

1 **IMPROVED CHROMATE ESTER CATALYST AND METHOD OF USING**
2 **SAME TO PRODUCE HIGH PERFORMANCE POLYETHYLENE**
3 **PRODUCTS**

4

5 **CROSS REFERENCE TO RELATED APPLICATIONS**

6 This application is a continuation-in-part of co-pending US Patent Application
7 serial number 09/222,080 filed December 29, 1998.

8 **FIELD OF THE INVENTION**

9 The present invention relates to an improved chromate ester catalyst,
10 especially a bis (triphenylsilyl) chromate catalyst useful for the polymerization
11 of ethylene, a method of using the improved catalysts to produce high
12 performance polyethylene products, such as polyethylene pipe, and the high
13 performance polyethylene products made using the method.

14 **BACKGROUND OF THE INVENTION**

15 The use of silyl chromate as a polymerization catalyst has been known in the
16 art for many years. See, for example, U.S. Patent No. 3,324,095 (Carrick
17 et al.) and U.S. Patent No. 3,324,101 (Baker et al.) which teach the use of a
18 silyl chromate catalyst system for olefin polymerization. Furthermore, in U.S.
19 Patent No. 3,642,749 (Johnson) and U.S. Patent No. 3,704,287 (Johnson
20 et al.) teach silyl chromate catalyst systems and disclose the deposition of
21 chromate ester or di-tertiary polyalicyclic catalyst on activated silica and
22 treatment with selected organo-metallic reducing agents. However, recently
23 chromate ester catalyst have fallen out of favor due to their limited
24 effectiveness in polymerization processes when compared with newer

1 catalysts, such as the new generation of catalysts used to make bi-modal
2 polyethylene products. The present invention is directed to a new chromate
3 ester catalyst that may be used to make very high performance polyethylene
4 products; such as polyethylene pipe, polyethylene liner systems, and high
5 molecular weight film. In a preferred embodiment of the invention the
6 polyethylene product comprises a copolymer.

7 SUMMARY OF THE INVENTION

8 The present invention relates to a supported chromium containing catalyst
9 which comprises (a) a highly porous silica support having a minimum surface
10 area of at least about 300 m²/gr., an average pore volume of at least 2.0
11 cc/gr., and an average meso pore diameter of between about 350 Å and 1000
12 Å; and (b) a promoter comprising a chromate ester treated with a reducing
13 agent. The catalyst of the present invention is particularly useful for the
14 polymerization of mono unsaturated alpha-olefins having from two to eight
15 carbon atoms in the molecule. The catalyst is especially useful for the
16 polymerization of ethylene. The chromate ester present in the catalyst is
17 usually a silyl ester compound such as bis (triphenylsilyl) chromate.
18 Preferably the chromate ester will be present in an amount within the range of
19 from about 0.15 weight percent to about 0.70 weight percent when calculated
20 on the basis of elemental chromium metal, and more preferably will be
21 present in an amount of between about 0.25 weight percent and 0.60 weight
22 percent when calculated on the basis of elemental chromium metal and most
23 preferably from about 0.45 weight percent to about 0.55 weight percent.

24 The support used in the catalyst of the present invention is a highly porous
25 silica which comprises not less than about 93 weight percent silica.
26 Preferably the support will consist essentially of silica with only traces other
27 materials, such as impurities, present. The term "meso pore" refers to only
28 those pores in the high silica support which have a diameter of between 20 Å

1 and 1000A. Pores present in the support smaller than 20A are referred to as
2 micropores, while pores larger than 1000A are referred to as macropores.
3 While not wishing to be bound by any particular theory, it is believed that the
4 average size of the mesopores are critical to the present invention, since the
5 mesopores are believed to be the primary sites where catalytic reactions, such
6 as polymerization, occur in the finished catalyst. Likewise surface area and
7 the average pore volume also have been shown to be critical limitations of the
8 support used in the present invention. For the highly porous silica support, it
9 is preferred that the surface area be at least 300 m²/gr., the average pore
10 volume be within the range of from about 2.0 cc/gr. to about 4.0 cc/gr., and
11 the mean meso pore diameter be within the range of from about 350 A and
12 about 700A.

13 Average pore diameters given in this disclosure were measured by the
14 adsorption isotherm method. Total pore volume may be determined by the
15 amount of liquid nitrogen adsorbed at a partial pressure of or near 0.99.
16 Surface area may be determined by the BET surface area method (ASTM
17 D3663). One skilled in the art will recognize that the average pore diameter
18 and pore volume may be somewhat different for the finished catalyst as
19 compared to the support prior to addition of the promoter.

