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(54) Title: LOOP REACTOR WITH VARYING DIAMETER FOR OLEFIN POLYMERIZATION

(57) Abstract: Process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension medium and this suspension is circulated by means of an axial pump, wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous product discharge, and wherein the polymerization is carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium. The loop reactor has a diameter which varies by at least 10% and in which there is at least one widening and narrowing in a region other than that of the axial pump.



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LOOP REACTOR WITH VARYING DIAMETER FOR OLEFIN POLYMERIZATION

The present invention relates to a process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a
5 pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension medium and this suspension is circulated by means of an axial pump.

Suspension polymerization processes for polymerizing olefins have been known for a long time. A suspension polymerization in which the polymerization is carried out in a loop reactor has been
10 found to be particularly useful for the polymerization of ethylene in particular, usually together with further comonomers. In such loop reactors, the polymerization mixture is pumped continuously through a cyclic reactor tube. The pumped circulation firstly achieves continual mixing of the reaction mixture, and also distributes the catalyst metered in and the feed monomers in the reaction mixture. Secondly, the pumped circulation prevents sedimentation of the suspended
15 polymer. The removal of the heat of reaction via the reactor wall is also promoted by the pumped circulation.

The polymer is generally discharged from the loop reactor in a discontinuous fashion in sedimentation legs. These sedimentation legs are projections which branch off vertically from the
20 lower part of the reactor tube and in which the polymer particles can settle. After sedimentation of the polymer has reached a particular point, a valve at the lower end of the sedimentation legs is opened briefly and the polymer which has settled is discharged discontinuously.

Since loop reactors have been used for production purposes for many years, numerous efforts
25 have been made to improve the economics of these reactors and the polymerization processes carried out therein. An increase in the space-time yield of the process is particularly desirable. The space-time yield is, in particular, limited by removal of the heat of reaction via the reactor wall and by the polymer content of the reaction suspension. An increase in the proportion of solids in the reactor will, in particular, make discharge of the polymer more effective and increase the
30 mean residence time of the polymer in the reactor.

US-A-6,239,235 describes a polymerization process in a loop reactor, in which an increase in the average proportion of solids in the reactor is achieved by means of a continuous discharge system. This continuous discharge system was able to achieve an average proportion of solids in
35 the reactor of 53% by weight, whereas the conventional discontinuous discharge achieved an average solids concentration of only 45% by weight. In accordance with conventional teachings, the document makes no reference to a varying reactor diameter; in contrast, disturbance-free flow is said to be achieved by means of gentle curves. Only in the region of the impeller pump does there seem to be, apparently for reasons of impeller construction, a short widening of the reaction

tube diameter. The process described in this document, too, leaves something to be desired in respect of the solids concentration in the reactor. The document also confirms the prevailing view that it is generally not possible to achieve polymer solids concentrations of more than 37-40 percent by weight in suspension polymerization processes.

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It is an object of the present invention to find a process for polymerizing olefinic monomers in a loop reactor, which process makes higher solids concentration in the reactor and higher space-time yields possible.

- 10 We have found that this object is achieved by the process described at the outset wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous
- 15 product discharge, and wherein the polymerization is carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium.

- In addition, we have found a process described at the outset wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the
- 20 total mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous product discharge, and wherein the loop reactor used comprises a cyclic reactor tube whose diameter varies by at least 10%, based on the predominant reactor tube diameter, and in which there is at least one widening and
- 25 narrowing in a region other than that of the axial pump. It is also advantageous if the reactor tube additionally has a widening and narrowing in the region of the axial pump.

- The process of the present invention is suitable for polymerizing various olefinic monomers, in particular for polymerizing ethylene, propylene and 1-butene or mixtures of these monomers. It is
- 30 also possible to use additional monomers as comonomers, e.g. further α -olefins such as 1-pentene, 1-hexene, 1-octene or 1-decene.

- Particular preference is given to a process in which ethylene is used as monomer and at least one α -olefin having from 3 to 8 carbon atoms, preferably 1-butene, 1-hexene or 1-octene, is used as
- 35 comonomer. The amount of comonomer depends on the incorporation behavior of the particular catalyst in respect of the comonomer and on the desired density of the copolymer. The more comonomer incorporated into the polymer, the lower the density of the copolymer will be. A person skilled in the art can readily set the monomer:comonomer ratio on the basis of these considerations.

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If the catalyst permits, vinylaromatic comonomers such as styrene or polar comonomers such as vinyl acetate, vinyl alcohols, acrylic acid or acrylic esters can also be polymerized. Cyclic monomers such as norbornene and dienes such as butadiene, 1,5-hexadiene or 1,7-octadiene are also possible as comonomers.

