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(54) CATALYST COMPOSITIONS, METHOD FOR PRODUCING SAME AND METHOD FOR POLYMERISATION OF 1-OLEFINS WITH SAME

(71) We, NATIONAL PETRO CHEMICALS CORPORATION, a corporation organised and existing under the laws of the State of Delaware, United States of America, of 99 Park Avenue, City and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to catalyst compositions, their production, and their use in the polymerisation of 1-olefins.

Molded articles, and particularly blow molded structures such as bottles, are commonly formed from polymers of 1-olefins such as polyethylene. It is important to the commercial utilization of a given polymer system that the converted product such as a bottle exhibit an optimized balance of properties, including for example, acceptable stress crack resistance and flexural stiffness. In addition, and in a contributing sense, it is necessary that the polymer exhibit suitable processability i.e. satisfactory rheological behavior under flow and deformation during fabrication. Although the viscoelastic behavior of polymer melts has been the subject of considerable study, it has not proven possible to translate performance during fabrication to end use articles in such manner as to selectively determine polymerization and particularly catalyst requirements. In any case catalyst performance must also be measured in terms of efficiency or productivity and stability over a sensible life.

In our U.S. Patent 3,474,080 there are described compounds useful in the catalysis of 1-olefins which prepared by the reaction of organophosphates and chromium trioxide.

Through further research we found that such compounds lend themselves to the production of supported catalyst systems which are useful for the polymerization of 1-olefins, and the polymerization activity of which is promoted by heating the catalyst in a dry oxygen containing atmosphere. By an extension of this research it was also found that the resulting activated catalysts, used alone or in conjunction with certain reducing agents, can produce polymers of 1-olefins and copolymers or interpolymers thereof having a favorable blend of properties. The use of the organometallic and/or organic non-metallic reducing agents with the air/heat treated catalyst gives latitude in obtaining variety in polymer property balance in addition to promoting catalytic activity.

In our U.S. Patent 3,493,554 there is disclosed the polymerization of 1-olefins in the presence of a reducing agent and a bis (diorgano) chromate compound as a catalyst.

Other researchers have also investigated certain other chromium compounds and phosphorous compounds and their use in olefin polymerization. For example U.S.

Patent 2,825,721 describes a polymerization process for olefins using as a catalyst chromium oxide and at least one material selected from silica, alumina, zirconia, and thoria, at least part of the chromium being in the hexavalent state at the initial contact of the hydrocarbon with the catalyst. Related U.S. Patent 2,951,816 describes a method ~~for~~ preparing such catalysts by depositing chromium oxide on a support of the just recited group and heating at an elevated temperature under anhydrous conditions to impart increased catalytic activity.

In U.S. Patent 2,945,015 a process is described for polymerizing 1-olefins using a chromium oxide-phosphorous oxide supported catalyst, at least a portion of the chromium in the catalyst being in the hexavalent state. Supported chromium catalysts of limited productivity are disclosed in U.S. Patent 3,349,067 as esters of chromyl chloride with e.g. tricresyl orthophosphate.

Other researchers have reported the use as catalysts for olefin polymerization of various silylchromate and polyalicyclic chromate esters — see, inter alia, U.S. Patents 3,324,095, 3,324,101, 3,642,749, and 3,704,287. The last of this group discloses placing the phosphorus chromate esters of U.S. Patent 3,474,080 on a support and then reducing the catalyst prior to contact with the olefin by heating at elevated temperatures in the presence of an aluminium, magnesium or gallium organometallic compound.

The preparation and use of improved high pore volume silica xerogel materials suitable as catalyst supports is described in Belgium Patent No. 741,437 and U.S. Patent Nos. 3,652,214, 3,652,215 and 3,652,216.

The present invention provides a catalyst composition comprising a solid inorganic support material having deposited thereon an organophosphoryl chromium product obtained by the reaction of chromium trioxide with an organophosphorus compound, said composition having been heated in a dry oxygen-containing atmosphere at a temperature above 400°F and below the temperature at which the structure of the support is impaired, and for a period of time sufficient to promote the polymerisation activity of said catalyst composition for the polymerisation of 1-olefins. It also provides a composition according to the invention wherein organophosphoryl chromium product is obtained by reaction of said organophosphorus compound with chromium trioxide in equimolar ratio. It further provides a process for the polymerisation of a 1-olefin comprising contacting said 1-olefin, alone or together with at least one copolymerisable comonomer, under polymerisation conditions of temperature and pressure, with a catalyst composition according to the invention. The preferred support materials have a surface area of 100 to 1000 m²/g or more.

We have found that the aforementioned catalyst compositions, usually used in conjunction with certain organometallic and/or organo non-metallic reducing agents, e.g. triethylaluminium, tri-isobutyl aluminium or triethylboron, permits the production of polymers of 1-olefins having a variety of properties, especially with respect to MWD (molecular weight distribution-shear response), and can thus complement and extend the utility of the original or basic catalyst system. These reducing agents may be brought into contact with the air/heat treated catalyst in a variety of ways, e.g., by having the agent in the solvent stream to the reactor, or by precontacting the catalyst with the agent prior to introducing it to the reactor, or by introducing the agent with some dilution directly to the reactor independently of the solvent stream. Particularly advantageous catalyst systems are obtained when using as a support a silica xerogel of high pore volume, e.g., >1.96 cc/g, such as xerogel is commercially available under the trade name "POLYPOR".

In addition to pore volume greater than 1.96 cc/g, the POLYPOR support material is characterized by the major portion of said pore volume being provided by pores having pore diameters of 300—600 Å, and by a surface area of 200—500 m²/g. The pore volume is determined by the well known nitrogen adsorption-desorption technique described, for example, Catalysis, Vol. II, pages 111—116, Emmett, P. H., Reinhold Publishing Corp., New York, N.Y., 1955 (Run to a P/Po of 0.967 which is equivalent to 600 Å pore diameter), and elsewhere.

The catalyst compositions of this invention, when used in known polymerization processes (e.g., suspension, solution and vapor phase processes) can produce polymers of a variety of molecular weights and molecular weight distributions suitable for the major applications of high and medium density polyethylene, especially blow molding and extrusion (e.g. sheeting, film) applications.

There follows a description of a preparative method for a catalyst composition according to the invention. For further information on the preparation of the compounds involved, reference may be had to the above mentioned U.S. Patent 3,474,080.