20 The present invention further relates to a continuous process for polymerizing
21 ethylene which comprises contacting a reaction system comprising ethylene
22 with a catalytic amount of a promoter comprising a chromate ester treated
23 with a reducing agent, said promoter being deposited on a highly porous silica
24 support having a minimum surface area of at least about 300 m²/gr., an
25 average pore volume of at least about 2.0 cc/gr., and an average meso pore
26 diameter of between about 350 A and 1000 A for a time and under process
27 conditions selected to produce an extrudable polyethylene product. In
28 carrying out the process of the present invention the reaction system may

1 contain only ethylene as a reactant, but in one preferred embodiment of the
2 invention, in addition to the ethylene, the reaction system may also contain
3 from about 0.002 mole ratio to ethylene to about 0.020 mole ratio to ethylene
4 of a mono unsaturated alpha-olefin having from three to eight carbon atoms in
5 the molecule. Preferably the mono unsaturated alpha-olefin present in the
6 reaction system will have from about four to six carbon atoms in the molecule.
7 The process of the present invention is particularly useful in the manufacture
8 of high performance polyethylene products, i.e., polyethylene exhibiting very
9 high PENT, NCTL or other slow crack growth test values as compared to
10 polyethylene products made using conventional chromate ester catalysts.

11 The present invention is further directed to a polyethylene product obtainable
12 by a process which comprises contacting a feedstream containing ethylene
13 with a catalytic amount of a promoter comprising a chromate ester treated
14 with a reducing agent, said promoter being deposited on a highly porous silica
15 support having a minimum surface area of at least about 300 m²/gr., an
16 average pore volume of is at least about 2.0cc/gr., and an average meso pore
17 diameter of between about 350 A and 1000 A for a time and under process
18 conditions selected to produce an extrudable polyethylene product. The
19 polyethylene product may consist essentially of only ethylene homopolymer,
20 i.e., a polymer resin containing only ethylene monomer, or the polyethylene
21 product will preferably contain co-monomers such as other mono unsaturated
22 olefins besides ethylene. Such co-monomers, if present will usually contain
23 from three to eight carbon atoms in the molecule and more preferably will
24 contain from about four to six carbon atoms in the molecule. Polyethylene
25 products, such as polyethylene pipe, within the scope of the present invention
26 have been demonstrated to have PENT values in excess of 1000 hours and
27 even in excess of 2000 hours.

1 As used in this disclosure a polyethylene product refers to either a
2 polyethylene resin made using the present invention, or a product formed,
3 usually by extrusion, from the polyethylene resin. Thus as used herein the
4 term "polyethylene product " may be used to refer to a polyethylene
5 homopolymer resin, a polyethylene copolymer resin, or to manufactures
6 made therefrom, such as, for example, polyethylene pipe, polyethylene liner
7 systems, and high molecular weight film.

8 PENT values used in this disclosure refer to the Pennsylvania Notched Test
9 (ASTM F1473) which measures slow crack growth in the products produced
10 using the resin. PENT values for conventional polyethylene pipe typically fall
11 within the range of 50 to 500 hours. High performance pipe made using bi-
12 modal polyethylene resins typically exhibit PENT values of about 1000 hours.
13 Thus it is particularly surprising that polyethylene pipe may be manufactured
14 using the present invention with PENT values in excess of 1000 hours and
15 even in excess of 2000 hours. In addition, polyethylene pipe made using the
16 process of the present invention has been shown to have good tensile
17 properties (ASTM D638) and superior melt strength (as shown by an
18 internally developed method).

19 As used in this disclosure the words "comprises" or "comprising" is intended
20 as an open-ended transition meaning the inclusion of the named elements,
21 but not necessarily excluding other unnamed elements. The phrase "consists
22 essentially of" or "consisting essentially of" is intended to mean the exclusion
23 of other elements of any essential significance to the combination. The
24 phrase "consisting of" is intended as a transition meaning the exclusion of all
25 but the recited elements with the exception of only minor traces of impurities.

