	6.9	2,300	89	65	22,500	119	59.0
20	AlEt <sub>3</sub> / AA-TiCl <sub>3</sub>	0.5/1	165	1,000	7.0	1.39	3.2	7.6	3,300	89	69	15,750	104	64.0



TABLE II  
ADHESIVE PROPERTIES OF APH MADE WITH DIFFERENT CATALYSTS

Ex.	Catalyst System	Mole Ratio	Temp., °C	Viscosity @ 190°C, CP	RBSP, °C	Hexene, wt %	APH Properties			
							Probe Tack, G	Quick Stick, Lb/In	180° Peel, Lb/In	Static Shear, Hr.
1	AlEt <sub>3</sub> / LYNX 900	1/1	162	42,000	112	60.0	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED
2	"	1/1	171	21,250	96	69.5	620	0.8	2.3	2.6
3	"	1/1	168	25,000	111	64.0	695	0.7	2.0	28.0
4	"	0.5/1	163	20,000	94	62.0	713	1.4	2.2	30.1
5	"	0.5/1	162	26,500	105	57.0	663	1.2	2.0	31.3
6	"	0.5/1	161	26,500	108	56.0	624	1.0	1.6	27.0
7	"	0.25/1	161	8,500	80	64.0	706	1.5	2.1	0.8
8	"	0.25/1	156	15,500	94	59.0	626	1.2	2.3	10.9
9	AlEt <sub>3</sub> / LYNX 705	4/1	140	8,125	98	51.0	780	1.3	3.0	1.1
10	AlEt <sub>3</sub> / 50% LYNX 900 50% LYNX 705	1.5/1	154	8,475	121	60.5	662	1.3	2.3	12.8

Table 11 (Continued)

Ex.	Catalyst System	Mole Ratio	Temp., °C	Viscosity		RBSF, °C	API Properties				
				@ 190°C, CP	@ 190°C, CP		Hexene, Mt. %	Probe Tack, G	Quick Stick, Lb/In	180° Peel, Lb/In	Static Shear, Hr.
11	AlEt <sub>3</sub> 75% LYNX 900 25% LYNX 705	0.5/1	153	7,500	113	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED
12	"	1/1	162	20,000	119	60.0	659	1.5	2.5	22.1	
13	"	1/1	162	18,500	107	62.5	585	1.1	2.0	32.0	
14	"	1/1	162	20,000	96	65.0	507	0.6	1.4	3.0	
15	"	1.25/1	163	19,000	118	59.0	693	1.7	2.8	19.3	
16	AlEt <sub>3</sub> 90% LYNX 900 10% LYNX 705	0.5/1	155	10,500	96	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED	NOT TESTED	
17	"	0.75/1	161	18,000	106	60.0	680	1.5	2.4	20.0	
18	"	0.75/1	158	20,000	111	57.0	366	0.8	1.7	22.4	
19	AlEt <sub>3</sub> AA-TiCl <sub>3</sub>	0.5/1	165	22,500	119	59.0	454	0.3	0.8	37.0	
20	AlEt <sub>3</sub> AA-TiCl <sub>3</sub>	0.5/1	165	15,730	104	64.0	472	0.4	1.8	21.0	

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We claim:

1. A catalyst mixture comprising:
  - (a) about 5 to about 50 weight percent (based on the weight of (a) plus (b)) of a supported catalyst comprising  $\text{TiCl}_4$  supported on an inorganic halide salt,
  - (b) about 95 to about 50 weight percent (based on the weight of (a) plus (b)) of a preactivated catalyst comprising preactivated  $\text{TiCl}_3$ , and
  - (c) an aluminum-alkyl cocatalyst at a molar ratio of aluminum-alkyl: Ti-chloride of about 0.25:1 to about 2:1.
2. The catalyst of Claim 1 wherein said supported catalyst comprises about 1 to about 15 weight percent  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$ .
3. The catalyst of Claim 1 wherein said preactivated catalyst comprises  $\text{TiCl}_3$  plus about 10 to 50 weight percent polypropylene.
4. The catalyst of Claim 1 wherein said aluminum-alkyl cocatalyst is selected from the group consisting of triethyl aluminum, tributyl aluminum, and triisobutyl aluminum.

