

POLYMERIZATION PROCESSES

The present invention relates to the polymerization of ethylene using a chromium/titanium-containing catalyst, and to the production of polyethylene resins suitable for blow molding resins.

BACKGROUND OF THE INVENTION

The polymerization of ethylene and ethylene copolymers using various methods and catalysts is known in the art. For blow molding applications, it is important for the polyethylene resin to exhibit a relatively high melt flow ratio. Melt flow ratio as used herein is the ratio of high load melt index to melt index. The melt index in g/10 min. at 190°C is run according to ASTM method D-1238 65T using a weight of 2.16 kg. The high load melt index in g/10 min. at 190°C is run according to ASTM method D-1238 65T using a weight of 21.6 kg.

Melt flow ratios can be increased by various compounding methods. However, these methods increase the final cost of the resin, require additional steps and adversely affect certain desired properties of the resin.

It would therefore be desirable to provide a simple economical polymerization process capable of preparing ethylene homopolymers and copolymers having a high melt flow ratio while still maintaining other desired properties.

-2-

SUMMARY OF THE INVENTION

It is thus an object of the present invention to provide a simple economical polymerization process which produces ethylene polymers having a relatively high melt flow ratio.

It is another object of the present invention to provide a polymerization process for preparing ethylene polymers suitable for blow molding applications.

According to the present invention, a polymerization process is provided comprising contacting under polymerization conditions a catalyst, a taming agent, ethylene and optionally an olefin comonomer, wherein the catalyst comprises chromium oxide, titanium oxide and an inorganic refractory oxide, wherein the taming agent is selected from the group consisting of water, alcohols, aldehydes, ketones, esters, and organic acids and mixtures thereof. The process is especially suited for polymerizing ethylene to produce resins suitable for blow molding use.

DETAILED DESCRIPTION

The taming agent used in the process of the present invention is selected from the group consisting of water, alcohols, esters, aldehydes, ketones, and organic acids and mixtures thereof. Preferably, the taming agent is water, an alcohol, or an ester. It is also within the scope of the invention to employ oxygen as a taming agent in combination with the above defined taming agents.

-3-

1 Suitable alcohols generally contain from 1 to 12 carbon atoms and include
2 methanol, ethanol, n-propanol, isopropanol, butanol, amyl alcohol, hexanol,
3 and others and mixtures thereof.

4

5 Suitable esters generally contain from 1 to 12 carbon atoms and include
6 methyl formate, ethyl formate, methyl acetate, ethyl acetate, n-propyl acetate,
7 n-butyl acetate, n-amyl acetate, methyl propanoate, methyl butanoate, ethyl
8 ethanoate, and others and mixtures thereof.

9

10 Suitable aldehydes generally contain from 1 to 12 carbon atoms and include
11 formaldehyde, acetaldehyde, propionaldehyde, n-butyraldehyde,
12 isobutyraldehyde, α -methylbutyraldehyde, and others and mixtures thereof.

13

14 Suitable ketones generally contain from 1 to 12 carbon atoms and include
15 acetone, ethyl methyl ketone, methyl isobutyl ketone, 3-pentanone,
16 3-hexanone, cyclopentanone, cyclohexanone and others and mixtures
17 thereof.

18

19 Suitable organic acids generally contain from 1 to 12 carbon atoms and
20 include formic acid, acetic acid, propionic acid, n-butyric acid, isobutyric,
21 pentanoic acid and hexanoic acid and others and mixtures thereof.

22

23 The amount of taming agent employed can vary broadly depending on the
24 particular taming agent, reactants, reaction conditions employed, and desired
25 results. Preferably, the amount of taming agent is adjusted in combination
26 with the catalyst and product properties desired.

27

28 Generally, the taming agent is present in an amount in the range of from
29 about 0.01 mole to about 10 moles taming agent per million moles of fresh
30 ethylene feed, preferably from 0.01 mole to 5 moles, and more preferably

1 from 0.01 mole to 3 moles taming agent per million moles of fresh ethylene
2 feed. The term "fresh" ethylene feed is used to distinguish from the total
3 ethylene feed to the reaction zone, which includes fresh, as well as recycle
4 ethylene.