1 DETAILED DESCRIPTION OF THE INVENTION

2 When chromate esters, such as silyl chromate, are supported on a highly
3 porous silica base as described herein, the resulting catalyst displays
4 significantly greater total catalyst productivity than chromate ester catalysts
5 previously known. Polymers produced with the catalysts of the present
6 invention have been found to have outstanding properties when used in high
7 performance polyethylene applications, such as polyethylene pipe. For
8 example, PENT values for polyethylene pipe made using the process of the
9 present invention have been shown to exceed 1000 hours. In addition, melt
10 strength was also found to be extremely desirable being more than 30%
11 greater than other high performance pipe resins. The properties of
12 polyethylene pipe made using the present invention suggest that the
13 improved polyethylene resins of the invention are at least equivalent to the
14 new generation bi-modal products made with other catalysts and processes.

15 Silyl chromate catalysts made using the highly porous silica support of the
16 present invention have demonstrated an increased total catalyst productivity
17 that is equal to about twice that seen using conventional silyl chromate
18 catalysts. Using the conventional silyl chromate catalysts productivity levels
19 of around 3000 lb/lb of total catalyst are typical. In contrast, the improved
20 process of the present invention has given productivity values as high as
21 6000 lb/lb of total catalyst. In addition, polyethylene pipe products made by
22 the improved process have demonstrated PENT values in the 3000 – 4000
23 hour range while the pipe made using conventional processes typically yield
24 PENT values of in the 50 – 500 hours range. The improved total catalyst
25 productivity and pipe performance levels demonstrated using the present
26 invention have not been observed using current processes.

27 Surprisingly, it has been found that the highly porous silica support allows
28 effective loading of the chromate promoter at higher levels than conventional

1 supports. While, it has been possible to load equivalent levels of chromate
2 promoter on conventional supports, studies indicate that the higher levels of
3 promoter do not improve total catalyst productivity of the process or produce
4 a higher performance product. Thus the present invention represents a
5 significant breakthrough in the manufacture of both high performance
6 catalysts and high performance polyethylene products.

7 In carrying out the present invention the chromate esters used as a promoter
8 may include any of the chromate esters which have been described in the
9 literature as useful in the polymerization of ethylene. See, for example US
10 Patents 3,324,101 and 3,704,287, the contents of which are herein
11 incorporated by reference. Preferred promoters are silyl ester compounds
12 having pendent hydrocarbyl groups of from one to about fourteen carbon
13 atoms attached to the silicon atom of the molecule. Illustrative promoters
14 within the scope of the broad invention include, but are not necessarily limited
15 to bis (trimethylsilyl) chromate, bis (triethylsilyl) chromate, bis (tributylsilyl)
16 chromate, bis (trisopentylsilyl) chromate, bis (tri-2-ethylhexylsilyl) chromate,
17 bis (tridecylsilyl) chromate, bis (tri-tetradecyl-silyl) chromate, bis (tribenzylsilyl)
18 chromate, bis (triphenethylsilyl) chromate, bis (triphenylsilyl) chromate, bis
19 (tritolylsilyl) chromate and the like. Especially preferred as a promoter is bis
20 (triphenylsilyl) chromate.

21 In carrying out the present invention the amount of chromate ester present on
22 the catalyst should be at least a catalytic amount, i.e., an effective amount
23 sufficient to catalyze the polymerization reaction. Preferably, the amount of
24 chromate ester should constitute at least about 0.15 wt % but could be as
25 high as 0.70 wt% of the catalyst composition expressed as elemental
26 chromium metal. More preferably, the amount of chromate ester should be
27 within the rang of from about 0.25 weight % to about 0.60 weight percent
28 expressed as chromium metal present and even more preferably within the

1 range from about 0.45 to about 0.55 weight percent expressed a chromium
2 metal present. As shown in the examples below, higher levels of chromate
3 exhibited the best catalyst performance and resulted in polyethylene products
4 having superior properties.

5 In preparing the catalysts of the present invention the chromate ester must be
6 reduced with an organometallic reducing agent, such as, for example, one or
7 more of a variety of alkyl aluminum compounds. Generally preferred in
8 reducing the chromate promoter when carrying out the present invention is di-
9 ethyl aluminum ethoxide. However, the reducing agent selected for preparing
10 the catalyst may not be the most critical element of the invention, and the
11 choice of reducing agent will often depend on other factors such as cost,
12 availability, ease of handling, and stability. Such reducing agents are well
13 known to those skilled in the art and should not require further elaboration
14 here.