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5. The catalyst of Claim 1 wherein said aluminum-alkyl cocatalyst is triethyl aluminum.
- 5 6. The catalyst of Claim 1 wherein the amount of supported catalyst is about 15 to about 45 weight percent, the amount of preactivated catalyst is about 85 weight percent to about 55 weight percent, and the  
10 molar ratio of aluminum-alkyl:Ti-chloride is about 1:1 to about 1.5:1.
7. The catalyst of Claim 1 wherein the amount of supported catalyst is about 25 weight  
15 percent, the amount of preactivated catalyst is about 75 weight percent and the molar ratio of aluminum-alkyl:Ti-chloride is about 1.25:1.
- 20 8. The catalyst of Claim 1 wherein the supported catalyst additionally contains up to about 25 weight percent organic esters and ethers.
- 25 9. The catalyst of Claim 8 wherein said organic esters and ethers are selected from the group consisting of anisole, ethyl benzoate and methyl benzoate.
- 30 10. A process for preparing an amorphous propylene higher 1-olefin copolymer comprising contacting propylene and a higher 1-olefin with a catalyst mixture comprising:  
35 (a) about 5 to about 50 weight percent  
(based on the weight of (a) plus (b))

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of a supported catalyst comprising  
TiCl<sub>4</sub> supported on an inorganic  
halide salt),

5 (b) about 95 to about 50 weight percent  
(based on the weight of (a) plus (b))  
of a preactivated catalyst comprising  
preactivated TiCl<sub>3</sub>, and

10 (c) an aluminum-alkyl cocatalyst at a  
molar ratio of aluminum-alkyl:  
Ti-chloride of about 0.25:1 to about  
2:1;

15 said process occurring for a sufficient  
reaction period and under conditions such  
that the desired copolymer is formed.

20 11. The process of Claim 10 wherein said higher  
1-olefin is 1-hexene.

25 12. The process of Claim 10 carried out in an  
inert atmosphere at a temperature of about  
140°C to about 200°C, a pressure of about  
400 to about 2000 psig, in the presence of  
a suitable solvent and for a reaction  
period of about 1/2 to about 10 hours.

30 13. The process of Claim 10 carried out in an  
inert atmosphere at a temperature of about  
150°C to about 180°C, a pressure of about  
1000 to about 1500 psig in the presence of  
a suitable solvent, and for a reaction  
period of about 2 to about 4 hours.

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14. The process of Claim 10 wherein said supported catalyst comprises about 1 to about 15 weight percent  $\text{TiCl}_4$  supported on  $\text{MgCl}_2$ .
- 10
15. The process of Claim 10 wherein said preactivated catalyst comprises  $\text{TiCl}_3$  plus about 50 weight percent polypropylene.
- 15
16. The process of Claim 10 wherein said aluminum-alkyl cocatalyst is selected from the group consisting of triethyl aluminum, tributyl aluminum, and triisobutyl aluminum.
- 20
17. The process of Claim 10 wherein said aluminum-alkyl cocatalyst is triethyl aluminum.
- 25
18. The process of Claim 10 wherein, in the catalyst mixture, the amount of supported catalyst is about 15 to about 45 weight percent, the amount of preactivated catalyst is about 85 to about 55 weight percent, and the molar ratio of aluminum-alkyl:Ti-chloride is about 1:1 to about 1.5:1.
- 30
19. The process of Claim 10 wherein, in the catalyst mixture, the amount of supported catalyst is about 25 weight percent, the amount of preactivated catalyst is about 75 weight percent, and the molar ratio of aluminum-alkyl:Ti-chloride is about
- 35
- 1.25:1.


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20. The process of Claim 10 wherein the supported catalyst of said catalyst mixture additionally contains up to about 25 weight percent organic esters and ethers.
21. The process of Claim 20 wherein said organic esters and ethers are selected from the group consisting of anisole, ethyl benzoate, and methyl benzoate.
22. A hot-melt, pressure-sensitive adhesive comprising an amorphous propylene-hexene copolymer containing about 40 to about 75 weight percent 1-hexene, having a melt viscosity of about 5,000 to about 50,000 cp at 190°C, a softening point of about 90°C to about 125°C, a probe tack of at least about 500 grams, a quick stick of at least about 1.5 pounds per inch, a 180° peel adhesion of at least about 2.5 pounds per inch, and a static shear adhesion of at least about 10 hours.
23. The adhesive of Claim 22 containing about 55 to about 65 weight percent 1-hexene and wherein the melt viscosity is about 15,000 to about 25,000 cp at 190°C, and the softening point is about 95°C to about 120°C.

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# INTERNATIONAL SEARCH REPORT

International Application No PCT/US 88/03637

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : C 08 F 210/06; C 08 F 210/14; C 08 F 4/64		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	C 08 F	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
A	GB, A, 951579 (DEPUTY MINISTER OF THE MINISTERUL INDUSTRIEI PETROLULUI SI CHIMIEL) 4 March 1965 see the whole document	1
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A	US, A, 4072812 (EASTMAN KODAK) 7 February 1978, see the claims	1
	--	
A	US, A, 3954697 (EASTMAN KODAK) 4 May 1976, see the claims	1
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<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
15th March 1989	11. 04. 89	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 <b>P.C.G. VAN DER PUTTEN</b>	



ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.

US 8803637  
SA 25699

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 05/04/89. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
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		FR-A, B 2306248	29-10-76
		DE-A- 2613587	14-10-76
		GB-A- 1529895	25-10-78
		JP-A- 51122136	26-10-76
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