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"METHOD OF PREPARING ALUMINIUM PHOSPHATE GEL, AND USE THEREOF AS A SUPPORT FOR OLEFIN POLYMERISATION CATALYSTS"

This invention relates to the production of aluminium phosphate. The production of aluminium phosphate by combining aqueous solutions of an aluminium salt and a source of phosphate ions, such as phosphoric acid, followed by neutralisation with a base to give a precipitate or a true hydrogel is well known in the art. The resulting phosphate has been disclosed to have several utilities including use as a support for chromium oxide catalysts. There is considerable progression in the art with regard to the preparation of aluminium phosphate catalysts and the newer art suggesting forming the gel at a relatively high pH in order to obtain a higher surface area product. Generally, the art suggests converting the hydrogel to a xerogel by means of simple oven or tray drying or spray drying although it is incidentally taught in the art to wash with a water miscible liquid, such as an alcohol.

At least as it relates to a base for chromium catalysts, even the most advanced teachings of the prior art still do not produce a base which has found favour as a chromium catalyst support for olefin polymerization. Thus, chromium catalysts are generally supported on silica-containing bases similar to those used decades ago when the chromium catalyzed polymerisation of olefin polymers first became commercial.

The present invention seeks to produce a superior aluminium phosphate for use as a support for chromium- or vanadium- containing olefin polymerisation catalysts. In broad terms, this method comprises reacting an aluminium salt with a source of orthophosphate ions in a concentrated reaction mass containing no more than 40% by weight of added water, based on the weight of the aluminium salt, and thereafter neutralising the reaction mass with a base to precipitate the gel. In this method the concentrated reaction mass can be either a molten reaction mass comprising an aluminium salt in the molten state, preferably an aluminium salt having a melting point at or below the boiling point of water, or a concentrated syrup comprising a water-soluble aluminium salt and a very small amount of water i.e. not exceeding 40% by weight.

The method of this invention, whether using a molten reaction mass or a concentrated aqueous syrup, can be carried out according to either of two techniques, referred to herein as the first and second embodiments respectively.

In the first embodiment, the concentrated reaction mass, i.e. melt or syrup, comprising the aluminium salt and the source of orthophosphate ions is combined with a base to form a hydrogel, which can then be converted to a xerogel by the removal of water.

In the second embodiment, the concentrated reaction mass is partially neutralised by reaction with a neutralising agent, and then aged until gellation occurs. In this embodiment, the gel is formed at a strongly acid pH.

Generally, hydrated aluminium salts such as hydrated aluminium nitrate are most susceptible to being melted and thus are preferred as the source of aluminium ions for the melt method. Aluminium bromide and hydrated aluminium bromate can also be used as can, broadly, any aluminium salt which will melt. If desired, up to 20 weight percent additional water can be present based on the weight of the aluminium salt or there can be no water except the water, if any, from the water of hydration and the water, if any, from the base used in the subsequent neutralisation, i.e., no extraneous water is added. By additional water is meant water

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actually added as water and does not count the water, if any, from the water of hydration of the ingredients and/or the water, if any, from the base. There may be some advantage to adding 1 to 15 weight percent water based on the weight of the aluminium salt, however. The percentages of water are based on the actual weight of the aluminium salt including any water of hydration.

In the syrup method aluminium sulfate is ideally suited as the aluminium salt although aluminium salt such as aluminium nitrate can be used.

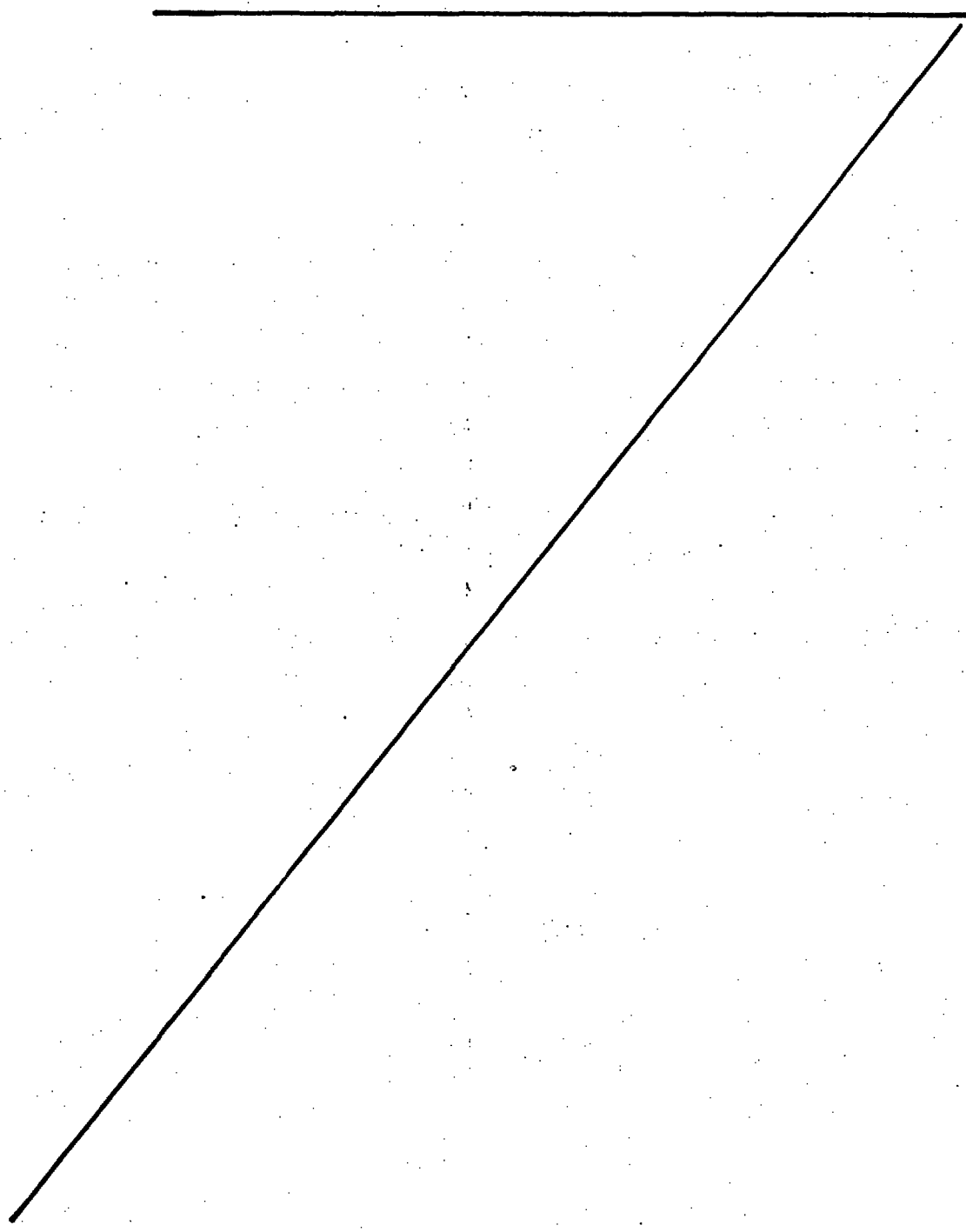
10 In the second embodiment there is an interrelation between the amount of water used, if any, and the degree of neutralisation. Less water or more neutralisation agent gives faster gellation, while more water and less neutralisation agent gives slower gellation. If no water, or an amount within the preferred range of 5 to 40 percent is used, then the 60 to 70 percent neutralisation is quite satisfactory to form the gel on aging with possibly even a little leeway on each end thereof. Generally, no gel will form at 56 percent neutralisation (56 percent of the stoichiometric amount of neutralising agent added) and generally gellation will occur spontaneously at about 72 percent so these extremes must be avoided. With these guidelines, it is easy to use the right combination of water, if any, and percentage neutralisation to give gellation on aging for 1 minute to 48 hours, preferably 5 minutes to 10 hours, more preferably 10 minutes to 3 hours.