15 The highly porous silica support used to prepare the catalysts of the present
16 invention should comprise at least about 93 weight percent silica. The support
17 will generally consist essentially of only silica, except for non-essential
18 impurities; however, other types of silicas containing other elements, such as
19 titanium co-gels, could be expected to work in certain instances. The support
20 should have a high surface area, preferably of at least about 300 m²/gr. and
21 alternatively can have a surface area of at least about 450 m²/gr.. The
22 average pore volume should be at least about 2.0 cc/gr. and more preferably
23 will have an average pore volume of at least 3.0 cc/gr.. The upper limit on
24 pore volume does not appear to be critical to the invention, but usually the
25 average pore volume of the support will not exceed about 4.0 cc/gr.. The
26 average meso pore diameter of the support should fall within the range of
27 from about 350 Å to about 1000 Å as measured by the adsorption method.
28 Generally, higher surface area and higher pore volume and a pore diameter

1 falling in the lower part of the range are preferred.

2 At least one family of microspherical-type supports meeting the requirements
3 of the invention is commercially available, and is produced by The PQ
4 Corporation of Valley Forge, Pennsylvania. Two supports from this family
5 have been used to carry out the process of the invention. Their designations
6 are MS 3030 and MS 3050. The surface area of MS 3030 has been
7 measured at 320 m²/gr. and the pore volume and average meso pore
8 diameter have been measured as 2.95 cc/gr. and about 610A, respectively.
9 The MS 3050 support has been found to have a surface area of 467 m²/gr., a
10 total pore volume of 2.8 cc/gr., and an average meso pore diameter of about
11 400A. Although the two cited supports are of the microspheroidal type, silicas
12 of a granular or spray-dried type are available and possess similar properties
13 to the microspheroidal varieties. They would thus be expected to find
14 application within the areas described herein.

15 In carrying out the invention, it may be advantageous to include between
16 about 0.002 mole ratio to ethylene and about 0.030 mole ratio to ethylene of
17 a co-monomer to ethylene in the reaction system. The co-monomer is
18 typically a mono unsaturated alpha-olefin having from three to eight carbon
19 atoms in the molecule. More preferably the co-monomer will have from four
20 to six carbon atoms in the molecules. One skilled in that art will recognize
21 that the reaction system may also contain a mixture of co-monomers,
22 hydrogen, and inert materials, in which case the invention is not restricted to
23 only the presence of a single monomer in addition to the ethylene. Co-
24 monomers which may be included in the reaction system are, for example,
25 propylene, 1-butene, 1-pentene, 3-methylbutene, 1-hexene, 1(4-
26 methylpentene), 1-heptene, 1-octene, and the like. Preferred for use as co-
27 monomers with ethylene are 1-butene and 1-hexene, with 1-hexene being
28 particularly preferred.

1 The polymerization reaction is preferably carried out in the gaseous phase,
2 but the process may also be carried out as a slurry or solution polymerization.
3 In gas phase polymerization, catalyst particles are fluidized by a continuous
4 flow of gaseous mixture which also acts as a coolant. See US Patents
5 4,876,320 and 5,473,027 for a discussion of gas phase polymerization, the
6 entire contents of which are incorporated herein by reference. The
7 polymerization process may be conducted over a wide range of temperatures
8 and pressures, but usually the polymerization reaction is conducted at a
9 temperature of between about 40 degrees C and about 200 degrees C and
10 within a pressure range of from about 20 psig to about 600 psig. The
11 polymerization process may also be used in high condensation and high
12 productivity mode. When the process is conducted as a gas phase
13 polymerization, the reaction is preferably conducted at a temperature of
14 between about 90 degrees C and about 110 degrees C and within a pressure
15 range of from about 150 psig and about 450 psig.

16 The invention will be further illustrated by the following examples, which set
17 forth preferred embodiments of the invention and compare the performance of
18 the improved catalysts of the invention to conventional catalysts. While the
19 Examples are provided to illustrate the present invention, they are not
20 intended to limit it.

21 Example 1

22 The performance of three different catalysts using conventional supports were
23 compared to two catalysts prepared using MS 3030 and MS 3050 as the
24 supports in a continuous gas phase system. Table 1 below shows a
25 comparison of total catalyst productivity, i.e., pounds of polyethylene per
26 pound of total catalyst, and PENT results.