In a typical general embodiment of this invention the organophosphorus compound and the chromium trioxide are brought together in a suitable inert solvent, e.g., cyclohexane, n-hexane, methylene dichloride or carbon tetrachloride. In this step the solid CrO_3 is slurried in the solvent and the organophosphorus compound added. Over a period e.g., about one hour, a reaction between the compounds ensues and the chromium trioxide disappears. During this period the solution becomes reddish-brown. It is ordinarily filtered to ensure the absence of any unreacted solid CrO_3 . This solution is then applied to the support to effect the deposition of the catalyst solution thereon, suitably by any wet coating technique, e.g., spraying. Typically, the solution is added to a dispersion of a silica gel support. The solvent is removed from the base by drying, e.g., using heat, inert gas stripping, or reduced pressure alone or in combination. It is considered significant that the organophosphoryl chromium reaction product is preformed i.e. the reacting entities are combined prior to the introduction to the support. The active catalyst is therefore understood not to derive from chromium trioxide but the organophosphoryl chromium reaction product as described.

The supported catalyst is then heated in a dry oxygen-containing atmosphere, such as dry air, resulting in a marked promotion of polymerization activity. Heating is conducted at temperatures above 400°F , e.g., from 400 to 2000°F , and preferably 1000 to 1790°F . The time period of the heating will vary depending on the temperature, but usually is conducted for from 2 to 18 and preferably from 6 to 12 hours.

When using the POLYPOR supported catalysts, heat treatment in dry air for the promotion of polymerization activity may be carried out at temperatures of from 1000°F , to 2000°F . for at least 2 hours, and preferably at temperatures in the range of from 1500°F . to 1650°F . for from 6 to 12 hours.

The supported reaction product, after heat treatment, is then used alone or in conjunction with organometallic and/or organo non-metallic reducing agents, e.g., a trialkylaluminum, dialkylzinc, dialkylmagnesium, dialkylaluminum chloride, dialkylaluminum alkoxides or triethylboron, to polymerize 1-olefins. When used with such reducing agents, the catalyst compositions provide a method for securing a desirable latitude of polymer properties, particularly molecular weight distribution.

In the following detailed description of the invention and operative Example, a measure of the viscoelastic behaviour of the polymer melt is expressed in values for melt index (M.I., determined in accordance with ASTM—D—1238, at 2 kg load and 190°C) and high load melt index (HLMI, 10X), and the shear sensitivity, (response of melt viscosity to the differential shear rates) is reflected in the HLMI/MI ratios. In general, the broader the molecular weight distribution, the more sensitive is the viscosity to shear rate i.e. the higher the HLMI/MI ratio. The lowest value for melt index that was measured at reasonable accuracy is about 0.1, but in many cases qualitative observation of a significantly lower rate is reported as 'low' herein, which may represent an actual value of as little as 0.05 or less. Performance testing indicates an HLMI/MI ratio consistent with other quantified results. Preferred polymer products have a melt index of less than 2, a high load melt index of at least 25 and an HLMI/MI ratio of at least 40.

Among the organic phosphorus compounds which may be used in making catalyst compositions of this invention are the triorganophosphates and diorganophosphates including such compounds as triphenyl phosphate, tributyl phosphate, triethyl phosphate, trioctyl phosphate and trimethyl phosphate. Also suitable are the mono-(dihydrogen) phosphate or phosphite and di(hydrogen) phosphate derivatives, e.g. monobutyl phosphate, dibutyl phosphate and monoethyl phosphite) and these materials may of course be in admixture. Organophosphoryl chromium reaction products are also formed with such phosphorus based compounds as phenylphosphonic acid, diethyl ethyl phosphonate and trioctylphosphine oxide. The preferred compounds are believed to be represented by the following formula:



where X is $\text{P}-(\text{OR})_3$ or $\text{PH}(\text{OR})_2$ and the R's are selected independently from alkyl, aralkyl, aryl, cycloalkyl, and hydrogen, but at least one R is other than hydrogen.

The alkyl derivatives and particularly the trialkyl phosphates are especially preferred. Typical examples of the preparation of the catalyst systems follow.

CATALYST PREPARATION 1

a. 125 ml of dichloromethane were placed in a 3-neck 500 ml flask equipped with a nitrogen inlet for blanketing, a gas outlet tube, magnetic stirring means, and a 100 ml dropping funnel. Under a nitrogen cover, 9.70 gms CrO_3 (0.097 m) were added to the stirred flask containing the dichloromethane solvent. From the dropping funnel 17.5 gms triethyl phosphate (0.097 m) dissolved in 75 ml dichloromethane were added over a period of 20 minutes. Within five minutes of the beginning of the addition of the triethyl phosphate the solution in the flask turned dark reddish-brown. At the end of one hour of stirring all the CrO_3 had disappeared and the solution was dark reddish-brown. Upon weighing, the solution was found to weigh 217.6 gms.

In order to place the compound on a support, 210 grams of microspheroidal silica gel (Davison MS 952) were placed in a 2000 ml round bottom flask, equipped with a stirrer and provided with a nitrogen blanket. Then 800 ml dichloromethane were added to the flask containing the gel and stirring was commenced in order to insure a uniform wetting of the gel. Then 90 grams of the dark reddish-brown filtered solution were added to the flask containing the gel and dichloromethane solvent. After stirring for about 15 minutes, the stirrer was turned off and the gel was allowed to settle. At this time, it was observed that the gel had a brownish color and the dichloromethane solvent was almost colorless. This indicated that the catalyst compound was very strongly and preferentially adsorbed on the gel. The supernatant liquid was removed by filtration and the gel was dried in a rotary evaporator at 55°C . and 29 inches Hg vacuum. The dried and catalyst coated gel containing 0.99% wt. chromium and 0.60% wt. phosphorus was then treated at 1110°F . for 6 hours while simultaneously passing dry air through the catalyst.

b. Chromium dioxide was found not to react with triethyl phosphate under identical conditions where chromium trioxide does react.

CATALYST PREPARATION 2

250 ml of dichloromethane were placed in a 3-neck 500 ml flask equipped with a nitrogen inlet for blanketing, a gas outlet tube, magnetic stirring means, and a 100 ml dropping funnel. Under a nitrogen cover 2.9 gms CrO_3 (0.029 m) were added to the stirred flask containing the dichloromethane solvent. From the dropping funnel 5.4 gms dibutyl phosphite (0.029 m) dissolved in 25 ml dichloromethane were added over a period of 20 minutes. Within five minutes of the beginning of the addition of the dibutyl phosphite the solution in the flask turned dark reddish-brown. Stirring was continued for 2 hours and the CrO_3 disappeared and the solution was dark reddish-brown. Upon weighing, the solution was found to weigh 353 gms.