25 In the second embodiment by complete (theoretical) neutralisation is meant that the final pH is 7. The range of about 60 to 70 percent neutralisation is based on the use of aluminium nitrate, monobasic ammonium phosphate and a P/Al ratio of 0.8. This would vary depending on the aluminium salt used, the phosphorus to aluminium ratio and would, of course vary in a manner easily calculated if dibasic ammonium phosphate or phosphoric acid were used. That is, if dibasic ammonium phosphate is used, then one less mole of base per mole of phosphate is needed and if phosphoric acid is used one more mole of base per mole of phosphate is needed.

35 In any event enough is used to give a pH below 4 and to cause gellation after a reasonable period of aging.

The source of the phosphate ions can be any source of orthophosphate ions and is generally orthophosphoric acid or orthophosphates, such as monobasic ammonium phosphate or dibasic ammonium phosphate or mixtures thereof. Of the ammonium phosphates, the monobasic is preferred.

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The temperature, if a melt is used, can be any temperature at or above which the aluminum salt chosen will melt. The reaction can be carried out in any atmosphere including air or can be carried out under an inert atmosphere for instance. Generally, temperatures of 65-200°C, preferably 65-100°C are used. Although, since the preferred aluminum salt is $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ which melts at 73°C, the most preferred temperatures based on the use of this aluminum salt is about 80°C + 5°C. If a very concentrated syrup of a water soluble aluminum salt and water is used, any temperature up to the boiling point of the syrup under the conditions employed can be used, preferably about 20 to about 150°C or 20 to about 100°C.

Since very little water, if any, is present during the formation of the aluminum phosphate, it is not necessary to utilize azeotropic distillation or washing with a normally liquid water miscible organic solvent to remove the water gently although azeotropic distillation or washing with a normally liquid water miscible organic solvent can be the preferred method of removing water. Also, the concentrated mass gives a gel with greater physical strength. Finally, olefin polymerization chromium catalysts supported on such a base have higher activity and less tendency for activity to drop off during polymerization of the monomer.

It has been found that low pore volume hydrogels usually give the highest porosity xerogels after drying because they have superior internal strength to withstand the compression of surface tension during the drying. Thus, if the hydrogel occupies 10 cm^3 per gram of aluminum phosphate or less, generally 3 to 6 cm^3 per gram, it will give a xerogel having improved porosity for a catalyst base than will a hydrogel conventionally prepared from a dilute aqueous solution which will occupy about 11 cm^3 per gram or more. By 6 cm^3 per gram, for instance is meant that each gram of any aluminum phosphate occupied 6 cm^3 in the hydrogel stage. Thus, another way to define the concentrated mass is that the aluminum salt melt/phosphate mass or aluminum syrup/phosphate mass is sufficiently concentrated so as to give a hydrogel which occupies 3 to 6 cm^3 per gram. The theoretical minimum if no extraneous water is added is about 3 cm^3 per gram with aluminum nitrate.

The following representative calculations of the volume per gram of concentrated mass of invention preparations, the further calculation showing the same mathematics for a run of the prior art and the two further calculations showing the same mathematics for a dilute system are presented to facilitate an understanding of the meaning of the concept of

the final dry aluminum phosphate having occupied a relatively small number of cm^3 per gram in the prior hydrogel stage. These calculations are based on the use of one quarter mole of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and about one-fifth mole monobasic ammonium phosphate plus sufficient $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ to give one weight percent chromium in the final catalyst. The slight disparity between the mole ratio of aluminum nitrate to aluminum phosphate reflects the desire to have a phosphorus to aluminum ratio of 0.8 in the final phosphate. It has been found experimentally that this amount of material when the aluminum nitrate is melted and the other ingredients added thereto occupies about 90 cm^3 . If it is gelled, by partial neutralization in the second embodiment, with ammonia gas, the ammonia gas will add no appreciable amount to the volume and the volume of the gel is approximately equal to the volume of the melt. This, then, gives one quarter mole of low phosphorus aluminum phosphate which weighs 27 grams when washed of salts and dried. As previously set out, this amount of material in the hydrogel stage occupied 90 cm^3 . Ninety cm^3 divided by 27 cm^3 is 3.3 cm^3 per gram representing approximately the theoretical minimum space which one gram of dry aluminum phosphate can occupy when in the hydrogel state. This might vary slightly if other proportions or types of starting ingredients were used.