1 The first entry in the table represents a conventional catalyst using Crosfield
2 EP10X as a support. This silica support may be described as having medium
3 surface area and medium pore volume. Catalysts of this type have been
4 used commercially to manufacture polyethylene pipe for many years. It
5 should be noted that increasing the loading of chromium on the support was
6 not effective in increasing either total catalyst productivity within the process
7 or the performance of the resulting product.

8 A second catalyst tested was prepared from Crosfield EP50 base. This
9 support has a high surface area and is described by the manufacturer as a
10 titanium modified cogel. Table 1 shows that the total catalyst productivity of
11 EP50 did not improve with increased chromium loading. However, some
12 improvement in PENT values were observed.

13 The third catalyst in the Table used a base produced by Grace Davison
14 designated SMR 49. High chromium loading gave improved total catalyst
15 productivity. Unfortunately, PENT results on the polymer were only slightly
16 improved over those obtained from the standard EP10X base.

17 The fourth catalyst in Table 1 was prepared using MS 3030. This catalyst
18 which is an embodiment of the invention is shown with high chromium
19 loading. The high chromium catalyst exhibited very good total catalyst
20 productivity and PENT values were exceptional. The PENT failure for product
21 made with this catalyst was recorded at 6000 hours. As noted above this
22 support has a surface area in the lower end of the range for the present
23 invention, but it does have very large diameter meso pores and a high pore
24 volume.

25 The final catalyst tested was prepared using MS 3050 as a support. Again the
26 performance of the catalyst was tested at both high and low levels of
27 chromium loadings. The high chromium version of the catalyst had excellent

- 1 total catalyst productivity and displayed superior PENT values. Some of the
 2 butene copolymers gave PENT values in excess of 1700 hours.

3

Table 1

4

Comparison of Catalyst and Pipe Performance Properties

Catalyst Base (comonomer)	Chromium Level	Total Catalyst Productivity lb. PE/lb. total Catalyst	PENT Test Results, hrs ⁴	Surface Area m ² /g	Pore Volume cc/g Silica
Crosfield EP10X (1-butene)	Low	2700	60-90	290- 370	1.8
Crosfield EP10X (1-butene)	High	2300	60-90	290- 370	1.8
Crosfield EP10X (1-hexene)	Low	3100	300-400	290- 370	1.8
Crosfield EP50 (1-butene)	Low	3100	>500	440- 540	2.2
Crosfield EP50 (1-butene)	High	2900	>700	440- 540	2.2
Davison SMR 49 (1-butene)	High	4350	135	500	2.6
PQ MS 3030 (1-butene)	High	3000	6000	300	3.0
PQ MS 3050 (1-hexene)	Low	3360	>1200	500	3.0
PQ MS 3050 (1-hexene)	High	5920	>3500	500	3.0
PQ MS 3050 (1-butene)	High	5700	>1700	500	3.0

5

1 Example 2

2 Comparative data shown in Table 2 was obtained for various properties of
3 polyethylene pipe resins produced using the catalyst of the present invention
4 in a continuous gas phase system and for polyethylene pipe resins made
5 using a conventional catalyst. Specifically, the data shown in Table 2 was
6 obtained for standard gas phase butene based pipe grade HiD 9346 (referred
7 in the table as HiD 9346 B) which was made with a catalyst using EP10
8 catalyst base, LX4838 (1-hexene comonomer) which was made with a
9 catalyst using MS 3050 catalyst base (bis(triphenyl silyl chromate) catalyst),
10 and HiD 9346 commercially prepared resin using MS 3050 and 1-hexene.
11 (The hexene version of HiD 9346 is referred to in the table as HiD 9346 H.)

12 The most obvious difference between the pipe resins is in the PENT data.
13 The PENT (Pennsylvania Notched Test, ASTM F1473) test assesses slow
14 crack growth for pipe resins. The PENT values for LX4838 exceed 3100
15 hours with no failures. HiD 9346 B (1-butene, EP10) failed PENT at 60 hours
16 which is typical for pipe manufactured using conventional catalyst.
17 Commercially prepared HiD 9346 H with 1-hexene and MS 3050 has PENT
18 values in excess of 2700 hours with no failures. Typical PENT values for
19 PE3408 type pipe grades (such as HiD 9346B) are in the 50-500 hour range.
20 The highest PENT values for commercially available PE3408 pipe grades
21 have been for bi-modal resins such as Fina 3344. Fina 3344 has PENT
22 values typically in the 1000 hour range. LX4838 and commercial HiD 9346 H
23 (1-hexene, MS 3050) have far superior PENT values.