In order to place the compound on a support, 42 grams of Polypor Silica Gel (Pore Volume 2.5 cc/gm) were placed in a 2000 ml round bottom flask, equipped with a stirrer and provided with a nitrogen blanket. Then 100 grams of the reddish-brown filtrate (the solution was passed through a filter to ensure the absence of unreacted CrO_3) were added to the flask containing the Polypor Silica Gel. After about 15 minutes, the gel had turned brownish and the dichloromethane solvent was almost colorless. This indicated that the catalyst compound was very strongly and preferentially adsorbed on the gel. The supernatant liquid was removed by filtration and the gel was dried in a rotary evaporator at 55°C . and 29 inches Hg vacuum. The dried and catalyst coated gel containing 1.02% wt. chromium and 0.60 wt. phosphorus was then treated at 1650°F . for 6 hours while simultaneously passing dry air through the catalyst.

CATALYST PREPARATION 3

In a manner of preparation similar to that of Catalyst Preparation 2 but utilizing 3.66 gms CrO_3 (0.0366 m) and 7.23 gm dibutyl phosphite (0.0373 m) in a total of 373 gms of dichloromethane as solvent a solution of the dibutyl phosphite chromium trioxide compound was prepared. This solution was used to coat 195 gm of Polypor silica gel with 0.97% wt. chromium and 0.6% wt. phosphorus. This coated Polypor silica gel after removal of the dichloromethane was then treated at 1650°F for 6 hours while passing dry air through the sample.

The foregoing catalysts are utilized in the polymerization of ethylene in the Polymerization Examples which follow, with and without various reducing agents such as tri-isobutylaluminum and triethylboron.

The amounts of organophosphoryl chromium compound deposited on the support may vary widely depending on the nature of the compound and the desired levels of chromium and phosphorus. Likewise the amount of reducing agents used in conjunction with the organophosphoryl catalyst may vary.

The most effective catalysts have been found to be those containing the organophosphoryl chromium compound in an amount such that the amount of Cr by weight on the support is from 0.25 to 2.5% and preferably is from 0.5 to 1.25%, although amounts outside the foregoing ranges still yield usable catalysts. The catalyst is commonly prepared at equimolar ratio, although an excess of the organophosphorus compound may be employed. Cr/P ratios calculated on an elemental weight basis in the supported catalyst are typically 1:0.6.

In proportioning the amount of reducing agent to the amount of organophosphoryl chromium compound used as the catalyst, fairly wide latitude is available, but some guidelines have been established consistent with good yield, favorable polymer properties, and economic use of materials. For example, in the use of organometallic and organo non-metallic reducing agents with an amount of organophosphoryl chromium compound sufficient to yield about 1% Cr by weight of the support the parameters set forth below are representative. The atomic ratios are based upon a calculation of the metal in the organometallic reducing agent and the non-metal in the organo-non-metallic reducing agent versus the chromium content present in the organophosphoryl chromium compound.

For example, based upon an amount of organophosphoryl chromium compound containing about 1% by weight of Cr based upon the weight of the support, the preferred amount of an organometallic reducing agent for use therewith, e.g., triisobutylaluminum (TIBAL), is about 11.4% by weight giving an Al/Cr atomic ratio of about 3/1. The preferred range of atomic ratios of Al to Cr is from 1/1 to 5/1, or from 3.8% to 19% by weight TIBAL. A wider practicable range of TIBAL in terms of the Al/Cr atomic ratio is from 0.1/1 to 20/1, and in terms of weight from 0.4% to 75% by weight.

Another example of an organometallic reducing agent for use in conjunction with the organophosphoryl chromium compound is triethylaluminum. Again based upon an amount of organophosphoryl chromium compound containing about 1% by weight of Cr based upon the weight of the support, the preferred amount of triethylaluminum (TEA) is about 6.6% by weight giving an Al/Cr atomic ratio of about 3/1. The preferred range of atomic ratios of Al to Cr is from 1/1 to 5/1, or from 2.2% to 11% by weight of TEA. A wider practicable range of TEA, in terms of an Al/Cr atomic ratio, is from 0.1/1 to 20/1, and in terms of weight from 0.22% to 44% by weight.

Triethylboron (TEB) may be taken as the preferred example to illustrate the proportions of non-metallic reducing agent for use in conjunction with the organophosphoryl chromium compound. Again based upon an amount of organophosphoryl chromium compound containing about 1% by weight of Cr based upon the weight of the support. The preferred amount of TEB is about 5% by weight giving a B/Cr atomic ratio of about 2.7/1. The preferred range of atomic ratios of B to Cr is from 0.1/1 to 10/1, or from 0.19 to 19% TEB. A wider practicable range, in terms of a B/Cr atomic ratio, is from 0.01/1 to 20/1, and in terms of weight, from 0.02% to 38% by weight.

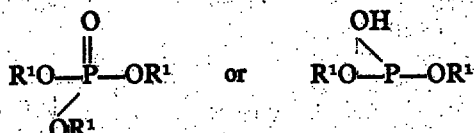
The conditions of treatment at elevated temperatures of the supported organophosphoryl chromium compound may be varied. In general, the catalyst is heated in dry air or other dry oxygen-containing gas at a temperature above 400°F. and preferably over 650°F. for a period of 2 hours or more. Using the preferred high pore volume silica gel support described above, heating in the range of from 1450°F. to 1650°F. for up to 6 hours is desirable. For other supports a regimen of heating at above 400°F. and preferably 1000°F. for about 6 hours is effective.

The dry air or other oxygen-containing gas should preferably be dehumidified down to a few parts per million (ppm) of water to obtain maximum productivity from the catalyst. Typically the air used in the processes described in this application is dried to less than 3 ppm or less than 2 ppm of water.

As indicated above, the catalysts of this invention are suitable for use in conventional polymerization processes under temperature and pressure conditions generally employed in the art, e.g. temperature of 100°F to 400°F. and preferably from 160°F to 230°F., and pressures of from 200 to 1000 psig and preferably from 300 to 800 psig, as are used in slurry polymerizations.