In the first embodiment more typically, however, neutralization will be carried out in accordance with the invention by neutralizing with 46 cc of ammonium hydroxide per one quarter mole. This then will add 46 cc to the 90 cc volume obtained with no water added in the neutralization to give a total of 136 cc which will still produce the same 27 grams of ammonium phosphate when washed of salts and dried. One hundred thirty-six divided by 27 equals 5.0 which is the volume in cc occupied in the hydrogel state by one gram of final dry ammonium phosphate in this preparation.

In the first embodiment in many runs, a very small amount of water, for instance 10 cc were added to the melt giving a total volume of 100 cc instead of 90. Then on adding 46 cc of ammonium hydroxide, the total volume would be 146 which would still produce 27 grams of dry ammonium phosphate. One hundred forty-six divided by 27 equals 5.4 cc of hydrogel which give one gram of final dry aluminum phosphate.

In the first embodiment even if 40 percent water based on the aluminum salt is used this is still a very small amount of water overall. For instance, 40 percent of 93 grams, the weight of one quarter mole $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is only 37 cc which added to 136 cc gives a total volume of hydrogel of 173 cc, which divided by 27 grams is 6.4 cc per gram.

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Compared to the first embodiment, in the prior art, typically 0.2 to 2 liters of water are utilized with one quarter mole of ingredients. Taking the lower end of this typical preparation of 0.2 liter, this added to the 136 cc obtained when no water is added would give 336 cc total volume divided by the 30 grams of product would give about 11 cc per gram. A more typical prior art preparation utilizing about one liter of water with one quarter mole of ingredients would give 1136 cc which divided by 27 would be 42 cc per gram.

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In the first embodiment if it is desired to wash the hydrogel with water, then ^{AZEOTROPIC}azeotropic distillation or washing with a volatile, oxygen-containing watermiscible organic solvent having a relatively low surface tension is desirable (adding water after the gel is formed does not harm the pore structure if it is removed gently as just described). After drying of water in this manner, the gel is preferably dried of solvent under mild conditions, for instance by heating at a temperature of 25° to about 150°, most preferably under vacuum.

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In the second embodiment more typically, however, neutralization of the concentrated mass will be carried out by partially neutralizing it with concentrated ammonium hydroxide. Complete neutralization (obtaining 30 g of hydrogel of pH 7) would require 46 cm³ of ammonium hydroxide per one quarter mole. Partial neutralization with, for instance, two-thirds of this would require 31 cm³. This then will add 31 cm³ to the 90 cm³ volume obtained with no water added in the neutralization to give a total of 121 cm³ which will still produce the same 27 grams of ammonium phosphate when washed of salts and dried. One hundred twenty-one cm³ divided by 27 cm³ equals 4.5 which is the volume in cm³ occupied in the hydrogel state by one gram of final dry ammonium phosphate in this preparation. By concentrated ammonium hydroxide is

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meant an aqueous solution containing about 30 weight percent ammonia.

5 In the second embodiment if a very small amount of water, for instance 10 cm^3 were added to the melt, this would give a total volume of 100 cm^3 instead of 90 cm^3 . Then on adding 31 cm^3 of ammonium hydroxide, the total volume would be 131 cm^3 which would still produce 27 grams of dry ammonium phosphate. One hundred thirty-one cm^3 ^{DIVIDED} ~~divided~~ by 27 cm^3 equals 4.9 cc of hydrogel which give one gram of final dry aluminum phosphate.

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In the second embodiment even if 40 percent water based on the aluminum salt is used, this is still a very small amount of water overall. For instance, 40 percent of 93 grams, the weight of one quarter mole $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ is only 37 cm^3 which added to 121 cm^3 gives a total volume of hydrogel of 158 cm^3 , which divided by 27 grams is 5.9 cm^3 per gram.

Compared to the second embodiment, in the conventional dilute systems, typically 0.2 to 2 liters of water are utilized with one quarter mole of ingredients. Taking the lower end of this typical preparation of 0.2 liter, this added to the 136 cm^3 obtained when no water is added (the prior art would use complete neutralization which would require 36 cm^3 not 31 cm^3) would give 336 cm^3 total volume divided by the 27 grams of product would give about 12 cm^3 per gram. A more typical conventional preparation utilizing about one liter of water with one quarter mole of ingredients would give 1136 cm^3 which divided by 27 cm^3 would be 42 cm^3 per gram. Thus, even the largest amount of water contemplated in this invention, 200 percent based on the aluminum salt is a relatively small amount.

While low phosphorus aluminum phosphate may be thought of for convenience as a mixture of alumina and aluminum phosphate, it is not, but rather is a gel with some of the trivalent PO_4 groups replaced with trivalent AlO_3 groups.

It may be desirable in some instances to coprecipitate other materials such as titania with the phosphate or have other materials present during the gellation and/or activation such as fluoride. For instance, if the purpose is to produce a support for a chromium catalyst, the chromium compound such as chromium nitrate or CrO_3 or chromium acetate can be introduced with the reactants. Similarly, a silicon compound, such as silicon tetraethoxide can be coprecipitated with the phosphate.

When the object is to produce a catalyst base, it is frequently preferred that a small amount of a boron compound, such as boric acid, be introduced into the concentrated mass to be coprecipitated with the aluminum phosphate. Other suitable boron compounds include borates, such as ammonium borate. By coprecipitated as it relates to the boron compound, it is meant that the aluminum phosphate is formed into a true hydrogel in the presence of the boron compound. It is not known to what extent the borate becomes incorporated in the hydrogel structure. The amount of boron compound present when the aluminum phosphate is gelled can vary widely but it is generally used in an amount so as to give 1 to 30 mole percent boron compound based on the moles of phosphate.