24 For the molecular weight data shown (GPC), LX4838 and HiD 9346 H are as
25 broad in molecular weight distribution (Mw/Mn value) as HiD 9346 B. This
26 means that LX4838 and HiD 9346 H have excellent processability into pipe.
27 There is also higher Mz (high molecular weight tail) values for LX4838 and
28 HiD 9346 H versus HiD 9346 B. This means that LX4838 and HiD 9346 H

- 1 will have good tensile properties, good melt strength, and better slow crack
- 2 growth resistance (PENT).
- 3 All grades meet PE3408 type resin requirements per ASTM D3350: HLMI
- 4 (typically in the 10 HLMI range); Density (0.941-0.955 range); Tensile
- 5 Properties (Tensile at Yield 3000-3500); and PENT (30 hours and up).

TABLE 2

Gas Phase Pipe Resins – MS3050 vs. EP10

Property	HiD 9346	LX4838A	LX4838B	HiD 9346
Density, gm/cc	0.9456	0.9456	0.9456	0.945
Melt Index 5, gm/10 min.	0.29	0.30	0.26	0.30
HLMI, gm/10 min.	9.0	9.4	8.5	9.0
MFR	31	31	33	30
PENT, hrs.	60	>3100	>3100	>2700
Tensile Strength at Yield, psi	3,190	3210	3300	3530
Tensile Strength at Break, psi	4,660	4030	5,220	5,400
Elongation, %	800	690	760	830
Charpy Impact, ft-lbs/in	4.5	9.0	8.5	8.0
Melt Strength at 190°C, gms	24	21	18	21
Melt Strength at 230°C, gms	14	12	15	12
Rheotens Tensile Force at Break, cN	38	90	89	N/A
OIT, minutes	50	55	65	75
Thermal Stability, C	265	265	265	265
Mn (GPC)	15,700	12,700	13,100	13,100

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Mw (GPC)	208,400	226,200	228,600	253,000
Mz (GPC)	1,144,400	1,196,700	1,195,100	1,744,300
Mw/Mn (GPC)	13	18	18	19
%<10 ⁴ (GPC)	14	17	17	15
%<10 ⁶ (GPC)	5	6	6	6
Catalyst Base	EP10X	MS3050	MS3050	MS3050
Comonomer Type	1-butene	1-hexene	1-hexene	1-hexene

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- 2 While the present invention has been described with reference to specific
3 embodiments, this application is intended to cover those various changes and
4 those may make those substitutions skilled in the art without departing from
5 the spirit and scope of the appended claims.

1 WHAT IS CLAIMED IS:

- 2 1. A supported chromium containing catalyst composition which
3 comprises:
4 (a) a highly porous silica support having a minimum surface area of
5 at least about 300 m²/gr., an average pore volume of at least
6 about 2.0 cc/gr., and an average meso pore diameter of
7 between about 350 A and 1000 A; and
8 (b) a promoter comprising a chromate ester treated with a reducing
9 agent.
- 10 2. The catalyst of claim 1 wherein the highly porous silica support
11 consists essentially of silica.
- 12 3. The catalyst of claim 2 wherein the surface area is at least 450 m²/gr.
- 13 4. The catalyst of claim 2 wherein the mean meso pore diameter of the
14 support is between about 350A and about 700 A.
- 15 5. The catalyst of claim 2 wherein the average pore volume of the support
16 is within the range of from about 2.8 cc/gr. and about 4 cc/gr..
- 17 6. The catalyst of claim 2 wherein the promoter is present in an amount
18 within the range of from about 0.15 to about 0.70 weight percent
19 calculated on the basis of elemental chromium metal.
- 20 7. The catalyst of claim 6 wherein the surface area of the support is at
21 least 450 m²/gr., the average pore volume is within the range of from
22 about 2.8 cc/gr. and about 3.5 cc/gr., and the average meso pore
23 diameter is in the range from about 375 A to about 425 A.