The 'organophosphoryl chromium' reaction products which form the basis for the supported catalysts of this invention may be empirically formed as seen in the above preparations from organophosphorus compounds in a reaction with chromium trioxide in an inert solvent, identifiable by the dissolution of the characteristic chromium trioxide. Suitable organophosphorus compounds may accordingly be readily selected for efficacy by reference to this test. Preferred materials are derived from compounds

containing at least one organic moiety directly bonded through carbon or oxygen to the phosphorus atom which is in the +3 or +5 oxidation state and has at least one valency satisfied by oxygen or a hydroxyl grouping. Such preferred compounds may be schematically represented by the formulae:



wherein the R¹'s are selected independently from alkyl, aralkyl, aryl, cycloalkyl, and hydrogen, but at least one R¹ is other than hydrogen. For ease of description the usable materials are referred to herein collectively and comprehensively as 'organophosphoryl chromium' reaction products.

The following Examples illustrate the use of catalyst systems of the invention in methods for polymerization of alpha olefins such as ethylene.

Polymerization Example 1.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, 0.33 gm hydrogen/kg solvent, 0.82 gms supported catalyst of Catalyst Preparation I and tri-isobutyl-aluminium sufficient to give a 1.4 to 1 atomic ratio of aluminium to chromium. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 435 psig. Polymerization began almost immediately as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all, 319 grams of polyethylene having a melt index of 0.21 and a high load melt index of 16 (HLMI/MI=76) (ASTM D-1238) before homogenizing were recovered. Based on the catalyst charge of 0.82 gms the yield was 390 gms polyethylene/gm cat/hour.

Polymerization Example 2.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, 0.33 gm hydrogen/kg solvent, 1.59 gms supported catalyst of Catalyst Preparation 1, and triethylboron sufficient to give a 3.8 to 1 atomic ratio of boron to chromium. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 435 psig. Polymerization began almost immediately as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all 439 grams of polyethylene having a melt index of 0.036 and a high load melt index of 10 (HLMI/MI=278) before homogenizing were recovered. Based on the catalyst charge of 1.59 gms the yield was 275 gms polyethylene/gm cat/hour.

Polymerization Example 3.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, 0.33 gm hydrogen/kg solvent, and 2.08 gms supported catalyst of Catalyst Preparation 1. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 435 psig. Following an induction period of about 30 minutes polymerization began as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all, 443 grams of polyethylene having a melt index of 0.05 and a high load melt index of 7.0 (HLMI/MI=140) before homogenizing were recovered. Based on the catalyst charge of 2.08 gms the yield was 212 gms polyethylene/gm cat/hour.

Polymerization Example 4.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, 1.0 gm hydrogen/kg solvent, 0.46 gms of the supported catalyst prepared as in Catalyst Preparation 2, and tri-isobutylaluminium sufficient to give a 1.4 to 1 atomic ratio of aluminium to

chromium. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 415 psig. Polymerization began almost immediately as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all, 298 grams of polyethylene having a melt index of 1.45 and a high load melt index of 75 (HLM₁/MI=52) before homogenizing were recovered. Based on the catalyst charge of 0.46 gms the yield was 650 gms polyethylene/gm cat/hour.

Polymerization Example 5.

In a manner similar to that of Polymerization Example 4 but utilizing 0.60 gms of the catalyst from Catalyst Preparation 2 and without the tri-isobutylaluminum a polymerization of ethylene was carried out at 220°F and at a total pressure of 490 psig. Polymerization began immediately and after 1 hour the reaction was terminated and 510 gms of polyethylene having a melt index of 1.5 and an HLM₁ of 71 before homogenizing were recovered. Based on the catalyst charge of 0.60 gms the yield was 850 gms polyethylene/gm catalyst/hour.

Polymerization Example 6.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, 0.57 gms of the supported catalyst of Catalyst Preparation 3, and triethylboron sufficient to give a 2.7 to 1 atomic ratio of boron to chromium. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 435 psig. Polymerization began almost immediately as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all, 648 grams of polyethylene having a melt index of less than 0.1 and a high load melt index of 16.7 before homogenizing were recovered. Based on the catalyst charge of 0.57 gms the yield was 1137 gms polyethylene/gm cat/hour.

Polymerization Example 7.

To a stirred autoclave there were added 0.9 kg of isobutane, ethylene to a pressure of 130 psig to give 10 mole % in the liquid phase, and 0.53 gms supported catalyst of Catalyst Preparation 3 and sufficient tri-isobutylaluminum to give an Al/Cr atomic ratio of 1.5. The stirred autoclave with the above contents was heated to 200°F. At this time the total pressure was 390 psig. Following an induction period of about 30 minutes polymerization began as noted by the ethylene coming from the ethylene demand supply system to the reactor. After one hour of polymerization the reaction was terminated by dropping the reactor contents into the pressure let-down system. In all, 652 grams of polyethylene having a melt index of 0.07 and a high load melt index of 10.5 before homogenizing were recovered. Based on the catalyst charge of 0.53 gms the yield was 1230 gms polyethylene/gm cat/hour.

The use of various organophosphoryl chromium compounds in supported, heat treated catalyst systems for the polymerization of 1-olefins is further illustrated in the data set forth in Table I. In each of Tables I to IX the heat treatment involves heating the supported catalyst at the indicated temperature for the indicated period by passing heated dry air therethrough at a superficial linear velocity of 0.2 feet per second.

TABLE I

Various Organophosphoryl Chromium Compounds as Polymerization Catalysts

Organophosphoryl Chromium Compound (1)	Support (2), (3) Treatment (7)	% Cr/Base	Catalyst (6) Treatment	Al/Cr (4)	Productivity (5) gm Polymer/gm Cat/hr.	MI	HLMl	HLMl/MI
triethyl phosphate	1000°F/6 hrs. (2)	1.0	1112°F/2 hrs.	5/1	950	0.15	17.6	117
triethyl phosphate	neat (2)	0.88	1112°F/6 hrs.	2.6/1	735	0.07	10.0	143
triphenyl phosphate	1000°F/6 hrs. (2)	1.0	1112°F/6 hrs.	2.6/1	400	0.18	28.5	160
dibutyl phosphite	neat (3)	1.02	1650°F/6 hrs.	2.70/1	1076	2.1	103.0	49
diethyl phosphite	neat (3)	1.05	1650°F/6 hrs.	1.50/1	1313	0.70	49.6	71

(1) Reacted mole/mole CrO_3 to form the desired reaction product.(2) Base SiO_2 is Davison MS 952. (7) Treatment performed prior to coating the organophosphoryl chromium compound on the base, except for the cases marked "neat", where the support is not pretreated.(3) Base is Polypor silica gel with P.V. about 2.5 cc/gm. and surface area about $350\text{m}^2/\text{gm}$.