In the first embodiment the gellation is generally brought about by neutralization carried out either by adding the acid phase, i.e., the aluminum salt/phosphate combination, to a base phase or vice versa. One suitable practice is to drip or spray or otherwise slowly introduce the acid phase into the base phase. This results in the production of small spheres or balls of the orthophosphate when the melt of the aluminum salt and the source of phosphate ions is dripped or sprayed or otherwise slowly added to a large excess of ammonium hydroxide. The spheres are subsequently collected, washed, dried, and if desired calcined.

In the first embodiment gellation occurs spontaneously at a pH of about 4, which is achieved by combining about 72 percent of the neutralizing agent, and it has been found that this is undesirable. Therefore, neutralization is preferably achieved by either: (1) combining slowly with stirring about 72 percent of the amount of neutralizing agent needed for complete neutralization and thereafter quickly adding the rest so as to quickly go through the 4 to 5 pH range and achieve gellation at a pH of 5 or greater, preferably at least 6, generally 6 to 10, or (2) combining 60 to 70 percent of the neutralizing agent needed for complete neutralization and aging until gellation occurs which will generally be 1 minute to 48 hours, more generally 5 minutes to 10 hours, more generally 10 minutes to 3 hours; thus, gellation occurs at a pH below 4, generally about 2.

Also ethylene oxide or propylene oxide or ammonium carbonate or any agent which will neutralize the acid can be used alone or in combination to effect gellation.

In the second embodiment the gellation must be brought about by partial neutralization followed by aging. This can be carried out either by adding the acid phase, i.e., the aluminum salt/phosphate combination, to a neutralizing agent phase or vice versa (or by adding both to a third vessel). One suitable practice is to slowly introduce the neutralizing agent into the acid phase with stirring.

In the second embodiment as stated above, the neutralization must be only partial neutralization so that gellation does not occur immediately but does occur after a reasonable aging time. Surprisingly, this is a relatively narrow range. While gellation can be brought about at a pH anywhere from 4 to 10 or more as is known in the prior art, if the pH is low, i.e., below 5, a poor quality gel forms. However, if about 60 to 70 mole percent of the theoretical amount of neutralizing agent is added, based on the exact amount needed for complete neutralization using monobasic ammonium phosphate, and the composition is allowed to sit, gellation occurs under acid conditions but without the bad characteristics associated in the prior art with gelling at an acid pH. Indeed, the results are superior even to gelling at an alkaline pH. The aging can be carried out at any convenient temperature from 0°C to 100°C, for instance, and in any nondeleterious atmosphere. For convenience and economy, this is generally done at room temperature in air. Of course, if the melt method is used and the gelling occurs in a matter of minutes, the composition will still be warm.

In the second embodiment the neutralizing agent is usually a base such as gaseous ammonia or concentrated ammonium hydroxide. Also, ammonia dissolved in alcohol can be used. Also ethylene oxide or propylene oxide or ammonium carbonate or any agent which will neutralize the acid can be used alone or in combination.

In the second embodiment if it is desired to wash the hydrogel with water, then azeotropic distillation or washing with a volatile, oxygen-containing water miscible organic solvent having a relatively low surface tension is desirable (adding water after the gel is formed does not harm the pore structure if it is removed gently). After drying of water in this manner (i.e. replacing the water with the organic liquid), the gel is preferably dried of solvent under mild conditions, for instance by heating at a temperature of 25° to about 150°C, most preferably under vacuum. Also, if the purpose is to make a catalyst, it is generally desirable to wash with a base after gellation, preferably ammonium hydroxide or a

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substituted ammonium hydroxide such as tetramethylammonium hydroxide. Generally, the base will be in water but it can be in an organic solvent. Thus, in this preferred sequence, the gel is washed with an aqueous base and then water removed with the normally liquid organic compound as previously described.

The resulting aluminum phosphate can be utilized as a filler in rubber or plastics, as a catalyst, or as a base for vanadium or chromium so as to produce a catalyst for olefin polymerization.

In the case of chromium, the chromium-containing xerogel must be activated in an oxidizing ambient. This can be carried out either by having chromium coprecipitated with the hydrogel or adding chromium to the hydrogel or adding an anhydrous solution of a chromium compound to the xerogel and thereafter heating in an oxidizing ambient such as air. The chromium or vanadium is present in an amount within the range of 0.001 to 10, preferably 0.1 to 5, more preferably about 1 weight percent based on the weight of the dried support. The activation of the thus formed xerogel can be carried out at a lower temperature than is generally required for activating silica-based chromium catalysts. Temperatures of 150-800°C, preferably 300-800°C, more preferably 300-700°C, and times of 1 minute to 48 hours, preferably 0.5 to 10 hours are suitable. Alternatively, the activation can be carried out in any ambient under dry conditions and thereafter a zerovalent chromium, for instance π -bonded organochromium compounds such as dicumene chromium or dibenzene chromium, added anhydrously. Any ambient can also be used when the support is used to carry vanadium.

If the purpose is to produce a chromium catalyst support, the aluminum and phosphorus components are selected so as to give an atom ratio of phosphorus to aluminum within the range of 0.2:1 to 1:1, preferably 0.6:1 to 0.9:1. Broadly, however, any ratio, for instance from 0.1:1 to 2:1 can be used.

Vanadium can be combined with the support by coprecipitating a vanadium compound with the phosphate-containing support, by adding a vanadium compound to the support at the hydrogel stage, or by adding a vanadium compound anhydrously to the xerogel. Suitable vanadium compounds include ammonium vanadate, vanadyl sulfate, vanadium tribromide, vanadium di or trichloride, vanadium tri or pentafluoride, vanadyl dibromide and vanadyl tribromide, vanadyl trichloride or other water soluble vanadium compounds. Vanadium acetylacetonate and other

hydrocarbon soluble vanadium compounds can be used to impregnate the xerogel.