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The polymerization process of the present invention can advantageously be carried out at from 20 to 150°C, preferably from 50 to 110°C, with an upper limit being imposed on the reaction temperature by the melting point of the polymer to be formed.

- 10 The reaction pressure is usually in the range from 5 to 100 bar, preferably from 10 to 80 bar. Low pressures are generally associated with low space-time yields, while higher pressures require an increased capital investment and lead to higher energy costs for compression. In general, a reaction pressure in the range from 20 to 50 bar represents a good compromise between apparatus cost and reaction yield. When supercritical suspension media such as supercritical
- 15 propane are employed, a higher pressure above the critical pressure can be appropriate from a technical point of view.

In a preferred embodiment of the process of the present invention, the polymerization is carried out at a pressure of from 43 to 80 bar, particularly preferably a pressure of 45-75 bar.

- 20 Polymerizations in a loop process are usually carried out at pressures of about 40 bar. An increase in the pressure has little effect. In the process of the present invention with high solids concentrations in the reactor, it has surprisingly been found that an increase in the pressure, in particular to pressures above 43 bar, has a significant influence on the solids concentration which can be increased further by means of the pressure increase. This effect appears to be due to the
- 25 proportion of suspension medium in the reactor contents becoming so small at high solids concentrations that the process of dissolution of ethylene in the suspension medium becomes a significant factor in determining the polymerization rate. A high ethylene pressure then leads to a higher concentration of dissolved ethylene.

- 30 Suitable suspension media for the process of the present invention are all media which are generally known for use in loop reactors. The suspension medium should be inert and be liquid or supercritical under the reaction conditions and should have a boiling point which differs significantly from those of the monomers and comonomers used in order to make it possible to recover the starting materials from the product mixture by distillation. Examples of customary
- 35 suspension media are isobutane, butane, propane, isopentane, pentane and hexane.

An important feature of the process of the present invention is that it allows polymerization at high ethylene concentrations. High proportions of solids in the reactor, in the present context also referred to simply as "reactor density", result in the proportion of the suspension medium in the

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reactor being correspondingly lower. In general, the smaller volume of the suspension medium results in the amount of ethylene in the reactor also being lower, which leads to reduced polymer formation. In contrast, the process of the present invention makes it possible to increase the ethylene concentration in the suspension medium and thus achieve higher polymer formation and a higher polymerization rate even at high reactor densities.

In the process of the present invention, the polymerization is therefore carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium. It is preferred to have an ethylene concentration of at least 11 mol%, more preferably at least 12 mol%, even more preferably of at least 13 mol%, most preferably of at least 14 mol%.

Ethylene concentrations of 15 mol% and even 17 mol%, based on the suspension medium, were achieved in the process of the present invention.

In this context, the term "suspension medium" refers not simply to the suspension medium used, e.g. isobutane, but to the mixture of this suspension medium with the monomers dissolved therein. The ethylene concentration can be determined easily by gas-chromatographic analysis of the suspension medium.

As mentioned at the outset, the technology of loop reactors has been known for a long time. In general, these reactors consist essentially of a cyclic reactor tube having one or more ascending and one or more descending segments which are surrounded by cooling jackets for removing the heat of reaction and also horizontal tube sections which connect the vertical segments. The lower tube section usually accommodates the axial pump, preferably an impeller pump, the feed facilities for catalyst and monomer and the discharge device, i.e. generally the sedimentation legs. However, the reactor can also have more than two vertical tube sections, so that a meandering arrangement is obtained.

The present invention makes it possible to carry out a suspension polymerization process in a loop reactor at solids concentrations of more than 53% by weight, based on the total mass of the contents of the reactor, and thus increase the production capacity of the loop reactor. These high solids concentrations can be achieved by various means.

In one embodiment of the present invention, the high solids concentration is achieved by the diameter of the cyclic reactor tube being varied by more than 10%, based on the predominant reactor tube diameter. A widening of the reactor tube in the region of the axial pump necessitated by the construction should not be taken into consideration here, since such a widening serves primarily to accommodate the axial pump, particularly the impeller of an impeller pump, in the reaction tube and highly turbulent flow prevails in this region in any case. Rather, the invention is

based inter alia on the observation that, contrary to prevailing opinion, deliberate nonuniform flow of the polymerization mixture in the region of the reaction tube even outside the region of the axial pump makes it possible to increase the solids concentration in the reactor. This effect appears, without wishing to be tied to this hypothesis, to be based on more effective mixing of the heterogeneous reaction mixture. In particular, the monomer fed in, e.g. ethylene, is apparently dispersed more quickly in the reaction mixture, is dissolved more quickly in the suspension medium and is available to a greater degree for the polymerization. The removal of the heat of reaction also appears to be aided, since the disturbance of the flow increases motion perpendicular to the flow direction, i.e. in the direction of the cooled reactor wall, which occurs to only a very limited extent in the case of uniform plug flow.