(4) Al added as tri-isobutylaluminum reducing agent.

(5) Polymerization temperature 200°F. Hydrogen concentration varied from 0.33 gm to 1.0 gm/kg solvent.

(6) Catalyst consists of the organophosphoryl chromium deposited on the support.

It is readily observable from the data shown in Table I that a variety of organo phosphorus/chromium trioxide reaction products are suitable for use in this invention, including those produced by the reaction of CrO_3 with phosphorus compounds having substituents which are alkyl or aryl.

In Tables II to IX the triethyl-, dibutyl- and diethylphosphoryl chromium compounds of the catalyst compositions used are obtained by the reaction of CrO_3 with triethyl phosphate, dibutyl phosphite and diethyl phosphite respectively.

Further illustration of the usage of this new catalyst is seen in Table II wherein polymerizations were conducted using triisobutylaluminium as reducing agent, but the Al/Cr ratio was varied. In addition it is also seen from the data in Table II that better catalyst productivity is found at an intermediate tri-isobutylaluminium concentration. Further the polymer flowability as indicated by the HLMI increases with increasing Al/Cr atomic ratios.

TABLE II

Effect of Tri-isobutylaluminium Concentration

Al/Cr	Productivity (gm Polymer/ gm Catalyst/Hr)	MI	HLMI
Triethyl phosphoryl Chromium (1)			
0.67	700	Low	4.8
1.33	1030	Low	5.8
2.63	342	Low	12.8
5.35	96	0.90	23.8
Dibutyl phosphoryl Chromium (2)			
1.35	644	1.45	75.9
2.70	1076	2.1	103

(1) Catalyst on POLYPOR silica gel (P.V. 2.3 cc/gm) air heat treated at 1110°F/6 hours. Catalyst contains approximately 1% chromium and 0.6% phosphorus.

(2) Catalyst on Polypor silica gel (P.V. 2.5 cc/gm) air heat treated at 1650°F/6hrs. Catalyst contains approximately 1% chromium and 0.6% phosphorus.

Polymerization Conditions

Temperature	— 200°F.
Solvent	— isobutane
Ethylene	— 10 mole %
Pressure (Total)	— 420 psig
H_2 Concentration	— 0.33 gm/kg solvent

As still further indication of the versatility of this catalyst, Table III shows the effect of increased polymerization temperature upon the MI of the polymer produced with the new catalyst system. In addition, it is to be noted that the triethyl phosphoryl chromium compound has been prepared using excess triethyl phosphate, for example, in a molar ratio of 2/1 of phosphate to CrO_3 without any deleterious effects.

TABLE III

Triethyl Phosphoryl Chromium (1)
Effect of Polymerization Temperature

Polymerization Temperature, °F.	Al/Cr (2)	Productivity gm Polymer/ gm Cat/Hour	MI
190	3.2	520	0.04
220	2.8	411	0.19

(1) Catalyst is triethyl phosphoryl chromium on Davison MS 952 at 1.0% chromium and 1.2% phosphorus air heat treated at 1110°F/6 hours.

(2) Aluminium as tri-isobutylaluminium.

Polymerisation Conditions

Solvent	— isobutane
Ethylene	— 10 mole %
Pressure (total)	— 380 psig
H ₂ Concentration	— 0.33 gm/kg solvent

A still further extension of this catalyst system is the type of base which may be used as support for the catalyst. In Table IV it is readily seen that either MgCO₃ or Al₂O₃ as well as SiO₂ are suitable supports for the catalyst. The heat treatment was conducted in air on the catalyst after deposition of the triethyl phosphoryl chromium compound on the indicated support.

TABLE IV

Triethyl Phosphoryl Chromium on Various Supports

Support	Air/Heat Treat Temperature °F/Hrs.	%Cr	%P	Al/Cr (1) Atomic Ratio	Productivity (g Polymer/ gm Catalyst/Hour)	Polymer	
						MI	HLMI
Al ₂ O ₃	1110/6 hours	1.0	0.6	3/1	70	—	0.43
MgCO ₃ (3)	1110/6 hours	1.0	0.6	3/1	8	—	NA
SiO ₂ (MS 952)	1110/2 hours	1.0	0.6	2.8/1	367	0.12	16.9

(1) Al as tri-isobutylaluminum

(2) Polymerization Conditions:

Solvent : Isobutane

Polymerization temperature °F. : 190–200°F.

Ethylene : 10 mole %

H₂ Pressure : 10–50 psig

Total Pressure : 370–435 psig

(3) Hydromagnesite from Newall's Ltd., England.

Still further work showing the broad scope of the air/heat treated supported catalyst is shown in Table V where a variety of reducing agents are used in conjunction with the air/heat treated supported catalysts.

TABLE V

Use of Various Reducing Agents with the Triethyl Phosphoryl Chromium Catalyst

Reducing Agent	X/Cr (7)	Polymer		Productivity (gm Polymer/gm Catalyst/Hour)
		MI	HLMI	
tri-isobutylaluminum (1)	2.7 (2)	0.20	26.5	400
triethylaluminum (1)	2.7 (2)	0.18	27.6	400
diethylaluminum ethoxide (1)	5.0 (2)	0.96	77.5	150
triethylboron (1)	4.0 (3)	0.11	19.9	280
triethylaluminum + triethylamino (m/m) (1)	2.8 (2)	0.32	70.2	55
triethylboron + tri-isobutylaluminum (10/1 m) (1)	3.7 (4)	—	7.0	320
triethylaluminum + dibutylmagnesium (1/6 m) (6)	3.5 (4)	—	12.5	2500
diethyl zinc (6)	2.0 (5)	0.21	26.6	610

(1) MS 952 supported triethylphosphoryl chromium (1% Cr) air/heat treated 1110°F./6 hours.

(2) Al/Cr (3) B/Cr (4) $\frac{B + Al}{Cr}$ or $\frac{Al + Mg}{Cr}$ (5) Zn/Cr (6) Catalyst on high pore volume (2.5 cc/gm) silica gel and air/heat treated at 1650°F/h hours

Polymerization Conditions

Solvent — Isobutane
10 mole % Ethylene
1.65 g H₂/Kg solvent, 435 psig total pressure
200°F. Polymerization Temperature.

(7) X/Cr is atomic ratio of metal or non-metal to Cr

The effect of TEB on silica gel supported organophosphoryl chromium catalysts is set forth in the data in Table VI.