The catalysts produced using the base prepared by the novel method of this invention containing a chromium or vanadium compound thereon can be used to polymerize at least one mono-1-olefin containing 2 to 8 carbon atoms per molecule, such as ethylene, propylene, 1-butene, 1-pentene, 1-hexene and 1-octene. Such catalysts are of particular applicability in producing ethylene homopolymers and copolymers of ethylene and one or more comonomers selected from 1-olefins containing 3 to 8 carbon atoms per molecule such as propylene, 1-butene, 1-pentene, 1-hexene and 1-octene. These polymers can be produced by solution polymerization, slurry polymerization, and gas phase polymerization using conventional equipment in contact and processes. Contacting of the monomer or monomers with the catalyst can be effected by any manner known in the art of solid catalyst. One convenient method is to suspend the catalyst in an organic medium and to agitate the mixture to maintain the catalyst in suspension throughout the polymerization process. Typically, predominantly ethylene copolymers are prepared using 0.5-20 weight percent comonomer as described above in the feed, preferably sufficient comonomer to give 97 to 99.6 weight percent polymerized ethylene units in the resulting copolymer.

When the novel method of making a phosphate of this invention is used to make a phosphate for a catalyst base for a chromium or vanadium olefin polymerization catalyst, the resulting catalyst can be used in conjunction with a cocatalyst if desired. Suitable cocatalysts include organometal compounds primarily aluminum and boron alkyls. The most preferred boron compounds are trihydrocarbylboron compounds, particularly trialkylboron compounds, such as tri-n-butylborane, tripropylborane, and triethylborane (TEB). Suitable aluminum alkyls include R_3Al , R_2AlX , and RA_2X_2 where R is a 1 to 12 carbon atom hydrocarbyl radical and X is a halogen preferably chlorine. Triethylaluminum and diethylaluminum chloride are particularly suitable.

Hereinafter Examples I to III relate to embodiment 1 and Examples IV and V to embodiment 2.

Example I

A number of samples of aluminum phosphate were made in accordance with this invention and used as a base for a chromium catalyst by the following general techniques. The desired quantity of an aluminum salt such as $Al(NO_3)_3 \cdot 9H_2O$, e.g., about 1 lb. (454 g), was heated to about 80°C to form a melt. The desired quantity of an ammonium phosphate, e.g., $NH_4H_2PO_4$, was dissolved in the melt to provide the

atomic ratio of P/Al needed, and finally the desired amount of chromium(III) acetate or chromium(III) nitrate was added to the melt mixture to provide about 1 weight percent chromium based on the weight of the dry, finished catalyst. Sufficient concentrated NH_4OH , e.g., 30 weight percent NH_3 , was mixed with the melt mixture to neutralize it giving a pH of about 6 to 7. The resulting mixture was washed with sufficient deionized water to remove substantially all of the ammonium nitrate by-product and the washed product in turn was washed with isopropyl alcohol or other volatile water-miscible organic liquid to displace the water or azeotrope dried. The resulting product was further dried in a vacuum oven and activated in a fluidized bed in dry air for about 5 hours at the specified temperature.

Alternatively, the melt containing the $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, the $\text{NH}_4\text{H}_2\text{PO}_4$ and the $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ can be treated with NH_4OH to obtain a pH of about 6 to 7 to form the gel and the gel dried in the presence of the by-product NH_4NO_3 . While this is essentially a non-aqueous system, there is a small amount of water present such that a sheet of pH indicator paper can be pressed into the gel and a pH reading obtained. The dry product can then be cautiously calcined to obtain the final catalyst. This procedure must be done carefully to avoid potential explosions or other undesired reactions.

Example II - Ethylene Polymerization

Each run was conducted in a clean, dry, air-free, stirred, stainless steel reactor of about a 2 L capacity. About 600 g of isobutane was used in each run as diluent with a catalyst charge ranging from about 0.03 to about 0.8 g. The reactor and its contents were heated to the desired operating temperature, ethylene was pressured in to give about 565 psia (3.9 MPa), and the run was started immediately as the catalysts, unlike the corresponding chromium oxide-silica catalysts, do not have an induction period. Ethylene pressure was maintained during the run by supplying additional ethylene as required from a reservoir.

Each run was terminated by stopping the ethylene flow and venting the gaseous reactor contents to a flare line for disposal. The polymer was recovered, dried and weighed to determine catalyst productivity which is expressed in terms of grams polyethylene per gram catalyst. When used as a reactor additive (add.) triethylborane (TEB) was added to the reactor as 1 weight percent solution in n-heptane. Hydrogen, when used, was admitted to the reactor to provide 50 psi (0.34 MPa) partial pressure of the total 565 psia reactor pressure.

The physical properties of each polymer, in this and subsequent examples, when given, were determined in accordance with the following ASTM test procedures.

- 5 Melt index (MI) ASTM D 1238-65T, Condition E.
 High load melt index (HLMI) ASTM D 1238-65T, Condition F.
 Density, g/cc ASTM D 1505-68.

10 The HLMI/MI ratio is thought to give an indication of the polymer molecular weight distribution or shear response. As the ratio increases, the molecular weight distribution is also thought to increase.

15 The heterogeneity index (HI) is thought to provide a more accurate representation of polymer molecular weight distribution. HI is determined from the weight average and number average molecular weight values obtained from size exclusion chromatography and is defined as the ratio of weight average to number average molecular weights. As the ratio increases, the molecular weight distribution is thought to broaden.

20 Ethylene polymerization was carried out with samples of the catalysts activated at different temperatures and the results are summarized in Table I.