5
6 The catalyst used in the process of the present invention contains a catalytic
7 amount of chromium. A "catalytic amount" as used herein is the amount
8 necessary to polymerize ethylene. Generally, the chromium will be present in
9 an amount greater than about 0.1 weight percent based on the total catalyst
10 weight, preferably in the range of from about 0.1 weight percent chromium to
11 about 10 weight percent, more preferably in the range of from about 0.1 to
12 about 8 weight percent, and most preferably in the range of from 0.2 to
13 6 weight percent. The weight percent chromium is given as the element.

14
15 Chromium compounds used in preparing the catalyst can be selected from
16 various organic or inorganic forms of chromium. The preferred chromium
17 compounds, which are used to prepare the catalysts for use in the process of
18 the present invention, are those which contain in addition to chromium, only
19 oxygen, and thermally degradable or volatile substituents, such as, for
20 example, is the case with chromium acetate. Chromium compounds, such as
21 chromium acetate and chromium trioxide, are two preferred sources for the
22 chromium.

23
24 Titanium in the catalyst will be present in an amount sufficient to increase the
25 melt index ratio of the polymer produced. Generally, the titanium will be
26 present in an amount greater than about 0.1 weight percent based on the
27 total catalyst weight. Preferably, the titanium content of the catalyst is in the
28 range of from about 0.1 to about 10 weight percent, preferably in the range of
29 from about 0.1 to about 8 weight percent, and more preferably in the range of

1 from 0.2 to 6 weight percent. The weight percent titanium is given as the
2 element.

3

4 Various titanium compounds can be used to prepare the catalysts. Suitable
5 titanium compounds include titanium oxides such as titanium tetramethoxide,
6 titanium tetraethoxide, titanium n-tetrapropoxide, titanium tetraisopropoxide
7 titanium tetra-n-butoxide and titanium isobutoxide. Excellent results have
8 been obtained with titanium tetraisopropoxide and it is preferred.

9

10 As indicated above, an important aspect of the present invention is the
11 attainment of higher melt flow ratio, using the taming agent with a chromium
12 and titanium catalyst, than would be achieved without the taming agent or
13 without the titanium. The melt flow ratio is the ratio of high load melt index
14 (HLMI) to melt index (MI). MI and HLMI in g/10 min. at 190°C are determined
15 in accordance with ASTM method D-1238 65T using a weight of 2.16 kg and
16 21.6 kg, respectively.

17

18 Although the melt flow ratio of a polymer can be increased by subsequent
19 compounding, the compounding conditions employed are often sufficiently
20 severe that other properties of the resin are damaged during the process.
21 Low melt flow ratios usually translate into greater processing difficulty in blow
22 molding applications.

23

24 Preferably, the amount of taming agent, chromium and titanium employed is
25 sufficient to raise the melt flow ratio of the product off the reactor by at least
26 2 units, more preferably by at least 5 units, and most preferably by 8 units or
27 more compared to product obtained off the reactor without the taming agent
28 and titanium.

29

1 The catalyst contains the foregoing metals on an inorganic refractory oxide,
2 such as silica, silica alumina, zirconia, thoria, etc. Silica is particularly
3 preferred, for example, finely divided silica available from Davison Chemical
4 Company and commonly designated as "952" silica support.

5
6 Preferably, the catalyst is prepared by impregnating the chromium compound
7 onto finely divided high surface area, silica support, drying at 200°F to 450°F
8 for several hours, then adding the titanium compound and activating in air or
9 other oxygen-containing gas at 800°F to 1600°F.

10
11 Suitable catalysts can be prepared by alternative procedures, for example, by
12 a cogel procedure where, instead of post-titanating the preferred silica base
13 after the base is formed, the titanium and silica are formed together in a cogel
14 procedure.