TABLE VI

Effect of Triethylboron

B/Cr (2)	Productivity (g Polymer/ g Total Catalyst/Hour)	Mi	HLMI	HLMI/Mi
<u>Triethyl phosphoryl chromium (1)</u>				
No TEB	1030	0.1	11.0	110
2.7	1210	0.08	11.5	144
<u>Diethyl phosphoryl chromium (3)</u>				
2.7	418	low (4)	0.5 (4)	—
5.4	400	low (4)	5.5 (4)	—

(1) Catalyst on MS 952 gel (% wt. Cr + 0.6% wt. P) and air-heat treated at 1470°F. for 6 hours.

Polymerization condition (A)

(2) B/Cr atomic ratio. Boron as triethylboron.

(3) Catalyst on Polypor silica gel, air/heat treated at 1650°F/6 hours.

Polymerization conditions (B).

(4) Powder samples.

Polymerization Conditions	(A)	(B)
Reactor Temperature :	210°F.	200°F
H ₂ Pressure :	10 psig.	None
Total Pressure :	435 psig.	370 psig.
Solvent :	Isobutane	Isobutane
Ethylene :	145 psig.	145 psig.

The effect of using high pore volume silica xerogel as the support material is illustrated in Table VII.

TABLE VII

Triethyl Phosphoryl Chromium Catalyst On Silica Gels of Various Pore Volume

Silica Gel	P.V. (cc/gm)	Reducing Agent	P. Productivity (gms. Polymer/ gm Catalyst/Hour)	MI	Polymer Properties	
					HLMI	Density
MS 952 (1)	1.5	None	1030	0.1	11.0	.9558
POLYPOR (1)	2.3	None	1245	0.26	22.6	.9586
POLYPOR (1)	2.3	2.7/1 (2)	1798	0.23	18.6	.9515
POLYPOR (1)	2.3	5.4/1 (2)	1360	0.12	18.2	(not available)

(1) Catalyst on gel at 1% Cr and 0.6% P. MS 952 air/heat treated 1470°F./6 hours POLYPOR silica gel air/heat treated 1650°F./6 hours.

(2) B/Cr atomic ratio. Boron as triethylboron.

Polymerization Conditions

Reactor Temperature : 210°F.

H₂ Pressure : 10 psig.

Total Pressure : 435 psig.

Solvent : Isobutane

Ethylene : 145 psig.

The effect of TEB as a reducing agent using the high pore volume silica gel as catalyst support is also observed in Table VII. Here it is found that with only a slight change in the MI of the polymer an appreciable change occurs in the density when TEB is used as a reducing agent, i.e., the density of the polymer produced with this catalyst on the high pore volume silica gel may be controlled by using TEB as reducing agent. In addition, the effect of the use of triethylboron on the molecular weight distribution of the produced polymer is seen from Table VII. The molecular weight distribution (as measured by the HLMI/MI ratio) is increased from 91 when using the triethyl phosphoryl chromium catalyst on POLYPOR to 151 when triethylboron is included at 5.4/1 B/Cr ratio. This broadening of the molecular weight distribution contributes significantly to improved polymer shear response.

A further illustration of the versatility of this catalyst placed on high surface area silica gel (POLYPOR) is its response to hydrogen which results in an increase in the MI of the polymer produced with increased hydrogen pressure during the polymerization. This effect is illustrated in Table VIII.

TABLE VIII

Hydrogen Effect on Organophosphoryl Chromium Catalyst on POLYPOR (1)

H ₂ Pressure psig	Productivity (gms Polymer/ gm Catalyst/Hour)	B/Cr (2)	MI	HLMI
Triethyl Phosphoryl Chromium				
10	1363	5.4	0.12	18.2
20	992	5.4	0.21	20.4
50	1052	5.4	0.43	3.2
Diethyl Phosphoryl Chromium				
0	400	5.4	low	5.5
30	510	5.4	low	15.0
75	505	5.4	0.15	21.2

(1) Catalyst on POLYPOR silica gel at 1.0% Cr and 0.6% P and then air/heat treated 1650°F./6 hours. Polymerization condition (A).

(2) B/Cr atomic ratio: Boron as triethylboron.

Polymerization Conditions	(A)	(B)
Reactor Temperature	210°F.	200°F.
Solvent	Isobutane	Isobutane
Ethylene	137 to 145 psig	137 to 145 psig
Total Pressure	435 to 465 psig	435 to 465 psig

Compared with polymers produced with prior art catalyst systems, the polymers produced using the catalyst of this invention exhibit a better balance of end use

properties, including stiffness, stress crack resistance, and processability needed for blow molding resin.

For example, the following Table IX presents a comparison of properties for three resins produced under optimum commercial reactor conditions. Specifically, Resin A, the resin produced in accordance with this invention using triethylboron as part of the catalyst system is compared with polyethylene resins produced using conventional CrO_3 on SiO_2 catalysts.

TABLE IX

Comparison of Polymer End Use Properties

Resin Type	A	B	C
Melt Index	0.40	0.28	0.21
Density	0.954	0.953	0.953
Viscosity (1)	3.67	3.92	3.75
Stress Crack Resistance (2)	230	36	94
Flexural Stiffness, psi	115,000	110,000	111,000

(1) Poises $\times 10^{-3}$ at 1000 sec^{-1} shear rate.

(2) Hours to 50% failure, ASTM D-1693 Condition B (Modified)

Resin A was produced in a continuous slurry reaction system using catalyst prepared by supporting the triethyl phospheryl chromium compound on POLYPOR silica gel, and treated with dry air at 1650°F . for 6 hours and used in combination with triethylboron at a B/Cr atomic ratio of 2.4/1. Resin density was controlled by TEB addition only.

Resin B was produced in a continuous slurry reaction system using a state-of-the-art CrO_3 on SiO_2 catalyst prepared and run under optimum conditions. Density of the resin was controlled by the separate addition to the reaction of hexene-1 for copolymerization with ethylene.

Resin C is a melt blend of two resins both produced in a continuous slurry reaction system. For both component resins, state-of-the-art CrO_3 on SiO_2 type catalysts were utilized under conditions which resulted in optimum blend properties. Basically, Resin C is a blend of two different molecular weight resins which give a broader MWD product than Resin B. Density of the product is controlled by the separate addition of butene-1 for copolymerization of butene-1 in the high molecular weight component.