Table I

Gel Mass Concentration

Run No.	Act. Temp. °C	Prep.	P/Al	Add.	Run Temp. °F	Prod. g/g	Time min.	MI	HUMI/MI
5									
1 Control	500	Aq-Az (1)	1.0	None	205	1725	90	0 (.74 H) (6)	-
2 Control		Aq-Az (1)		8 ppm TEB	(96°C)	3565	65	.43	373
3 Control		Aq-Az (1)		H ₂		1400	90	.30	152
4 Control		Aq-Az (1)		8 ppm TEB + H ₂		2515	50	11.4	57
10									
5 Control	700	Aq-OD (2)	0.9	None	225	605	90	0 (.86 H)	-
6 Control		Aq-OD (2)		8 ppm TEB	(107°C)	509	60	1.2	144
7 Control		Aq-OD (2)		H ₂		427	100	0.95	104
8 Control		Aq-OD (2)		8 ppm TEB + H ₂		605	90	32	47
15									
9 Invention	700	Melt-Az (3)	.8	None	205	3844	60	0 (.76 H)	-
10 Invention		Melt-Az (3)		4 ppm TEB	(96°C)	9420	60	1.41	122
11 Invention		Melt-Az (3)		4 ppm TEB + H ₂		5340	60	6.8	64
20									
12 Invention	500	Melt-Az (3)	.8	None	205	3135	60	0 (.37 H)	-
13 Invention		Melt-Az (3)		4 ppm TEB	(96°C)	5440	60	.51	143
14 Invention		Melt-Az (3)		4 ppm TEB + H ₂		5605	60	3.15	73
15									
15 Invention	600	Melt-OD (4)	.8	4 ppm TEB	205	3010	90	.03	533
16 Invention	600	Melt-Az (5)	.8	4 ppm TEB	205	2230	60	.04	511

- (1) Aqueous precipitation and azeotrope drying, i.e., a conventional dilute mass.
- (2) Aqueous precipitation and oven drying, also a conventional dilute mass.
- 5 (3) Hydrogel formed from melt but then water added to wash followed by azeotropic drying. This demonstrates the effect of a concentrated mass at the critical time, i.e., when the reactants are combined and shows subsequent addition of water not being harmful.
- (4) Hydrogel formed from melt but then water added to wash followed
10 by oven drying, i.e., also a concentrated mass during gellation. In this run, 469 g (1.25 mole) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and 3.98 g boric acid were used with sufficient monobasic ammonium phosphate to give the P/Al ratio of 0.8. Some water (125 mL) was in the melt and the melt was dripped into concentrated ammonium hydroxide.
- 15 (5) Like (4) except washed in alcohol and the alcohol removed in a vacuum oven. While the productivity is not outstanding in this run, other runs gave better overall results. One other run similar to this except without boric acid and using aluminum sulfate instead of aluminum nitrate gave 3,200 grams polymer
20 per gram of catalyst in 25 minutes.
- (6) "H" indicates HLMI.

Runs 9-16 show a general advantage to the use of the melt technique in productivity and/or melt index.

Example III

25 A series of aluminum phosphate gels was prepared by employing the melt technique and several variations thereof as shown below in which a melt was formed from 94 g (0.25 mole) of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 23 g (0.2 mole) of $\text{NH}_4\text{H}_2\text{PO}_4$, and 2.4 g (0.006 mole) of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ by application of gentle heat to give a volume of about 100 mL at a temperature of about
30 80°C. The calculated P/Al atomic ratio is about 0.8:1. To the melt was added with vigorous stirring, 46 mL (0.72 mole NH_3) of concentrated NH_4OH (30 weight percent NH_3). The reaction mass at a pH of about 6 to 7 set to a hard gel, which was thoroughly washed with hot, deionized water and the washed product divided in two approximately equal portions.

35 Portion 1 (catalyst 1 base or support) was dried overnight (about 15 hours) in a vacuum oven at 80°C.

Portion 2 (catalyst 2 base) was dried of water by azeotrope distillation with isoamyl alcohol. The alcohol was removed by heating at 60°C in a vacuum oven.

Catalyst 3 base was prepared in the manner used for catalyst 2 base except that in the gelling step the 100 mL of melt was diluted to 200 mL with water (100 mL water) and to it was added 46 mL of concentrated NH_4OH .

5 Catalyst 4 base was prepared in the manner used for catalyst 2 base except that in the gelling step the 100 mL of melt was diluted to 400 mL with water (300 mL of water) and to it was added 46 mL of concentrated NH_4OH .

10 Catalyst 5 base was prepared in the manner used for catalyst 2 base except that gelling occurred before all the ammonium hydroxide solution was added because of slow addition right up to the end. The pH was about 3 to 4 at this stage and the gel was washed and dried as for catalyst 2 base. This shows that the pH during gelling should be about 5 or above if gellation is to be forced by combination with base until
15 gellation occurs. Partial neutralization followed by aging will give a good product, however.

Catalyst 6 base was prepared by gelling 100 mL of the melt with 46 mL of concentrated ammonium hydroxide as described at the beginning of this Example. The resulting gel was dried overnight in a vacuum oven at
20 80°C without removal of the salt by-product.

Catalyst 7 base was prepared in the manner used for catalyst 2 base except that in the gelling step the 100 mL of melt was gelled with a solution of 46 mL of NH_4OH diluted to 100 mL.

A portion of each catalyst base was then activated at 500°C for
25 5 hours as before. The surface areas of the recovered, activated catalysts were then determined by the B.E.T. nitrogen sorption method as known in the art.

A portion of each catalyst was tested in ethylene polymerization at 96°C using 4 ppm TEB as adjuvant in each run.

30 The surface area of each catalyst and its productivity in terms of grams polymer per g catalyst per hour are given in Table II.

Table II

Effect Of Gel Mass Concentration

	Catalyst Base	Catalyst Base	Catalyst Surface Area, m ² /g	Productivity g/g cat/hr	Remarks
5	1 Invention	Concentrated	330-380 (a)	2540	washed, oven dried
	2 Invention	Concentrated	330-380 (a)	3955	washed, azeotrope dried
	3 Control	Dilute	254	3540	diluted before gelling
	4 Control	Dilute	223	3020	diluted before gelling
	5 Invention	Concentrated	493	dead	gel at acid pH
10	6 Invention	Concentrated	330-380 (a)	4160	unwashed, oven dried
	7 Control	Dilute	269	2485	diluted before gelling

(a) Estimated surface area based on similar preparations.