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- 1 8. The catalyst of claim 6 wherein the chromate ester is present in an
2 amount of about .25 weight percent to about 6.0 weight percent
3 calculated on the basis of elemental metal.
- 4 9. The catalyst of claim 8 wherein the chromate ester is present in an
5 amount of about 0.45 weight percent to about 0.55 weight percent
6 calculated on the basis of elemental metal.
- 7 10. The catalyst of claim 1 wherein the chromate ester is bis (triphenylsilyl)
8 chromate.
- 9 11. A polyethylene product obtainable by a continuous process which
10 comprises contacting a reaction system containing ethylene with a
11 catalytic amount of a promoter comprising a chromate ester treated
12 with a reducing agent, said promoter being deposited on a highly
13 porous silica support having a minimum surface area of at least about
14 300 m²/gr., an average pore volume of is at least about 2.0 cc/gr., and
15 an average meso pore diameter of between about 350 Å and 1000 Å
16 for a time and under process conditions selected to produce an
17 extrudable polyethylene product.
- 18 12. An extruded polyethylene pipe product made using the polyethylene
19 product of claim 11.
- 20 13. The polyethylene product of claim 11 wherein the reaction system also
21 contains co-monomer comprising at least one mono unsaturated
22 alpha-olefin having from three to eight carbon atoms in the molecule or
23 a mixture thereof.
- 24 14. The polyethylene product of claim 13 wherein the co-monomer
25 comprises a mono unsaturated alpha-olefin having from four to six
26 carbon atoms in the molecule or a mixture thereof.
- 27 15. The polyethylene product of claim 14 wherein the co-monomer is 1-
28 butene.

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* C L M S *

- 1 16. The polyethylene product of claim 14 wherein the co-monomer 1-
2 hexene.
- 3 17. The polyethylene product of claim 14 exhibiting a PENT value of at least
4 1000 hours.
- 5 18. An extruded polyethylene pipe product made using the polyethylene
6 product of claim 17.
- 7 19. The polyethylene product of claim 16 exhibiting a PENT value of at
8 least 2000 hours.
- 9 20. An extruded polyethylene pipe product made using the polyethylene
10 product of claim 19.
- 11 21. A continuous process for polymerizing ethylene which comprises
12 contacting a reaction system comprising ethylene with a catalytic
13 amount of a promoter comprising a chromate ester treated with a
14 reducing agent, said promoter being deposited on a highly porous
15 silica support having a minimum surface area of at least about 300
16 m²/gr., an average pore volume of is at least about 2.0 cc/gr., and an
17 average meso pore diameter of between about 350 Å and 1000 Å for a
18 time and under process conditions selected to produce an extrudable
19 polyethylene product.
- 20 22. The process of claim 21 wherein the chromate ester on the catalyst is
21 present in an amount of at least 0.15 and as much as 0.70 weight
22 percent calculated on the basis of elemental metal.
- 23 23. The process of claim 21 wherein the chromate on the catalyst is bis
24 (triphenylsilyl) chromate treated with a reducing agent.
- 25 24. The process of claim 21 wherein the highly porous silica support on the
26 catalyst consists essentially of silica
- 27 25. The process of claim 24 wherein the surface area of the highly porous



- 1 silica support is at least 450 m²/gr.
- 2 26. The process of claim 24 wherein the mean meso pore diameter of the
3 highly porous silica support is between about 350A and about 700 A
- 4 27. The process of claim 24 wherein the average pore volume of the highly
5 porous silica support is within the range of from about 2.0 cc/gr. and
6 about 4 cc/gr..
- 7 28. The process of claim 24 wherein the surface area of the highly porous
8 silica support is at least 450 m²/gr., the average pore volume is within
9 the range of from about 2.8 cc/gr. and about 3.5 cc/gr. and the average
10 meso pore diameter is in the range from about 375 A to about 425 A.
- 11 29. The process of claim 21 wherein the reaction system also contains a
12 co-monomer comprising at least one mono unsaturated alpha-olefin
13 having from three to eight carbon atoms in the molecule or a mixture
14 thereof.
- 15 30. The process of claim 29 wherein the co-monomer comprises a mono
16 unsaturated olefin having from four to six carbon atoms in the molecule
17 or a mixture thereof.
- 18 31. The process of claim 29 wherein the co-monomer comprises between
19 about 0.002 mole ratio to ethylene and about 0.30 mole ratio to
20 ethylene.
- 21 32. The process of claim 30 wherein the reaction system contains 1-
22 butene.
- 23 33. The process of claim 30 wherein the reaction system contains 1-
24 hexene.
- 25 34. The process of claim 21 wherein the polymerization is carried out as a
26 gas phase polymerization.



- 1 35. The process of claim 34 wherein the polymerization is carried out in
2 condensation mode.



This Sheet Has Been Replaced