Inspection of Table IX clearly shows that Resin A has a better balance of properties than does the single reactor product, Resin B, or even the more expensive and difficult to prepare product, Resin C. That is, with at least equivalent processability (as noted by viscosity) the resin of this invention has superior stiffness and stress crack resistance. Thus, utilizing the polymer prepared in accordance with the precepts of this application permits blow molded articles of special value to be prepared efficaciously. While not wishing to be bound by any proposed mechanism, it is believed that the desirable properties of these structures may be attributed at least in part to the rheological behavior of the polymers produced in accordance with this invention under flow and deformation involved in the fabrication of end use articles, and the contribution of molecular weight balance to product characteristics. Control of polymer properties is achieved in this invention by selective utilization of catalyst systems as disclosed.

Optimally, polymer of significant shear sensitivity represented by HLMI/MI ratios of 40 or 50 or more is prepared, at melt indices ranging from below the measurable to 1 or 2.HLMI values will preferably range from 5 to 75.



WHAT WE CLAIM IS:—

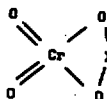
1. A catalyst composition comprising a solid inorganic support material having deposited thereon an organophosphoryl chromium product obtained by the reaction of chromium trioxide with an organophosphorus compound, said composition having been heated in a dry oxygen-containing atmosphere at a temperature above 400°F and below the temperature at which the structure of the support is impaired, and for a period of time sufficient to promote the polymerisation activity of said catalyst composition for the polymerisation of 1-olefins.

2. A composition according to claim 1 wherein said organophosphorus compound is an organophosphate or organophosphite.

3. A composition according to claim 2 wherein the organophosphorus compound is a trialkyl phosphate.

4. A composition according to any of claims 1 to 3 wherein organophosphoryl chromium product is obtained by reaction of said organophosphorus compound with chromium trioxide in equimolar ratio.

5. A composition according to any of claims 1 to 4 wherein said organophosphoryl chromium product is represented by the formula:



wherein X is $P(OR)_3$ or $PH(OR)_2$ and the R's are selected independently from alkyl, aralkyl, aryl cycloalkyl and hydrogen, at least one R being other than hydrogen.

6. A composition according to any of claims 1 to 5 wherein said organophosphoryl chromium product is present on the support material in an amount sufficient to provide from 0.25 to 2.5% by weight of Cr based upon the weight of the support material.

7. A composition according to any of claims 1 to 6 wherein said support material comprises silica gel.

8. A composition according to claim 7 wherein the support is a silica xerogel having a surface area of 200 to 500 m^2/g , a pore volume greater than 1.96 cc/g and wherein the major portion of said pore volume is provided by pores having pore diameters of 300 to 600 Å, said composition having been heat treated in a dry oxygen containing atmosphere at a temperature of 1000 to 2000° F for a period of from 2 to 12 hours.

9. A composition according to any of claims 1 to 8 including an organic reducing agent.

10. A composition according to claim 9 wherein the reducing agent is an organo-aluminium compound, and the atomic ratio of the aluminium of said reducing agent to the chromium of said organophosphoryl chromium reaction product is between 0.1/1 and 20/1.

11. A composition according to claim 10 wherein said reducing agent is an alkyl aluminium.

12. A composition according to claim 9 wherein the reducing agent is an organo-boron compound, and the atomic ratio of the boron of said reducing agent to the chromium of said organophosphoryl chromium reaction product is between 0.01/1 and 20/1.

13. A composition according to claim 12 wherein said reducing agent is triethyl-boron.

14. A process for the preparation of a catalyst composition comprising reacting chromium trioxide with an organophosphorus compound and depositing the resultant organophosphoryl chromium product upon a solid inorganic support material, heating said support material and said organophosphoryl chromium product in a dry oxygen containing atmosphere at a temperature above 400° F and below the temperature at which the structure of the support is impaired for a period of time sufficient to promote the activity of the composition for the polymerisation of 1-olefins.

15. A process according to claim 14 wherein the chromium trioxide and organo-phosphorus compound are reacted at a molar ratio of at least 1:1.

16. A process according to claim 14 or 15 wherein said organophosphorus compound is an organophosphate or organophosphite.

17. A process according to claim 16 wherein the organophosphorus compound is an alkyl phosphate.

18. A process according to claim 17 wherein the alkyl phosphate is triethyl phosphate.



19. A process according to any of claims 14 to 18 wherein the organophosphoryl chromium product is deposited from a solution in an inert solvent, and the deposition is proportioned such that there is provided on the support from 0.25 to 2.5% by weight of Cr based upon the weight of the support material.

20. A process according to any of claims 14 to 18 which includes reacting the chromium trioxide with an organophosphorus compound in an inert solvent medium to form a solution of dissolved organophosphoryl chromium product, contacting said solution with a solid inorganic support material of surface area of at least 100 m²/g, and removing the solvent, the organophosphoryl chromium product being in such proportion as to provide on the support from 0.25 to 2.5% by weight of Cr based upon the weight of the support material.

21. A process according to any of claims 14 to 20 wherein said support material is a silica gel.

22. A process according to claim 21 wherein said support material is a silica xerogel having a surface area of 200 to 500 m²/g, a pore volume greater than 1.96 cc/g, the major portion of said pore volume being provided by pores having pore diameters of 300 to 600 Å.

23. A process according to claim 22 wherein the heating in a dry oxygen containing atmosphere is conducted at a temperature of 1000 to 2000°F for a period of 2 to 12 hours.

24. A catalyst composition obtained by a process according to any of claims 14 to 23.

25. A process for the polymerisation of a 1-olefin comprising contacting said 1-olefin, alone or together with at least one copolymerisable comonomer, under polymerisation conditions of temperature and pressure, with a catalyst composition according to any of claims 1 to 13 and 24.

26. A process according to claim 25 wherein said support material comprises a silica xerogel having a pore volume in excess of 1.96 cc/g, the major portion of said pore volume being provided by pores having pore diameters of 300 to 600 Å.

27. A process according to claim 25 or 26 wherein the 1-olefin is contacted with said catalyst composition in the presence of an organic reducing agent.

28. A process according to claim 27 wherein said organic reducing agent comprises an organometallic compound.

29. A process according to claim 28 wherein said organometallic compound is an alkylaluminum, alkylaluminum halide or alkylaluminum alkoxide.

30. A process according to claim 29 wherein said reducing agent comprises triethylaluminum.

31. A process according to claim 29 wherein said reducing agent comprises triisobutylaluminum.

32. A process according to any of claims 29 to 31 wherein said organometallic compound is present in an amount sufficient to provide an aluminum to chromium atomic ratio of 1:1 to 5:1.

