

Description

The present invention relates to the improvement of Ziegler-Natta type alpha-olefin polymerisation catalysts based on one or more transition metal compounds.

More particularly, the invention relates to processes and apparatus for the liquid elutriation of particles of alpha-olefin polymerisation catalyst, and makes it possible to obtain catalysts having a relatively narrow particle size distribution. These catalysts can be used in the polymerisation of alpha-olefins under low pressure to produce polyolefin powders themselves possessing a relatively narrow particle size distribution.

According to French Patent No. 2 116 698, Ziegler-Natta catalyst systems comprise one or more transition metal compounds belonging to Groups IV, V or VI of the Periodic Table of Elements, and at least one organo-metallic compound of metals of Groups II or III of this Table. Generally, in the art of Ziegler-Natta polymerisation the transition metal-containing component of the catalyst system is referred to as the "catalyst", whilst the organometallic compound is referred to as the "co-catalyst". This terminology will be used in the present specification. The catalysts are frequently solid compounds consisting of titanium halides, preferably associated with compounds of magnesium, having a relatively high activity in the polymerisation of alpha-olefins, which advantageously makes it possible to avoid at the end of polymerisation the stage of removing the catalytic residues present in the polymers. The co-catalysts generally comprise organo-aluminium or organo-zinc compounds which are liquid or gaseous under the normal polymerisation conditions.

When the polymerisation of alpha-olefins is conducted in suspension in a liquid hydrocarbon medium, or in the gas phase, the solid polymer being formed develops inside and on each particle of catalyst. Provided that this development of polymer occurs in a uniform manner, the particle size distribution of the produced polymer particles remains similar to that of the catalyst, whilst the average particle size of the polymer particles increases as the reaction continues.

Highly active catalysts based on transition metal and magnesium compounds are generally prepared by contacting at least one transition metal compound with metallic magnesium or a magnesium compound, for example an organomagnesium compound, magnesium oxide, magnesium hydroxide, a magnesium alcoholate, magnesium hydroxychloride or magnesium chloride, such contacting being performed for example by chemical reaction, impregnation or grinding. The produced catalysts often have a comparatively broad particle size distribution associated with a high content of fine particles. This can cause problems in gas-fluidised bed polymerisation of olefins due to the fact that the fine particles are easily entrained by the fluidisation gas into parts of the apparatus not intended for carrying out on the polymerisation reaction.

Moreover the presence of fine particles of polyolefin, for example those possessing a diameter of less than 50 or 100 microns, provides a dust explosion risk during handling of the powders, can lead to losses of polyolefins during their conversion and can diminish the flowability of the polyolefin powders, thus hindering the feed to conversion machinery.

Large particles of polyolefin, for example those possessing a diameter up to several millimetres, provide difficulties in the pneumatic conveying of the powders.

It has been suggested that the fine and large catalyst particles should be removed by sieving or by elutriation using a flow of gas or liquid. However, having regard to the fineness of the catalyst particles, such a size segregation or "selection" operation has hitherto not been achieved under satisfactory industrial conditions.

In general, processes are known for segregating particles which use the physical principle of separating the particles by their differences in density. However, such processes cannot be applied to Ziegler-Natta type catalysts, whose particles are differentiated not by density, but by size.

Processes for segregating particles are also known which use the physical principle of separating particles by their differences in size. According to French Patent No. 1 179 079, such a segregation can be performed in an elutriation column in which an elutriation liquid flows in an ascending stream at a substantially constant speed and in laminar flow conditions - i.e., without turbulence. The segregation is performed by applying the physical principle of the variation in the speed at which the particles settle in the elutriation liquid in relation to their sizes. The largest particles settle towards the bottom of the column in relative contraflow with the elutriation liquid, while the finest particles are entrained to the top of the column with the elutriation liquid. Attempts to apply this type of elutriation technology to the segregation of Ziegler-Natta catalyst particles have encountered a number of difficulties, particularly due to the relatively low density of the catalyst particles, the relatively small average particle sizes involved and difficulties in relation to the selection of a suitable elutriation liquid. The elutriation liquid is desirably chemically inert in relation to the catalyst, and for practical reasons this restricts the choice of elutriation liquids essentially to non-polar liquids, for example, liquid hydrocarbons. However, it is found that the use of such non-polar liquids as elutriation liquids can cause aggregation or agglomeration of the catalyst particles making it difficult to achieve satisfactory particle segregation.

It is an object of the present invention to provide an improved process and apparatus for segregating Ziegler-Natta catalyst particles by liquid elutriation.

Accordingly the present invention provides a process for elutriation by a liquid or solid particles of a

Ziegler-Natta catalyst to obtain separation into at least two portions which differ in average particle size characterised in that in a preliminary stage (stage 1) a suspension of the solid catalyst particles is prepared in the elutriation liquid which is a non-polar liquid chemically inert in relation to the catalyst, at a concentration in the range 20 to 150 grammes per litre, and further in that the process comprises one or more of the following defined stages M and N,

wherein stage M is a process for separating large particles comprising introducing the catalyst suspension at a flow rate Q1 into a vertical elutriation column F1 having a height H', at a level between H'/2 and the bottom of the column, introducing the elutriation liquid at a flow rate R1 into the column F1 at a level lower than that of the introduction of the catalyst suspension, the liquid being caused to flow in the column in an ascending stream substantially under laminar flow conditions, withdrawing from the top of the column F1 a catalyst suspension substantially free from large particles and, withdrawing from the bottom of the column F1 a catalyst suspension mainly comprising large particles and wherein stage N is a process for separating fine particles comprising introducing the catalyst suspension at a flow rate Q2 into a vertical elutriation column F2 of height H at a level above H/2 and below 7H/8, introducing the elutriation liquid at a flow rate R2 into the column F2 at a level below H/2, the liquid being caused to flow in the column in an ascending stream and substantially under conditions of laminar flow, withdrawing from the top of the column F2 elutriation liquid charged with fine catalyst particles and withdrawing from the bottom of the column F2 catalyst particles substantially freed from fine particles.