Runs 1, 2, and 6 show an advantage for preparing the base in accordance with the invention utilizing the melt technique as compared with runs wherein the melt was diluted with water to give, in effect, a conventional aqueous system. Run 1 of Example II compared with run 5 of Example I shows even more the advantage for the melt preparation compared with the conventional aqueous preparation so far as productivity is concerned.

As can be seen, in every instance higher surface area was obtained by gelling from a concentrated mass.

10

Example IV

A melt of 1,230 grams of $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ plus 302 grams of $\text{NH}_4\text{H}_2\text{PO}_4$ and 75 grams $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (about 5 percent chromium in the final catalyst) plus 50 cm^3 water was made. The final volume after heating to melt to form a homogeneous syrup was 1,200 cm^3 .

Of this 1,200 cm³, a 200 cm³ first aliquot was put into a blender and very slowly 70 cm³ concentrated ammonium hydroxide was added. This is 56 percent of the theoretical 125 cm³ needed for complete neutralization. The liquid got hot and was poured into a beaker and
5 allowed to stand for 24 hours but did not gel.

A second 200 cm³ aliquot of the melt was put into a blender as above and very slowly 80 cm³ of concentrated ammonium hydroxide was added. After blending together the liquid is poured into a beaker. After 3 hours, it got thick. After 24 hours, it resembled jello. Eighty
10 cm³ is 64 percent of the theoretical amount needed for complete neutralization.

A third 200 cm³ aliquot of the basic melt was put in a blender and very slowly (over 2 minutes) 85 cm³ of concentrated ammonium hydroxide was added. The resulting liquid was poured out into a beaker.
15 It turned into a hard gel in about 10 minutes at a pH of about 2.

A fourth 200 cm³ aliquot of the basic melt was placed in a blender and very slowly 90 cm³ of concentrated ammonium hydroxide was added. It gelled before it could be taken out of the blender. This represents 72 percent of the theoretical amount of neutralizing agent
20 required for complete neutralization.

A fifth 200 cm³ aliquot of the melt was placed in a blender with 50 cm³ of water and 90 cm³ of the ammonium hydroxide was slowly added. The solution got hot and was poured into a beaker. Nothing happened in 10 minutes. It was put back in the blender, another 5 cm³ of
25 ammonium hydroxide added and it got thick. It was poured into a beaker and gelled during the operation of pouring it into the beaker.

The liquid from the first aliquot to which 70 cm³ of ammonium hydroxide were added and which had not gelled after 24 hours was put back in a blender and 10 cm³ additional ammonium hydroxide added whereupon it
30 gelled immediately in the blender. These runs demonstrate that about 56 percent neutralization is too little to effect gellation after a reasonable aging time and that about 72 percent is too much causing immediate gellation which would be, of course, under acid conditions which is believed in the prior art to be bad. These data further show
35 that when about two-thirds (60 to 70 percent) of the amount of base needed for gellation is used, gelling will occur under acid conditions after a waiting period. These results also show that there is an interrelationship between the amount of dilution and the amount of base

used with dilution tending to inhibit gellation and additional base, of course, tending to expedite it.

Example V

A melt was made as in Example IV and neutralized by slow addition with stirring of two-thirds of the ammonium hydroxide needed for complete neutralization. This made a solution with a pH of about 2 which was set aside to cool. Within an hour, it was hard. After about three hours, it was knocked out of the beaker as a hard brick. The next day, the brick was split into four pieces which were each crushed, washed and dried as follows:

A1: Washed with three volumes of hot water. The particles fell apart into a mush. It was then dried in a vacuum oven at 60°C.

A2: The same water wash was used as in A1 and then the gel was washed three times with acetone, and dried under a vacuum oven.

A3: The third aliquot was washed with three volumes of hot water to which had been added ammonium hydroxide to make a pH of 8 to 9 and was oven dried under vacuum at 60°C.

A4: This was treated in the same manner as A3 except it was washed three times with acetone before the oven drying.

All four samples were activated in air 5 hours at 700°C.

Ethylene was polymerized under particle form conditions in a stirred, stainless steel reactor of about 2 L capacity employing about 600 g of isobutane as diluent in each run with a catalyst charge ranging from about 0.03 to about 1.2 g, and in the presence of 1 mL of a hydrocarbon solution of triethylborane (TEB). The reactor and its contents were heated to the operating temperature of 205°F (96°C), ethylene was pressured in to give an ethylene pressure of about 550 psig and the run was started and continued for the time set out. Ethylene pressure was maintained during the run by supplying additional ethylene as required from a reservoir.

Each run was terminated by stopping ethylene flow and venting the gaseous contents to a flare line for disposal. The polymer was recovered,, dried and weighed to determine catalyst productivity which is expressed in terms of grams polyethylene per gram catalyst for the time period set out.

The polymerization results were as follows:

Polymerization Results

	<u>Sample</u>	<u>Productivity</u>	<u>Time</u>	<u>MI</u>	<u>HLMI/MI</u> ⁽¹⁾
	A1	Trace	30 min.	-	-
	A2	2,895	22 min.	.54	212
5	A3	453	60	-	-
	A4	7,470	30	.78	102
	A4	7,790	20	-	-
	A4	10,600	60	.49	229

(1) MI is Melt Index determined by ASTM D 1238-65T, Condition E
and High Load Melt Index (HLMI) by Condition F.

As can be seen, the catalyst produced in accordance with this invention had the ability to produce polymer with exceptional productivity and good melt index. In addition, the rate of polymerization held constant during the runs, as evidenced by a constant rotameter reading for rate of ethylene addition, thus giving better overall activity than in a conventional chromium/ AlPO_4 preparation.