15
16 Catalyst preparation procedures as described in U.S. Patent No. 3,622,521
17 can be used in preparing the chromium-titanium catalysts used in the process
18 of the present invention. The disclosure of the '521 patent is incorporated
19 herein by reference.

20
21 The taming agent can be combined with the catalyst prior to reacting with the
22 olefin or the taming agent can be injected into the reaction vessel prior to or
23 with the introduction of ethylene. One preferred embodiment is to introduce
24 the taming agent in the recycle gas stream prior to the introduction of the
25 recycle gas into the reactor vessel. Preferably, the taming agent is added in
26 mixture with nitrogen, such as in an amount of 4 to 10% taming agent to 96 to
27 90% nitrogen. Another preferred embodiment is to adsorb the taming agent
28 onto the catalyst. Another preferred embodiment is to combine the taming
29 agent with a diluent such as isopentane prior to or with the introduction of
30 ethylene.

-7-

1

2 The taming agent should be effective to reduce the productivity of the
3 catalyst. The productivity of the catalyst is the amount of polyethylene
4 produced per unit weight of fresh catalyst added to the reaction zone. For
5 example, productivity of the catalyst can be measured in terms of pounds of
6 polyethylene produced per hour divided by pounds of fresh catalyst
7 introduced to the reaction zone per hour.

8

9 The process of the present invention is especially useful in improving control
10 in carrying out a polymerization process to produce resins, such as blow
11 molding resins, film resins, and other polyethylene resins. The present
12 process employing a taming agent and a catalyst containing chromium oxide
13 and titanium oxide produces polymers having higher and more controllable
14 melt flow ratios.

15

16 The polymerization process can be carried out in various types of reactors.
17 Thus, a mechanically stirred reaction zone in a horizontal or vertical reactor
18 can be used or a fluidized bed in a vertically disposed reactor can be used.
19 A fluidized bed is preferred, such as described, for example, in U.S. Patent
20 No. 4,011,382. The bed of catalyst particles/polyethylene is fluidized by
21 upwardly flowing ethylene gas.

22

23 Temperatures and pressures used in the polymerization process of the
24 present invention are those sufficient for the polymerization of ethylene.
25 Generally, polymerization temperatures are in the range of from about 100°F
26 to about 250°F, preferably in the range of from 150°F to 250°F and more
27 preferably in the range of from 190°F to 230°F. Preferred pressures are
28 below 500 psig, more preferably between 100 and 500 psig, and still more
29 preferably between 150 and 400 psig, and most preferably between 250 and
30 350 psig.

1
2 The feed ethylene preferably is highly purified. Conventional processes can
3 be employed to purify the ethylene, such as by passing the ethylene through
4 beds of copper oxide or lead oxide on alumina, molecular sieves,
5 hydrogenation catalyst or all three of these, to remove impurities, such as
6 oxygen, carbonyl sulfide, carbon monoxide and arsenic, water, and
7 acetylene. Oxygen can be removed by treatment with a supported copper
8 catalyst. Carbon dioxide impurity can be removed by passing the ethylene
9 through a bed of solid caustic. Preferably, the feed ethylene contains no
10 more than 1 ppm, more preferably less than 0.5 ppm, and most preferably
11 less than 0.05 ppm of the foregoing impurities.
12
13 The high purity ethylene preferably fed to the process of the present
14 invention can contain nitrogen, for example, 1 to 50 mole percent nitrogen,
15 more preferably 5 to 45 mole percent.
16
17 The ethylene can be polymerized to a homopolymer, or to a copolymer using
18 an alpha-olefin containing from 3 to 8 carbon atoms as a comonomer feed.
19 Preferred alpha-olefins comonomers are propylene, butene-1, pentene-1, and
20 hexene-1. When employed, preferred amounts of the comonomer feed are in
21 the range of from 0.01 to 10 mole percent of the total (fresh plus recycle)
22 ethylene feed, more preferably 0.1 to 3 mole percent of the total ethylene
23 feed, and most preferably 0.25 to 2 mole percent of the total ethylene feed.
24
25 The process of the present invention is especially useful as applied to blow
26 molding resin production, but is applicable for other end-use areas such as
27 film and pipe. For blow molding resin production, melt flow ratio for the resins
28 as produced off the reactor are generally in the range of from about 75 to
29 about 150 and are dependent upon the Melt Index and end use. Preferably,
30 the melt flow ratio is in the range of from 85 to 150, and most preferably