The laminar flow conditions mentioned in stages M and N above is characterised by a Reynolds number (Re) lower than 2000 and preferably lower than 1000. In the case of cylindrical columns of circular section the Reynolds number is dimensionless and equal to:

$$Re = \frac{4 \cdot Q \cdot n}{\pi \cdot d \cdot v}$$

Where Q = flow rate of the liquid,

n = density of the liquid,

d = diameter of the column, and

v = viscosity of the liquid.

and pi is the universal constant 3.14159...

In the variants of the process according to the invention, therefore, the catalyst suspension in the elutriation liquid prepared during stage 1 can be subjected to an elutriation operation enabling either the large or fine particles of the catalyst to be separated. The suspension can also be subjected to a double elutriation operation enabling both the large and fine catalyst particles to be separated simultaneously, the large particles being separated in the elutriation column F1, preferably before the fine particles are separated in the elutriation column F2.

The catalyst suspension fed to the elutriation is preferably well dispersed and of substantially uniform constitution throughout.

The invention also relates to an apparatus for performing the elutriation process according to the invention and comprising:

- a tank M2 for the preliminary preparation of a catalyst suspension in an elutriation liquid and having means adapted to maintain uniformity in the suspension,
- a vertical elutriation column F1 having a height H' and a diameter D' such that the ratio H'/D' is equal to or greater than 5, such column having: (a) a tube for the introduction of catalyst suspension prepared in the tank M2 or of the catalyst suspension substantially freed from fine particles coming from the outlet of the top of column F2 as the case may be, at a level lying between H'/2 and the bottom of the column; (b) a tube for the introduction of the elutriation liquid at a level lower than that of the introduction of the catalyst suspension; (c) an outlet from the top of the column for catalyst suspension substantially freed from large particles; and (d) an outlet from the bottom of the column for catalyst suspension comprising mainly large particles, and/or

- a vertical elutriation column F2 having a height H and a diameter D such that the ratio H/D is equal to or greater than 10, the column having: (a) a tube for the introduction of the catalyst suspension prepared in the tank M2 or of the catalyst suspension substantially freed from large particles coming from the outlet at the top of the column F1, as the case may be, such tube being disposed at a level above H/2 and below 7H/8; (b) a tube for the introduction of the elutriation liquid at a level lying below H/2; (c) an outlet from the top of the column for catalyst particles substantially freed from fine particles.

The apparatus can also advantageously comprise means for separating the catalyst particles and the elutriation liquid, for example, a decantation or filtration device, or a liquid cyclone, and also means for recycling the elutriation liquid freed from the catalyst particles to the feed to the column F1 and/or F2.

The invention is further illustrated with reference to the accompanying drawing.

Fig. 1 is a simplified diagram of a liquid-phase elutriator according to the invention, in which elutriation can be carried out on the one hand of the fine particles and on the other hand of the large particles present in powdery catalyst.

The process may be implemented in an apparatus such as that shown in Fig. 1 and operating in the following manner:

A uniform suspension is produced of the solid catalyst in the elutriation liquid. This suspension, maintained in agitation in the tank M2, is pumped by the pump G2 so as to feed the column F1 in which elimination of the large particles is carried out; these latter are then conveyed to the tank M5. The suspension freed from large particles and leaving column F1 at the top then feeds column F2. The columns F1 and F2 are fed with decanted elutriation liquid coming from the tank M4 by means of the pump G3.

The elutriation liquid leaving the column F2 at the top entrains the fine particles separated from the elutriation liquid by means of the hydrocyclone Z. The fine particles separated are introduced into the tank M5 where decanting of the separated particles is performed, whilst the elutriation liquid separated in the hydrocyclone Z is sent to the tank M4.

The elutriated catalyst leaves the column F2 at the bottom. It is collected in the tank M3 in the form of a concentrated suspension.

In order to obtain good particle size separation of the fine particles and/or large particles in the catalyst the following provisions are preferred:

- the ratio between the height H' and the diameter D' of the elutriation column F1 is equal to or greater than 5, preferably equal to or greater than 10;
- the ratio between the height H and the diameter D of the elutriation column F2 is equal to or greater than 10, preferably about 20;
- the point at which the catalyst suspension is introduced into the elutriation columns F1 and F2 has an influence on the quality of separation; if H is the height of the elutriation column F2 adapted to separate the fine particles, the catalyst suspension is advantageously introduced above $H/2$, preferably at $3H/4$ or above, and below $7H/8$;
- moreover, in the case of the elutriation column F1 adapted to separate the large particles and having a height H' , the catalyst suspension is preferably fed at a level lying between $H'/2$ and the bottom of the column, preferably lying between $H'/4$ and the bottom of the column;
- also advantageously the elutriation liquid is introduced into the columns F1 and F2 at a point lying below the point where the catalyst suspension is introduced, preferably at a point such that the distance separating the points of introduction of the elutriation liquid and the catalyst suspension is equal to or greater than $H'/8$, preferably equal to or greater than $H'/4$ in the column F1, and equal to or greater than $H/4$, preferably equal to or greater than $H/2$ in the column F2, since it has been found that a sufficiently large distance separating the two points of introduction into a column enables the dispersion of the particles in the elutriation liquid to be improved and therefore improves the quality of the selection; the introduction of the elutriation liquid into the column F1 is therefore performed at a level lying preferably below $H'/4$;
- similarly, the elutriation liquid is advantageously introduced into the column F2 at a level preferably lying at $H/4$ or there below;
- the concentration of the catalyst suspension in the elutriation liquid prepared in the tank M2 must be relatively low, lying more particularly between 20 and 150 g/l, and preferably between 40 and 100 g/l; such a concentration enables the quality of the particle size selection to be improved and the elutriated catalyst yield to be enhanced;
- the catalyst concentration in the elutriation columns is advantageously low; more particularly, in the column F1 it lies between 10 and 100 g/l, preferably between 30 and 70 g/l, while in column F2 it lies between 2 and 60 g/l, preferably between 5 and 30 g/l; in these conditions the large and fine catalyst particles can be efficiently separated and then readily eliminated; the ratio between the flow rates $R1/Q1$ in the column F1 therefore advantageously lies between 0.2 and 5, preferably between 0.5 and 2; similarly, the ratio between the flow rates $R2/Q2$ in the column F2 is advantageously between 0.3 and 6, preferably between 0.5 and 4;
- the liquid used for elutriation must not impair the catalysts; preferably it is a dry liquid aliphatic hydrocarbon freed from oxygen, for example, n-heptane or n-hexane.