CLAIMS:

1. A method of forming an aluminium orthophosphate hydrogel which comprises reacting an aluminium salt with a source of orthophosphate ions in a ^{CONCENTRATED} ~~concentration~~ reaction mass containing no more than 40% by weight of added water, based on the weight of the aluminium salt, and ^{THEREAFTER} ~~thereafter~~ neutralising the reaction mass with a base to precipitate the gel.

2. A method according to claim 1, wherein, after precipitation the product hydrogel is treated to remove the water therefrom thereby to form a xerogel.

3. A method according to claim 1 or 2, wherein said mass contains no more than 20% by weight of added water, based on the aluminium salt.

4. A method according to claim 1, 2 or 3, wherein the hydrogel formed by said neutralisation occupies a volume of from 3 to 6 cm³ per gram of aluminium orthophosphate.

5. A method according to claim 1, 2, 3 or 4, wherein the base is ammonia or ammonium hydroxide.

6. A method according to any one of claims 1, 2 - 5, wherein the hydrogel is formed at a pH of at least 6.

7. A method according to any one of claims 1 - 6, wherein said concentrated mass comprises said aluminium salt in the molten state.



8. A method according to any one of claims 1 - 7, wherein the aluminium salt is hydrated aluminium nitrate.

9. A method according to claim 8, wherein the concentrated mass is formed and neutralised at a temperature of $80^{\circ}\text{C} \pm 5^{\circ}\text{C}$.

5 10. A method according to claim 7, 8 or 9, wherein the concentrated mass contains 1-15% by weight of added water based on the weight of the aluminium salt.

10 11. A method according to any one of claims 1 - 9, wherein the concentrated mass contains no additional water beyond water of hydration.

12. A method according to any one of claims 1-6, wherein the concentrated mass comprises said salt in the form of a concentrated aqueous syrup.

15 13. A method according to claim 12, wherein said syrup contains 5-20% by weight of water, based on the weight of the aluminium salt.

14. A method according to claim 12 or 13, wherein the salt is aluminium sulfate.

20 15. A method according to any one of claims 2-10, wherein the source of orthophosphate ions is orthophosphoric acid, or mono- or di-basic ammonium orthophosphate.

16. A method according to claim 1, which comprises forming a concentrated mass comprising an aluminium salt and a source of orthophosphate ions; partially neutralising the concentrated mass with a base; and aging the partially neutralised mass thereby to precipitate an aluminium phosphate hydrogel.



* C L N S *

17. A method according to claim 16, wherein said hydrogel occupies a volume of 3-6 cm³ per gram of aluminium orthophosphate.

18. A method according to claim 16 or 17 wherein said base is ammonia or ammonium hydroxide.

19. A method according to any one of claims 16-18, wherein the base is used in an amount to give a pH below 4.

20. A method according to any one of claims 16-19, wherein said mass comprises the aluminium salt in the molten state.

21. A method according to any one of claims 16-20, wherein the aluminium salt is hydrated aluminium nitrate.

22. A method according to claim 21, wherein the concentrated mass is formed and neutralised at a temperature of 80°C ± 5°C.

23. A method according to any one of claims 16-22, wherein the concentrated mass contains 1-15 per cent by weight added water based on the aluminium salt.

24. A method according to any one of claims 16-22, wherein the concentrated mass contains no added water beyond water of hydration.

25. A method according to any one of claims 16-19, wherein the concentrated mass contains said aluminium salt in the form of a concentrated aqueous syrup.

26. A method according to claim 25, wherein said syrup contains 5-40% by weight water based on the aluminium salt.

27. A method according to claim 25 or 26, wherein said salt is aluminium sulfate.

28. A method according to any one of claims 16-27, wherein the partially neutralised mass is aged for 5 minutes to 10 hours.



29. A method according to any one of claims 16-28, wherein the base is used in an amount of 60-70% of that theoretically required for complete neutralisation.

5 30. A method according to any one of claims 16-29, wherein the source of phosphate ions is monobasic ammonium phosphate.

31. A method according to any one of claims 16-30 including the additional step of removing water from the hydrogel to form a xerogel.

10 32. A method according to claim 31, wherein the hydrogel is washed with ammonium hydroxide, followed by removal of the water by washing with a water miscible organic solvent, and evaporating the solvent to form said xerogel.

33. An aluminium orthophosphate gel, when prepared by a method claimed in any one of the preceding claims.

15 34. An aluminium orthophosphate gel according to claim 33 which is a xerogel.

20 34. A supported chromium or vanadium-containing olefin polymerisation catalyst wherein the support material comprises a xerogel claimed in claim 34, which has been activated by heating in an oxidising atmosphere and into which the chromium or vanadium compound is incorporated prior to activation in an amount sufficient to provide from 0.001 to 10% by weight of vanadium or chromium, based on the weight of the support.

36. A catalyst according to claim 35, wherein the support contains



an atom ratio of phosphorus/aluminium in the range of 0.6:1 to 0.9:1.

37. A catalyst according to claim 35 or 36, which is a chromium containing catalyst and wherein the chromium is introduced by treating the xerogel under anhydrous conditions with a zerovalent chromium containing compound.

38. A process which comprises polymerising one or more mono-1-olefin of 2-8 carbon atoms which comprises contacting the olefin under polymerisation conditions with a catalyst according to claim 35, 36 or 37.

39. A process according to claim 38, wherein the olefin is ethylene, propylene, 1-butene, 1-pentene, 1-hexene or 1-octene.

40. A process according to claim 38, or 39, wherein the olefin consists of ethylene, or ethylene and sufficient comonomer to provide an ethylene copolymer containing 97-99.6 weight per cent of polymerised ethylene units.

41. A process according to claims 38, 39 40, or 42, wherein the catalyst is used in combination with an organometallic cocatalyst.

42. A process according to claim 41, wherein the cocatalyst is a trialkylborane.