1 between 90 and 150. Preferably, the melt index of such resins is in the range
2 of from about 0.1 to about 1.0, preferably from 0.1 to 0.75.

3

4

EXAMPLES AND FURTHER DESCRIPTION

5

6 A preferred catalyst preparation procedure for a catalyst for use in the
7 process of the present invention is as follows. The starting material
8 commonly is a commercially available chromium-silica catalyst, such as the
9 969MS product available from Davison Chemical Division of W. R. Grace &
10 Co. Suitable silica supports include silica "952", available from Davison. The
11 catalyst starting material preferably has a surface area between 200 and
12 500 m²/gm, for example, approximately 300 m²/gm and a pore volume
13 between about 1.0 and 2.0 cm³/gm, for example, approximately 1.6 cm³/gm.

14

15 The catalyst can be prepared at various chromium levels, preferably at least
16 0.4 weight percent, preferably between 0.7 and 2.0. For purpose of the
17 present procedure, preferably the catalyst is prepared to contain
18 approximately one weight percent chromium, for example, 0.8 to 1.2 weight
19 percent chromium. The chromium can be impregnated onto silica support
20 using various techniques, for example, chromium acetate can be impregnated
21 onto finely divided silica support.

22

23 After impregnating the chromium component onto the catalyst support, the
24 resulting catalyst base is dried in a fluidized bed at about 200 to 400°F,
25 preferably approximately 250°F, for several hours, preferably approximately
26 4 hours in air, nitrogen, or a mixture of air and nitrogen.

27

28 Titanium compound is next added to the dried catalyst base. This can be
29 done in a variety of ways. The titanium compound can be added in various
30 forms, such as titanium ester compounds, preferably, titanium

-10-

1 tetraisopropoxide. The dry catalyst base can be slurried in a hydrocarbon,
2 such as isopentane, and then the titanium compound added to it. For
3 example, 25 cm³ of titanium tetraisopropoxide can be slurried with 100 grams
4 of catalyst base and the temperature gradually raised to approximately 113°F
5 and then held for one-half hour.

6

7 Next, the solvent is evaporated by raising the temperature to approximately
8 158°F. Drying is continued until all of the hydrocarbon is removed and then
9 the catalyst material is cooled to ambient temperature.

10

11 Next, the dried, titanium-impregnated catalyst is transferred to a fluidized bed
12 catalyst activator wherein the catalyst is subjected to initial heat treatment at
13 approximately 250°F under nitrogen, or a mixture of air and nitrogen.

14

15 After one hour, the fluidizing gas is changed to air and the temperatures
16 programmed to rise to 1525°F at a rate of 100°F increase in temperature per
17 hour. When the temperature reaches 1525°F, the catalyst is held at this
18 temperature for 12 hours. Then the catalyst is cooled to 500°F. At 500°F,
19 the gas is changed to nitrogen and one hour later the catalyst is removed
20 from the activation step.

21

22 Because the catalysts are activated in the presence of oxygen at high
23 temperature, it will be understood that the chromium and titanium of the
24 catalyst are present in oxide form in the activated catalyst. However, the
25 oxidation state of the chromium and titanium can change during the ethylene
26 polymerization reaction. Also, it is believed that the chromium and titanium in
27 the catalyst are coordinated to at least some extent with each other, probably
28 through oxygen atoms, and that at least the chromium (and possibly the
29 titanium also) are coordinated with alkyl bonds and/or hydrogen bonds as
30 well as oxygen bonds when the catalyst is in the active form in the ethylene

-11-

1 polymerization process. The weight percent chromium and titanium are given
2 herein as the element rather than as the compound, such as chromium oxide
3 or titanium oxide.