The process according to the invention can be performed by continuous introduction of the catalyst suspension and elutriation liquid into the elutriation column or columns (permanent continuous conditions), or by continuous introduction for a predetermined period of the catalyst suspension into the elutriation column or columns and continuous introduction of the elutriation liquid until the whole of the catalyst charge has been elutriated (non-permanent continuous conditions).

Depending on the catalysts, one proceeds to a simple selection (fine or large) or to a double particle size selection (fine and large), each type of selection involving the elutriation characteristics peculiar to it (dimension of columns, throughput of solvent). These characteristics are determined experimentally within the limits disclosed hereinbefore.

It has been observed that the particle selection is improved when the elutriation is conducted in the presence of a small quantity of one or more special additives.

Accordingly, the present invention further comprises a process for elutriation of particles of a Ziegler Natta-type catalyst comprising performing the elutriation using a non-polar liquid elutriation medium in the presence of a polar aprotic compound, preferably an organometallic compound. The Ziegler Natta-type catalyst comprises a compound or compounds of one or more transition metals selected from metals of Groups IV, V or VI of the Periodic Table (Mendeleev). The Ziegler Natta-type catalyst preferably

comprises one or more transition metal compounds associated with or in chemical combination with one or more magnesium compounds. The preferred polar aprotic compounds are soluble in the elutriation liquid. Most preferably they are organo-metallic compounds of the type used as co-catalysts in Ziegler-Natta catalyst systems; these co-catalysts generally consist of organo-metallic compounds of metals belonging to Groups II or III of the Periodic Table, especially of organoaluminium, organozinc or organomagnesium compounds comprising at least one aluminium/carbon bond, such as trialkylaluminums, halides or alcoholates of alkylaluminium, dialkylzinc and dialkylmagnesium. Preferred compounds are triethylaluminium, triisobutylaluminium, tri-n-hexylaluminium, tri-n-octylaluminium, diethylaluminium chloride, ethylaluminium sesquichloride, ethoxydiethylaluminium or diethylzinc. These compounds are preferably used at concentrations in the range 0.1 and 100 millimoles per litre of elutriation liquid.

The polar aprotic compound employed as the special additive in the process of the present invention is preferably selected from compounds which do not deleteriously affect the catalyst. In the case in which the additive is an organometallic compound, some reduction and/or activation of the catalyst particles can take place. The use of the defined polar aprotic compounds can lead to improvements in the quality of the particle size selection, the yield of elutriated catalyst and the reproducibility of the operations.

The catalysts employed in the processes of the invention preferably consist essentially of halogenated compounds of transition metals belonging to Groups IV, V or VI of the Periodic Table of Elements and compounds of magnesium and optionally with aluminium compounds. Preferred catalysts have the general formula:



in which M is an atom of titanium and/or vanadium, R_1 is an alkyl group comprising 2 to 14 carbon atoms, X is an atom of chlorine and/or bromine, D is an electron donor compound comprising at least one atom of oxygen, or sulphur, or nitrogen, or phosphorus, but not comprising an atom of active hydrogen, wherein:

m lies in the range 1.5 to 50, preferably 2 to 10,

n lies in the range 0 to 2, preferably 0 to 1,

p lies in the range 0 to 3,

q lies in the range 4 to 100, preferably 5 to 27, and

r lies in the range 0 to 60, preferably 0 to 20.

These catalysts can be obtained by various processes in themselves known, in particular those according to which a magnesium compound, for example a magnesium halide, is ground in the presence of at least one halogenated compound of a transition metal and optionally an electron donor compound, or else a magnesium compound is precipitated at the same time as one or more halogenated transition metal compounds, optionally in the presence of an electron donor compound.

The catalysts can be obtained, for example, by reacting an organomagnesium compound with a halogenated transition metal compound taken at its maximum valency in the presence of a halogenating agent and optionally an electron donor compound D, having the same definition as above, chosen for example from amongst amines, amides, phosphines, sulphoxides, sulphones, ethers and thio-ethers. This reaction is advantageously performed using these compounds in quantities such that the molar ratio of the quantity of organomagnesium compound to the quantity of halogenated transition metal compound is greater than 1, the excess of organomagnesium compound being decomposed by the halogenating agent so that no substantial quantity of magnesium-carbon bonds remains.

The catalysts may also be obtained by reacting magnesium metal with an alkyl halide in the presence of a halogenated transition metal compound taken at its maximum valency and optionally an electron donor compound D having the same definition as above. This reaction is advantageously performed using a quantity of magnesium metal such the molar ratio of the quantity of magnesium metal to the quantity of halogenated transition metal compound is greater than 1, and a quantity of alkyl halide such that after the reaction substantial quantities of compounds comprising a magnesium-carbon bond are no longer present.

The processes of the present invention are particularly useful for size separation by liquid elutriation of Ziegler-Natta catalyst particles having a density in the range 1 to 2, preferably in the range 1.2 to 1.6, and having an average particle size in the range 10 to 100 microns. Such particles can have irregular shapes and rough surfaces.

The catalysts obtained by elutriation according to the present invention can be used in processes of polymerisation or copolymerisation of alpha-olefins, especially in gas-phase polymerisation or copolymerisation processes, and in particular in a fluidised bed.

The invention is illustrated by the following examples, in which Example 1 is given by way of comparison:

Example 1 (Comparison)

(a) Preparation of the catalyst

A 1-litre glass reactor, provided with a mechanical stirrer, a reflux condenser and a heating or cooling device is filled with dry nitrogen; there are introduced into it successively at ambient temperature:

- 12.15g (500 m.Moles) of magnesium in powder form

- 23.75 g (125 m.Moles) of titanium tetrachloride
- 92.5 g (1 Mole) of n-butyl chloride
- n-heptane, to make up the volume to 600 ml.