33. A process according to claim 27 wherein said reducing agent comprises triethylboron.

34. A process according to claim 33 wherein said triethyl boron is present in an amount sufficient to provide a boron to chromium atomic ratio of 0.1:1 to 10:1.

35. A process according to any of claims 25 to 34 wherein the polymerisation is conducted in the presence of hydrogen.

36. A process according to claim 35 wherein the hydrogen pressure is from 10 to 75 psig.

37. A process according to any of claims 25 to 36 from which there is recovered a polyolefin having a melt index of less than 2, a high load melt index of at least 25 and an HLMI/MI ratio of at least 40.

38. An olefin polymer comprising the product of a process according to any of claims 25 to 37.

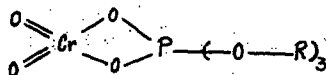
39. A structure blow moulded from an olefin polymer according to claim 38.

40. A blow moulded bottle according to claim 39.

41. A process for the preparation of a blow moulded article from an olefin polymer which employs an olefin polymer according to claim 38.

42. A catalyst composition comprising

(a) a compound having the general formula





wherein the R's are selected independently from alkyl, aralkyl, aryl and cycloalkyl, and

(b) a porous, solid, inorganic support material on which said compound is deposited, said composition having been heated in a dry oxygen containing atmosphere at a temperature above 400° F and below the temperature at which the structure of the support is impaired, and for a period of time sufficient to promote the polymerisation activity of said catalyst composition for the polymerisation of 1-olefins.

43. A composition according to claim 42 wherein said support material comprises at least one of silica, alumina and magnesium carbonate.

44. A composition according to claim 43 wherein said support material comprises silica gel.

45. A composition according to claim 44 wherein said support material comprises a silica xerogel having a pore volume in excess of 1.96 cc/g.

46. A composition according to any of claims 42 to 45 wherein said compound is a reaction product of chromium trioxide with a trialkyl phosphate or triphenyl phosphate.

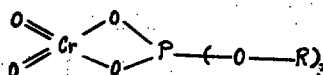
47. A composition according to claim 48 wherein said trialkyl phosphate is trimethyl, triethyl, tributyl or trioctyl phosphates.

48. A composition according to any of claims 42 to 45 wherein the R's are ethyl.

49. A composition according to any of claims 42 to 48 wherein said compound is present on said support material in an amount sufficient to provide from 0.25 to 2.5% by weight of Cr based upon the weight of the support material.

50. A process for preparing a catalyst composition comprising

(a) depositing upon a porous, solid, inorganic support material a compound having the general formula:



wherein the R's are selected independently from alkyl, aralkyl, aryl and cycloalkyl, and (b) heating the composition of step (a) in a dry oxygen containing atmosphere at a temperature above 400° F and below the temperature at which the structure of the support is impaired, for a period of time sufficient to promote the polymerisation activity of said catalyst composition for the polymerisation of 1-olefins.

51. A process according to claim 50 wherein said support material comprises at least one of silica, alumina and magnesium carbonate.

52. A process according to claim 51 wherein said support material comprises silica gel.

53. A process according to claim 52 wherein said support comprises a silica xerogel having a pore volume in excess of 1.96 cc/g.

54. A process according to any of claims 50 to 53 wherein said compound is a reaction product of chromium trioxide with a trialkyl phosphate or triphenyl phosphate.

55. A process according to claim 54 wherein said trialkyl phosphates is trimethyl, triethyl, tributyl or trioctyl phosphate.

56. A process according to any of claims 50 to 54 wherein the R's are ethyl.

57. A process according to any of claims 50 to 56 wherein said compound is present on said supporting material in an amount sufficient to provide from 0.25 to 2.5% by weight of Cr, based upon the weight of the support material.

58. A catalyst composition obtained by a process according to any of claims 50 to 57.

59. A process for the polymerisation of a 1-olefin comprising contacting said 1-olefin, alone or together with at least one copolymerisable comonomer, under polymerisation conditions of temperature and pressure, with a catalyst composition according to any of claims 42 to 49 and 58.

60. A process according to claim 59 wherein said 1-olefin is contacted with said catalyst composition in the presence of an organic reducing agent.

61. A process according to claim 60 wherein said organic reducing agent comprises an organometallic compound.

62. A process according to claim 61 wherein said organometallic compound comprises an alkylaluminium, alkylaluminium halide or alkylaluminium alkoxide.

63. A process according to claim 62 wherein said reducing agent comprises triethylaluminium.

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64. A process according to claim 62 wherein said reducing agent comprises tri-isobutylaluminium.

65. A process according to any of claims 61 to 64 wherein said organometallic compound is present in an amount sufficient to provide an aluminium to chromium atomic ratio in the range of from 1:1 to 5:1.

66. A process according to claim 60 wherein said reducing agent comprises triethylboron.

67. A process according to claim 66 wherein said triethylboron is present in an amount sufficient to provide a boron to chromium atomic ratio in the range of 0.1:1 to 10:1.

68. A heat-treated supported trialkyl- or triphenylphosphoryl chromium compound catalyst substantially as hereinbefore described in Catalyst Preparation 1, or in Example 1, 2 or 3, or in any one of Tables I to IX.

69. A process for preparing a heat-treated trialkyl- or triphenylphosphoryl chromium compound supported catalyst, the process being substantially as hereinbefore described in Catalyst Preparation 1 or in any of Tables I to IX.

70. An olefin polymerisation process employing a heat-treated supported trialkyl- or triphenylphosphoryl chromium compound catalyst, the process being substantially as hereinbefore described in Example 1, 2 or 3 or in any one of Tables I to IX.

71. An olefin polymer obtained by a process according to any one of claims 59 to 67 and 69.

72. A heat-treated supported dialkylphosphoryl chromium compound catalyst substantially as hereinbefore described in Catalyst Preparation 2 or 3, or in any one of Examples 4 to 7, or in any one of Tables I, VI and VIII.

73. A process for preparing a heat-treated supported dialkylphosphoryl chromium compound catalyst, the process being substantially as hereinbefore described in Catalyst Preparation 2 or 3, or in any one of Examples 4 to 7, or in any one of Tables I, VI and VIII.

74. An olefin polymerisation process employing a heat-treated supported dialkylphosphoryl chromium compound catalyst, the process being substantially as hereinbefore described in any one of Examples 4 to 7 or in any one of Tables I, VI and VIII.

75. An olefin polymer obtained by a process according to claim 74.

76. A blow moulded article comprising an olefin polymer according to claim 71.

77. A blow moulded article comprising an olefin polymer according to claim 75.

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