4
5 Catalysts were prepared using the procedure indicated above, and were
6 tested in polymerization runs at a temperature of from 210°F to 220°F. The
7 catalysts contained approximately one percent chromium and four percent
8 titanium. The test reactions were conducted in gas phase in a fluidized bed,
9 substantially like the fluidized bed system illustrated in U.S. Patent
10 No. 4,011,382.

11

12 In the Table below:

13

14 Taming Agent is the taming agent and the amount employed in $\mu\text{g/g}$
15 polyethylene.

16

17 MI is the melt index in g/10 min. at 190°C run according to ASTM method
18 D-1238 65T using a weight of 2.16 kg

19

20 MFR is the melt flow ratio and is the ratio of high load melt index to melt
21 index. The high load melt index in g/10 min. at 190°C was determined
22 according to ASTM method D-1238 65T using a weight of 21.6 kg.

23

24 Productivity is lbs polyethylene produced per lb catalyst.

25

Table 1

Run	Taming Agent $\mu\text{g/g}$ PE	MI	MFR	Productivity lbs PE/lb Cat.
101	None	0.28	82	20,000+

-12-

102	None	0.35	74	20,000
103	None	0.41	74	33,000
104	Oxygen 0.2-0.3	0.34	98	16,000
105	Oxygen 0.3	0.19	116	13,300
106	Oxygen 0.35	0.33	100	12,000
107	Water 0.24	0.32	98	16,700
108	Water 0.45	0.36	106	10,000
109	Water 0.49	0.33	97	9,000
110	Water 0.70	0.75	106	6,500
111	Water 0.5-0.8 + Oxygen 0.3	0.34	144	5,000
112	Ethanol 0.87	0.30	93	11,000
113	Ethanol 3.1	0.26	109	10,000
114	Ethanol 3.5	0.27	101	10,000
115	Ethyl Acetate 2.6	0.27	107	13,000
116	Water* 0.2-0.3	0.41	101	14,300
117	Water* 0.2-0.3	0.29	98	19,600
118	Water* 0.3-0.4	0.43	107	12,000
119	Water* 0.4-0.5**	0.52	110	10,000
120	Water* 0.2-0.3 + Oxygen 0.35	0.30	135	7,700
121	Water* 0.4-0.5 + Oxygen 0.3	0.68	109	5,500

-13-

1

2 * Water adsorbed on catalyst

3 ** Estimated from amount of water added to catalyst and productivity values.

4

5 The results in the Table above indicate that polymerizations conducted in the
6 presence of a taming agent employing a chromium/titanium-containing
7 catalyst produced a higher melt flow ratio than those with no taming agent.



-14-

1 **WHAT IS CLAIMED IS:**

2

3 **1. A polymerization process comprising contacting under polymerization**
4 **conditions a catalyst, a taming agent, ethylene and optionally an olefin**
5 **containing from 3 to 8 carbon atoms:**

6

7 **wherein the catalyst comprises chromium oxide, titanium oxide and an**
8 **inorganic refractory oxide; and**

9

10 **wherein the taming agent is selected from the group consisting of**
11 **water, alcohols, aldehydes, ketones, esters, and organic acids and**
12 **mixtures thereof.**

13

14 **2. A process in accordance with Claim 1 wherein the taming agent is**
15 **present in an amount in the range of from about 0.01 mole to about**
16 **10 moles per million moles of fresh ethylene.**

17

18 **3. A process in accordance with Claim 2 wherein the taming agent is**
19 **present in amount in the range of from 0.01 mole to 8 moles per million**
20 **moles of fresh ethylene.**

21

22 **4. A process in accordance with Claim 3 wherein the taming agent is**
23 **present in an amount in the range of from 0.01 mole to 5 moles per**
24 **million moles of fresh ethylene.**