After the addition of 1.26g of iodine, the reaction medium is heated with stirring to 75°C, so as to cause the reaction to commence. The reaction begins slowly after about an hour and a half and the reaction medium is maintained at 75°C for 3.5 hours. The resultant brown/black precipitate is washed several times with heptane. The catalyst A obtained has the following composition by weight:

Ti : 10.3% Mg : 19.2% Cl : 70.5%

(b) Polymerisation of ethylene

Into a 5-litre stainless steel reactor provided with mechanical stirring there are introduced under an atmosphere of nitrogen 2 litres of n-heptane at ambient temperature. After heating the n-heptane to 70°C, one introduces:

- 0.46 g (4 m.Moles) of triethylaluminium
- a quantity of catalyst corresponding to 1 milligram atom of titanium.

When the reaction medium has been heated to 75°C, hydrogen is introduced into it until a pressure of 0.6 MPa is obtained, then ethylene at a throughput of 160 g/hr.

After 7 hours of polymerisation, 1100 g of polymer are collected, the titanium content of which is 34 parts per million by weight (ppm).

The particle size distribution of the polymer is shown in Table I.

Table I.

Example 2

(a) Preparation of the elutriated catalyst

1 kg of the catalyst A is prepared using the same conditions as in Example 1(a).

The catalyst is subjected to liquid elutriation using the following conditions:

- apparatus	:	as shown in Fig. 1, but omitting the column (F1)
- diameter of the column (F2)	:	70 mm
- height of the column (F2)	:	1600 mm
- elutriation operation	:	continuous non-permanent
- nature of elutriation liquid	:	n-heptane
- level of introduction of the elutriation liquid into the column	:	150 mm above the bottom
- throughput of elutriation liquid (R2)	:	15 litres per hour
- catalyst concentration in the catalyst suspension	:	100 millimoles of titanium/litre - i.e. 60 g of catalyst per litre
- throughput of catalyst suspension (Q2)	:	4 litres per hour
- catalyst concentration in the column (F2)	:	13 millimoles of titanium per litre - i.e. 7.8 g of catalyst per litre
- level of introduction of the catalyst suspension into the column (F2)	:	1200 mm above the bottom
- yield of elutriated catalyst (based on titanium contained in the catalyst)	:	50%
- hourly production	:	0.2 millimoles of titanium/hour - i.e. 0.12 kg of catalyst per hour.

The catalyst B obtained after elutriation has the same chemical characteristics as catalyst A.

The catalyst B obtained after elutriation has the same chemical characteristics as catalyst A.

(b) Polymerisation

Example 1(b) was repeated using catalyst B instead of catalyst A.

1100 g of a polyethylene powder are obtained, the particle size distribution of which is shown in Table 1.

It is found that the polyethylene obtained from catalyst B has a content of particles with dimensions below 350 microns which is appreciably lower than that of the polyethylene obtained from catalyst A, this decrease being particularly significant for particles with dimensions below 50 microns.

Example 3

(a) Preparation of the elutriated catalyst

1 kg of the catalyst A is prepared in accordance with Example 1(a) is subjected to liquid elutriation under the following conditions:

- apparatus	:	as shown in Fig. 1, omitting the column (F1)
- diameter of the column (F2)	:	70 mm
- height of column (F2)	:	1600 mm
- elutriation operation	:	continuous non-permanent
- nature of elutriation liquid	:	n-heptane
- height of introduction of the elutriation liquid into the column (F2)	:	150 mm above the bottom
- throughput of elutriation liquid (R2)	:	15 litres/hour
- nature of additive contained in the elutriation liquid	:	tri-n-octylaluminium
- additive concentration in the elutriation liquid	:	0.7 millimole/litre
- catalyst concentration in the catalyst suspension	:	100 millimoles of titanium/litre - i.e. 60 mg of catalyst per litre
- throughput of catalyst suspension (Q2)	:	4 litres per hour
- catalyst concentration in the column (F2)	:	17 millimoles of titanium/litre - i.e. 10.4 g of catalyst per litre
- level of introduction of the catalyst suspension into the column (F2)	:	1200 mm above the bottom
- yield of elutriated catalyst (based on titanium contained in the catalyst)	:	65%
- hourly production	:	0.26 millimoles of titanium per hour - i.e. 0.12 kg of catalyst per hour

The catalyst C obtained after elutriation has the same chemical characteristics as catalyst A.

(b) Polymerization

Example 1(b) is repeated using catalyst C instead of the catalyst A.

1100 g of a polyethylene powder are obtained, the particle size distribution of which is shown in Table 1.

It is found that the polyethylene obtained from catalyst C has a content of particles with dimensions below 350 microns which is appreciably smaller than that of the polyethylene obtained from catalysts A and B, this decrease being particularly great for particles of dimensions below 50 microns.

It is also noted that the yield of catalyst C is appreciably higher than the yield of catalyst B obtained in Example 2.

Example 4

In order to determine the reproducibility of the elutriation operations described in Examples 2 and 3, each of these examples is reproduced 10 times from the same catalyst A, and one determines:

- the mean percentage by weight of particles of polyethylene with dimensions below 160 microns and the

corresponding standard deviation,

- the mean yield of elutriated catalyst and the corresponding standard deviation.

The results obtained are set out in Table II.

The standard deviation,

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$$\sqrt{\sum (\text{deviation})^2},$$

10 that is to say the square root of the sum of the squares of the deviations by comparison with the mean result, gives an indication of the dispersion of the results obtained and consequently of the reproducibility of the tests.

15 It is found that the standard deviations obtained according to Example 3 are smaller than those obtained in Example 2, both as regards the percentage of particles with dimensions below 160 microns and the catalyst yield, which indicates that the conditions of Example 3 provide appreciably more reproducible results than those of Example 2

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TABLE I
COMPARISON OF THE PARTICLE SIZES OF THE POLYETHYLENE OBTAINED WITH THE
NON-ELUTRIATED CATALYST (CATALYST A) AND THE POLYETHYLENE OBTAINED WITH
THE ELUTRIATED CATALYST (CATALYST B AND C)

Percentage by weight of particles retained between two sieves	Aperature of sieves (microns)	The elutriated catalyst (Catalyst B and C)									
		above 1000	710- 1000	500- 710	350- 500	250- 350	160- 250	125- 160	80- 125	50- 80	below 50
Catalyst A	1	7	16	23	21	16	5	6.5	2.5	2	
Catalyst B	2	10	24	26	17	12	3.5	4	1	0.5	
Catalyst C	3	15	24	26	16	10.5	2	2.5	1	0	

TABLE II

5	Example 2, reproduced 10 times		Example 3, reproduced 10 times	
	% by weight of particles with dimensions below 160 microns	Catalyst Yield	% by weight of particles with dimensions below 160 microns	Catalyst Yield
	Mean Result	9	5.5	65
10	Typical deviation	3	1.5	5

Claims

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1. A process for elutriation by a liquid of solid particles of a Ziegler-Natta catalyst to obtain separation into at least two portions which differ in average particle size characterised in that in a preliminary stage (stage 1) a suspension of the solid catalyst particles is prepared in the elutriation liquid which is a non-polar liquid chemically inert in relation to the catalyst, at a concentration in the range 20 to 150 grammes per litre, and further in that the process comprises one or more of the following defined stages M and N,

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wherein stage M is a process for separating large particles comprising introducing the catalyst suspension at a flow rate Q1 into a vertical elutriation column F1 having a height H', at a level between H'/2 and the bottom of the column, introducing the elutriation liquid at a flow rate R1 into the column F1 at a level lower than that of the introduction of the catalyst suspension, the liquid being caused to flow in the column in an ascending stream substantially under laminar flow conditions, withdrawing from the top of the column F1 a catalyst suspension substantially free from large particles and, withdrawing from the bottom of the column F1 a catalyst suspension mainly comprising large particles and wherein stage N is a process for separating fine particles comprising introducing the catalyst suspension at a flow rate Q2 into a vertical elutriation column F2 of height H at a level above H/2 and below 7H/8, introducing the elutriation liquid at a flow rate R2 into the column F2 at a level below H/2, the liquid being caused to flow in the column in an ascending stream and substantially under conditions of laminar flow, withdrawing from the top of the column F2 elutriation liquid charged with fine catalyst particles and withdrawing from the bottom of the column F2 catalyst particles substantially freed from fine particles.

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2. A process as claimed in claim 1, characterised in that the ratio of the flow rates R1/Q1 in the elutriation column F1 is between 0.2 and 5.

3. A process as claimed in claim 1, characterised in that the ratio of the flow rates R2/Q2 in the elutriation column F2 is between 0.3 and 6.

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4. A process as claimed in claim 1, characterised in that the catalyst concentration in the elutriation column F1 is between 10 and 100 g/l and the catalyst concentration in the elutriation column F2 is between 2 and 60 g/l.

5. A process as claimed in claim 1, characterised in that the elutriation liquid is an aliphatic hydrocarbon.

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6. A process as claimed in claim 1 characterised in that the elutriation is carried out using a non-polar liquid elutriation medium in the presence of a polar aprotic compound.

7. A process for elutriation of particles of a Ziegler Natta-type catalyst characterised in that the elutriation is performed using a non-polar liquid elutriation medium in the presence of a polar aprotic compound.

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8. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is an organo-metallic compound.

9. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is an organoaluminium, organozinc or organomagnesium compound.

10. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is employed at a concentration of 0.1 to 1000 millimoles per litre of elutriation liquid.

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11. A process as claimed in claim 6 or 7 wherein the Ziegler Natta-type catalyst comprises one or more transition metal compounds associated with or in chemical combination with one or more magnesium compounds.

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12. Apparatus for the liquid elutriation of a solid Ziegler-Natta type alpha-olefin polymerisation catalyst, consisting of at least one transition metal compound belonging to Groups IV, V or VI of the Periodic Table of Elements and a magnesium compound, characterised in that it comprises:

- a tank M2 for the preliminary preparation of a catalyst suspension in the elutriation liquid and having means adapted to maintain uniformity of the suspension,

- a vertical elutriation column F1 having a height H' and a diameter D' such that the ratio H'/D' is equal to or greater than 5, such column having: (a) a tube for the introduction of the catalyst suspension pre-

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TABLE II

	Example 2, reproduced 10 times		Example 3, reproduced 10 times	
	% by weight of particles with dimensions below 160 microns	Catalyst Yield	% by weight of particles with dimensions below 160 microns	Catalyst Yield
Mean Result	9	50	5.5	65
Typical deviation	3	10	1.5	5

Claims

1. A process for elutriation by a liquid of solid particles of a Ziegler-Natta catalyst to obtain separation into at least two portions which differ in average particle size characterised in that in a preliminary stage (stage 1) a suspension of the solid catalyst particles is prepared in the elutriation liquid which is a non-polar liquid chemically inert in relation to the catalyst, at a concentration in the range 20 to 150 grammes per litre, and further in that the process comprises one or more of the following defined stages M and N,

wherein stage M is a process for separating large particles comprising introducing the catalyst suspension at a flow rate Q1 into a vertical elutriation column F1 having a height H', at a level between H'/2 and the bottom of the column, introducing the elutriation liquid at a flow rate R1 into the column F1 at a level lower than that of the introduction of the catalyst suspension, the liquid being caused to flow in the column in an ascending stream substantially under laminar flow conditions, withdrawing from the top of the column F1 a catalyst suspension substantially free from large particles and, withdrawing from the bottom of the column F1 a catalyst suspension mainly comprising large particles and wherein stage N is a process for separating fine particles comprising introducing the catalyst suspension at a flow rate Q2 into a vertical elutriation column F2 of height H at a level above H/2 and below 7H/8, introducing the elutriation liquid at a flow rate R2 into the column F2 at a level below H/2, the liquid being caused to flow in the column in an ascending stream and substantially under conditions of laminar flow, withdrawing from the top of the column F2 elutriation liquid charged with fine catalyst particles and withdrawing from the bottom of the column F2 catalyst particles substantially freed from fine particles.