25

26 **5. A process in accordance with Claim 1 wherein the taming agent is**
27 **water, an alcohol, or an ester.**

28

29 **6. A process in accordance with Claim 5 wherein the taming agent is**
30 **water, ethanol, or ethyl acetate.**



- 1
- 2 7. A process in accordance with Claim 1 wherein the taming agent is
- 3 contacted with the catalyst prior to contacting with ethylene.
- 4
- 5 8. A process in accordance with Claim 1 wherein the melt flow ratio of the
- 6 polyethylene produced is in the range of from 85 to 150.
- 7
- 8 9. A process in accordance with Claim 4 wherein the taming agent is
- 9 present in amount sufficient to increase the melt flow ratio by at least
- 10 2 units compared to a polymer prepared under the same conditions
- 11 without the taming agent.
- 12
- 13 10. A process in accordance with Claim 1 wherein the chromium content of
- 14 the catalyst is greater than about 0.1 weight percent based on the total
- 15 catalyst weight.
- 16
- 17 11. A process in accordance with Claim 10 wherein the chromium content
- 18 of the catalyst is in the range of from about 0.1 to about 10 weight
- 19 percent based on the total catalyst weight.
- 20
- 21 12. A process in accordance with Claim 10 wherein the amount of titanium
- 22 is greater than about 0.1 weight percent based on the total catalyst
- 23 weight.
- 24
- 25 13. A process in accordance with Claim 12 wherein the amount of titanium
- 26 is in the range of from about 0.1 to about 10 weight percent based on
- 27 the total catalyst weight.
- 28
- 29 14. A process in accordance with Claim 12 wherein the inorganic
- 30 refractory oxide is silica.



- 1
- 2 15. A process in accordance with Claim 14 where oxygen is also present.
- 3
- 4 16. A process in accordance with Claim 1 wherein an alpha-olefin
- 5 comonomer containing 3 to 8 carbon atoms is also polymerized.
- 6
- 7 17. A process in accordance with Claim 16 wherein the comonomer is
- 8 butene-1 or hexene-1 and is present in an amount in the range of from
- 9 0.01 to 10 mole percent of the total ethylene.
- 10
- 11 18. A process in accordance with Claim 1 wherein the polymerization
- 12 conditions include a temperature in the range of from 100°F to 250°F
- 13 and a pressure in the range of from 100 and 500 psig.
- 14
- 15 19. A process in accordance with Claim 18 wherein the polymerization is
- 16 carried out under gas phase polymerization conditions in a fluidized
- 17 bed of catalyst and polyethylene.

PCTWORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C08F 10/02, 4/24	A1	(11) International Publication Number: WO 97/19963 (43) International Publication Date: 5 June 1997 (05.06.97)
(21) International Application Number: PCT/US96/19104 (22) International Filing Date: 25 November 1996 (25.11.96) (30) Priority Data: 08/566,453 1 December 1995 (01.12.95) US (71) Applicant: CHEVRON CHEMICAL COMPANY [US/US]; P.O. Box 5047, San Ramon, CA 94583-0947 (US). (72) Inventors: KELLUM, Gene, E.; Route 11, Box 917, Orange, TX 77632 (US). BATCHELOR, Robert, L.; 2000 Burton Avenue, Orange, TX 77630 (US). (74) Agents: MICHEL, Marianne, H. et al.; Chevron Corporation, Law Dept., P.O. Box 7141, San Francisco, CA 94120-7141 (US).		(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>
(54) Title: POLYMERIZATION PROCESSES (57) Abstract A polymerization process is provided comprising contacting under polymerization conditions a catalyst, a taming agent, ethylene and optionally a comonomer, wherein the catalyst comprises chromium oxide, titanium oxide and an inorganic refractory oxide, wherein the taming agent is selected from the group consisting of water, alcohols, aldehydes, ketones, esters, and organic acids and mixtures thereof. The process is especially suited for polymerizing ethylene resins suitable for blow molding use.		