2. A process as claimed in claim 1, characterised in that the ratio of the flow rates R1/Q1 in the elutriation column F1 is between 0.2 and 5.

3. A process as claimed in claim 1, characterised in that the ratio of the flow rates R2/Q2 in the elutriation column F2 is between 0.3 and 6.

4. A process as claimed in claim 1, characterised in that the catalyst concentration in the elutriation column F1 is between 10 and 100 g/l and the catalyst concentration in the elutriation column F2 is between 2 and 60 g/l.

5. A process as claimed in claim 1, characterised in that the elutriation liquid is an aliphatic hydrocarbon.

6. A process as claimed in claim 1 characterised in that the elutriation is carried out using a non-polar liquid elutriation medium in the presence of a polar aprotic compound.

7. A process for elutriation of particles of a Ziegler Natta-type catalyst characterised in that the elutriation is performed using a non-polar liquid elutriation medium in the presence of a polar aprotic compound.

8. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is an organo-metallic compound.

9. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is an organoaluminium, organozinc or organomagnesium compound.

10. A process as claimed in claim 6 or 7 wherein the polar aprotic compound is employed at a concentration of 0.1 to 1000 millimoles per litre of elutriation liquid.

11. A process as claimed in claim 6 or 7 wherein the Ziegler Natta-type catalyst comprises one or more transition metal compounds associated with or in chemical combination with one or more magnesium compounds.

12. Apparatus for the liquid elutriation of a solid Ziegler-Natta type alpha-olefin polymerisation catalyst, consisting of at least one transition metal compound belonging to Groups IV, V or VI of the Periodic Table of Elements and a magnesium compound, characterised in that it comprises:

- a tank M2 for the preliminary preparation of a catalyst suspension in the elutriation liquid and having means adapted to maintain uniformity of the suspension,

- a vertical elutriation column F1 having a height H' and a diameter D' such that the ratio H'/D' is equal to or greater than 5, such column having: (a) a tube for the introduction of the catalyst suspension pre-



pared in the tank M2 or of the catalyst suspension substantially freed from fine particles coming from the outlet of the top of column F2 as the case may be, at a level lying between $H'/2$ and the bottom of the column; (b) a tube for the introduction of the elutriation liquid at a level lower than that of the introduction of the catalyst suspension; (c) an outlet from the top of the column of a catalyst suspension substantially free from large particles; and (d) an outlet from the bottom of the column of a catalyst suspension comprising mainly large particles, and/or

- vertical elutriation column F2 having a height H and a diameter D such that the ratio H/D is equal to or greater than 10 such column having: (a) a tube for the introduction of the catalyst suspension prepared in the tank M2 or of the catalyst suspension substantially free from large particles coming from the outlet at the top of the column F1, as the case may be, such tube being disposed at a level above $H/2$ and below $7H/8$; (b) a tube for the introduction of the elutriation liquid at a level lying below $H/2$; (c) an outlet from the top of the column of the catalyst particles substantially freed from fine particles.

13. Apparatus according to Claim 12, characterised in that it also comprises means for separating the catalyst particles and the elutriation liquid, and means for recycling the elutriation liquid freed from the catalyst particles to the feed to the column (F1) and/or F2.

14. Apparatus according to Claim 12, characterised in that the distance separating the points of introduction of the elutriation liquid and the catalyst suspension is equal to or greater than $H'/8$ in the elutriation column F2 and is equal to or greater than $H/4$ in the elutriation column F2.

20 Revendications

1. Procédé d'élutriation, par un liquide, de particules solides d'un catalyseur Ziegler-Natta pour obtenir sa séparation en au moins deux portions qui diffèrent par leur granulométrie moyenne, caractérisé en ce que dans une étape préliminaire (étape 1) on prépare une suspension de particules solides de catalyseur dans le liquide d'élutriation qui est un liquide non-polaire, chimiquement inerte à l'égard du catalyseur, à une concentration allant de 20 à 150 grammes par litre, et en ce qu'en outre le procédé comporte une ou plusieurs des étapes définies suivantes M et N,

l'étape M étant un procédé de séparation des particules de grande dimension comportant l'introduction de la suspension du catalyseur au débit Q1 dans une colonne d'élutriation verticale F1 de hauteur H' , à un niveau situé entre $H'/2$ et le fond de la colonne, l'introduction de liquide d'élutriation au débit R1 dans la colonne F1 à un niveau inférieur à celui de l'introduction de la suspension du catalyseur, le liquide devant s'écouler dans la colonne en flux ascendant sensiblement sous des conditions d'écoulement laminaire, l'extraction de la partie supérieure de la colonne F1 d'une suspension du catalyseur sensiblement exempte de particules de grande dimension et l'extraction de la partie inférieure de la colonne F1 d'une suspension du catalyseur comprenant principalement des particules de grande dimension et

l'étape N étant un procédé de séparation des fines particules comportant l'introduction de la suspension du catalyseur au débit Q2 dans une colonne d'élutriation verticale F2 de hauteur H à un niveau situé au-dessus de $H/2$ et en dessous de $7H/8$, l'introduction du liquide d'élutriation au débit R2 dans la colonne F2 à un niveau situé en dessous de $H/2$, le liquide devant s'écouler dans la colonne en un flux ascendant et sensiblement sous les conditions d'écoulement laminaire, l'extraction de la partie supérieure de la colonne F2 du liquide d'élutriation chargé de fines particules du catalyseur et l'extraction de la partie inférieure de la colonne F2 des particules du catalyseur sensiblement exemptes de fines particules.

2. Procédé selon la revendication 1, caractérisé en ce que le rapport des débits $R1/Q1$ dans la colonne d'élutriation F1 est compris entre 0,2 et 5.

3. Procédé selon la revendication 1, caractérisé en ce que le rapport de débit $R2/Q2$ dans la colonne d'élutriation F2 est compris entre 0,3 et 6.

4. Procédé selon la revendication 1, caractérisé en ce que la concentration du catalyseur dans la colonne d'élutriation F1 est comprise entre 10 et 100 g/l et en ce que la concentration du catalyseur dans la colonne d'élutriation F2 est comprise entre 2 et 60 g/l.

5. Procédé selon la revendication 1, caractérisé en ce que le liquide d'élutriation est un hydrocarbure aliphatique.

6. Procédé selon la revendication 1, caractérisé en ce que l'élutriation s'effectue à l'aide d'un milieu d'élutriation liquide non polaire en présence d'un composé aprotique polaire.

7. Procédé d'élutriation de particules d'un catalyseur du type Ziegler-Natta, caractérisé en ce que l'élutriation s'effectue à l'aide d'un milieu d'élutriation liquide non polaire en présence d'un composé aprotique polaire.

8. Procédé selon la revendication 6 ou 7 dans lequel le composé aprotique polaire est un composé organo-métallique.

9. Procédé selon la revendication 6 ou 7 dans lequel le composé aprotique polaire est un organoaluminium, organozinc ou organomagnésium.

10. Procédé selon la revendication 6 ou 7, dans lequel le composé aprotique polaire s'emploie à une concentration de 0,1 à 100 millimoles par litre de liquide d'élutriation.

11. Procédé selon la revendication 6 ou 7 dans lequel le catalyseur du type Ziegler-Natta comporte un ou plusieurs composés d'un métal de transition associés avec, ou en combinaison chimique avec, un ou plusieurs composés de magnésium.



12. Appareil pour l'élutriation, par un liquide, d'un catalyseur de polymérisation de l'alpha-oléfine du type Ziegler-Natta, constitué d'au moins un composé d'un métal de transition appartenant aux groupes IV, V ou VI du Tableau périodique des éléments et un composé du magnésium, caractérisé en ce qu'il comporte:

- 5 - un réservoir M2 pour la préparation préliminaire d'une suspension du catalyseur dans le liquide d'élutriation, présentant des moyens conçus pour maintenir l'uniformité de la suspension,
- une colonne d'élutriation verticale F1 de hauteur H' et de diamètre D' tels que le rapport H'/D' soit égal ou supérieur à 5, ladite colonne comprenant: (a) un tube pour l'introduction de la suspension du catalyseur préparée dans le réservoir M2 ou de la suspension du catalyseur sensiblement exempte
- 10 de fines particules provenant de la sortie située à la partie supérieure de la colonne F2, selon le cas, à un niveau situé entre H'/2 et à la partie inférieure de la colonne; (b) un tube pour l'introduction du liquide d'élutriation à un niveau inférieur à celui de l'introduction de la suspension du catalyseur; (c) une sortie, par la partie supérieure de la colonne, une suspension du catalyseur sensiblement exempte de particules de grande dimension; et (d) une sortie, par la partie inférieure de la colonne, d'une sus-
- 15 pension du catalyseur comportant principalement des particules de grande dimension, et/ou
- une colonne d'élutriation verticale F2 de hauteur H et de diamètre D tels que le rapport H/D soit égal ou supérieur à 10, cette colonne comprenant: (a) un tube pour l'introduction de la suspension du catalyseur préparée dans le réservoir M2 ou la suspension du catalyseur sensiblement exempte de particules
- 20 de grande dimension provenant de la sortie prévue à la partie supérieure de la colonne F1, selon le cas, ce tube étant disposé à un niveau situé au-dessus de H/2 et en dessous de 7H/8; (b) un tube pour l'introduction du liquide d'élutriation à un niveau situé en dessous de H/2; (c) une sortie, par la partie supérieure de la colonne, des particules du catalyseur sensiblement exemptes de fines particules.

13. Appareil selon la revendication 12, caractérisé en ce qu'il comporte également des moyens pour séparer les particules du catalyseur et le liquide d'élutriation et des moyens pour recycler le liquide d'élutriation exempt des particules du catalyseur dans l'arrivée dans la colonne (F1) et/ou F2.

14. Appareil selon la revendication 12, caractérisé en ce que la distance séparant les points d'introduction du liquide d'élutriation et de la suspension du catalyseur est égale ou supérieure à H'/8 dans la colonne d'élutriation F1 et égale ou supérieure à H/4 dans la colonne d'élutriation F2.

30 Patentansprüche

1. Verfahren zur Aufschlammung von festen Teilchen eines Ziegler-Natta-Katalysators durch eine Flüssigkeit, um eine Auftrennung in mindestens 2 Teile zu erzielen, welche sich in der mittleren Teilchengröße unterscheiden, dadurch gekennzeichnet, daß in einer Vorstufe (Stufe 1) eine Suspension der festen Katalysatorteilchen in der Aufschlammungsflüssigkeit, welche eine nicht-polare, im Hinblick auf den Katalysator chemisch inerte Flüssigkeit ist, mit einer Konzentration im Bereich von 20 bis 150 g je Liter hergestellt wird, und ferner dadurch, daß das Verfahren eine oder mehrere der folgenden definierten Stufen M und N umfaßt, worin die Stufe

M ein Verfahren zum Abtrennen großer Teilchen ist, umfassend das Einbringen der Katalysatorsuspension mit einer Strömungsgeschwindigkeit Q1 in eine vertikale Aufschlammungskolonne F1, welche eine Höhe von H' besitzt, bei einer Höhe zwischen H'/2 und dem Boden der Kolonne, das Einbringen der Aufschlammungsflüssigkeit mit einer Strömungsgeschwindigkeit R1 in die Kolonne F1 bei einer Höhe, welche geringer als jene der Einbringung der Katalysatorsuspension ist, wobei die Flüssigkeit veranlaßt wird, in der Kolonne in einem aufsteigenden Strom im wesentlichen unter laminaren Strömungsbedingungen zu fließen, das Entnehmen einer Katalysatorsuspension, welche im wesentlichen von großen Teilchen frei ist, vom Kopf der Kolonne F1 und das Entnehmen einer Katalysatorsuspension, welche hauptsächlich große Teilchen umfaßt, vom Boden der Kolonne F1, und worin die Stufe

N ein Verfahren zum Abtrennen feiner Teilchen ist, umfassend das Einbringen der Katalysatorsuspension mit einer Strömungsgeschwindigkeit Q2 in eine vertikale Aufschlammungskolonne F2 mit der Höhe H, bei einer Höhe über

H/2 und unter 7H/8, das Einbringen der Aufschlammungsflüssigkeit mit einer Strömungsgeschwindigkeit R2 in die Kolonne F2 bei einer Höhe unter H/2, wobei die Flüssigkeit veranlaßt wird, in der Kolonne in einem aufsteigenden Strom und im wesentlichen unter laminaren Strömungsbedingungen zu fließen, das Entnehmen der mit feinen Katalysatorteilchen beladenen Aufschlammungsflüssigkeit vom Kopf der Kolonne F2 und das Entnehmen der im wesentlichen von feinen Teilchen befreiten Katalysatorteilchen vom Boden der Kolonne F2.

2. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Verhältnis der Strömungsgeschwindigkeit R1/Q1 in der Aufschlammungskolonne F1 von 0,2 bis 5 beträgt.

3. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß das Verhältnis der Strömungsgeschwindigkeiten R2/Q2 in der Aufschlammungskolonne F2 von 0,3 bis 6 beträgt.

4. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Katalysatorkonzentration in der Aufschlammungskolonne F1 von 10 bis 100 g/l beträgt und daß die Katalysatorkonzentration in der Aufschlammungskolonne F2 von 2 bis 60 g/l beträgt.

5. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Aufschlammungsflüssigkeit ein aliphatischer Kohlenwasserstoff ist.



6. Verfahren nach Anspruch 1, dadurch gekennzeichnet, daß die Aufschlammung unter Verwendung eines nicht-polaren flüssigen Aufschlammungsmediums in Gegenwart einer polaren aprotischen Verbindung ausgeführt wird.

7. Verfahren zur Aufschlammung von Teilchen eines Katalysators vom Ziegler-Natta-Typ, dadurch gekennzeichnet, daß die Aufschlammung unter Verwendung eines nicht-polaren flüssigen Aufschlammungsmediums in Gegenwart einer polaren aprotischen Verbindung ausgeführt wird.

8. Verfahren nach Anspruch 6 oder 7, worin die polare aprotische Verbindung eine organo-metallische Verbindung ist.

9. Verfahren nach Anspruch 6 oder 7, worin die polare aprotische Verbindung eine Organo-Aluminium-, Organo-Zink- oder Organo-Magnesiumverbindung ist.

10. Verfahren nach Anspruch 6 oder 7, worin die polare aprotische Verbindung in einer Konzentration von 0,1 bis 100 mmol je Liter Aufschlammungsflüssigkeit angewandt wird.

11. Verfahren nach Anspruch 6 oder 7, worin der Katalysator vom Ziegler-Natta-Typ eine oder mehrere Übergangsmetallverbindungen gemeinsam mit oder in chemischer Verbindung mit einer oder mehreren Magnesiumverbindungen umfaßt.

12. Vorrichtung zur flüssigen Aufschlammung eines festen alpha-Olefin-Polymerisationskatalysators vom Ziegler-Natta-Typ, bestehend aus mindestens einer zu den Gruppen IV, V oder VI des Periodensystems der Elemente gehörenden Übergangsmetallverbindung und aus einer Magnesiumverbindung, dadurch gekennzeichnet, daß sie:

– einen Tank M2 für die vorausgehende Herstellung einer Katalysatorsuspension in der Aufschlammungsflüssigkeit, welcher Mittel zum Aufrechterhalten der Einheitlichkeit der Suspension besitzt,
– eine vertikale Aufschlammungskolonne F1 mit einer Höhe H' und einem Durchmesser D' , sodaß das Verhältnis H'/D' gleich oder größer als 5 ist, welche Kolonne:

a) eine Rohrleitung zum Einbringen der im Tank M2 hergestellten Katalysatorsuspension oder der im wesentlichen von feinen Teilchen befreiten Katalysatorsuspension, welche vom Auslaß des Kopfes der Kolonne F2 kommt, wie es der Fall sein kann, in einer Höhe, die zwischen $H'/2$ und dem Boden der Kolonne liegt;

b) eine Rohrleitung zur Einbringung der Aufschlammungsflüssigkeit in einer Höhe, welche geringer als jene der Einbringung der Katalysatorsuspension ist;

c) einen Auslaß vom Kopf der Kolonne für eine Katalysatorsuspension, welche im wesentlichen von großen Teilchen frei ist; und

d) einen Auslaß vom Boden der Kolonne für eine Katalysatorsuspension, welche hauptsächlich große Teilchen umfaßt, aufweist, und/oder

– eine vertikale Aufschlammungskolonne F2, mit einer Höhe H und einem Durchmesser D , sodaß das Verhältnis H/D gleich oder größer als 10 ist, welche Kolonne:

a) eine Rohrleitung zur Einbringung der im Tank M2 hergestellten Katalysatorsuspension oder der im wesentlichen von großen Teilchen freien Katalysatorsuspension, welche vom Auslaß am Kopf der Kolonne F1 kommt, wie es der Fall sein kann, welche Rohrleitung in einer Höhe über $H/2$ und unter $7H/8$ angeordnet ist;

b) eine Rohrleitung zur Einbringung der Aufschlammungsflüssigkeit in einer Höhe unter $H/2$;

c) einen Auslaß vom Kopf der Kolonne für im wesentlichen von feinen Teilchen befreite Katalysatorteilchen, besitzt, umfaßt.

13. Vorrichtung nach Anspruch 12, dadurch gekennzeichnet, daß sie auch Mittel zum Trennen der Katalysatorteilchen und der Aufschlammungsflüssigkeit und Mittel zum Zurückführen der von den Katalysatorteilchen befreiten Aufschlammungsflüssigkeit zur Zuführung zu der Kolonne F1 und/oder F2 umfaßt.

14. Vorrichtung nach Anspruch 12, dadurch gekennzeichnet, daß der Abstand, welcher die Punkte der Einbringung der Aufschlammungsflüssigkeit und der Katalysatorsuspension trennt, gleich oder größer als $H'/8$ in der Aufschlammungskolonne F1 und gleich oder größer als $H/4$ in der Aufschlammungskolonne F2 ist.