To be able to influence the flow conditions in this desired way, the reaction tube diameter should be varied to a particular degree. The diameter of the tube should vary by at least 10%, based on the predominant diameter of the reactor tube. For the present purposes, the predominant diameter of the reactor tube is the tube diameter which is constant over the longest stretch of the reactor tube. The tube diameter should preferably vary by at least 20%, even better by at least 30% and very particularly preferably by at least 50%.

The conical widening of the reactor tube diameter in the flow direction should have a cone angle of about 0.5-10°, preferably 0.5-1.5°, and the cone angle at the narrowing of the tube diameter down to the predominant tube diameter should be about 0.5-10°, preferably 1-3°.

The length of the sections having a widened tube diameter is preferably from 2 to 30 times the predominant tube diameter, particularly preferably from 5 to 15 times this tube diameter.

In a preferred embodiment of the process of the present invention, there is also an additional widening and narrowing of the reaction tube in the region of the axial pump. As mentioned above, such widenings necessitated by the construction are already known. The effect of these widenings in accordance with the present invention can, however, be increased by making the widening greater and possibly also extending it over a longer section of the tube than is required by the construction.

The effect of the present invention in terms of enabling the solids concentration in the reactor to be increased appears to be based, inter alia, on better mixing of the monomer in the reaction mixture. It has been found that this inventive effect can be increased by feeding the monomer, i.e. for example ethylene, in at various points along the reaction tube. An advantageous embodiment of the process of the present invention therefore comprises feeding at least one olefinic monomer in at at least 2 points along the reactor tube. It has been found to be advantageous for the monomer to be fed in at, for example, 3 or 4 points along the reactor tube. These feed points can

be provided uniformly along the reactor tube, and it is advantageous for the feed points to be located in each case upstream of the widenings of the tube, but not in the region of the last vertical segment before the product discharge region.

- 5 It is known from US-A-6,239,235 that a continuous discharge system can also be useful for increasing the solids concentration in the reactor. This measure can be combined with the process of the present invention. Accordingly, the present invention also provides a process as described above in which the polymer formed is discharged continuously from the reactor.
- 10 The high solids concentration in the reactor which is sought according to the present invention can, as indicated above, be achieved by the abovementioned means. Particular preference is given to a process in which the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor. This solids concentration is preferably above 55% by weight, more preferably above 58% by
- 15 weight and particularly preferably above 60% by weight. As shown in the examples, solids concentrations of more than 62% by weight can be achieved. For the present purposes, the average solids concentration is then the solids concentration in the reaction tube. Even higher solids concentrations can be observed in the discharge system, whether continuous or discontinuous, due to sedimentation.
- 20 The high solids concentrations can be achieved by the measures provided by the present invention even without continuous discharge of the polymer product. One variant of the process of the present invention therefore comprises discharging the polymer formed from the reactor in a discontinuous fashion and carrying out the polymerization at an average solids concentration in
- 25 the reactor of more than 45% by weight, based on the total mass of the contents of the reactor. Under these conditions, the solids concentration in the reactor is preferably above 50% by weight, particularly preferably above 55% by weight.
- The process of the present invention can be operated as a single-stage process, but can also be
- 30 carried out as a multistage cascade process by combining it with further polymerization reactors. One embodiment of the process of the present invention is therefore a process for polymerizing at least one olefinic monomer in a loop reactor, wherein the polymerization in this loop reactor is preceded or followed by at least one further polymerization step in a loop reactor or a gas-phase reactor. Such cascade processes, albeit without the specific features of the present invention, are
- 35 described, for example, in EP-A-517 868 and US-A-6 355 741.

Apart from the above-described disturbance of the suspension flow in the reaction tube, a high reactor density can also be achieved by other measures, for example by selection of a particularly suitable catalyst.

Catalysts suitable for use in the process of the present invention are in principle all catalysts which are also used otherwise in loop reactors, i.e., for example, chromium catalysts of the Phillips type, Ziegler catalysts, Ziegler-Natta catalysts or single-site catalysts such as metallocene catalysts. Phillips catalysts have become particularly widespread in loop reactors, and can also be
5 used particularly advantageously in the process of the present invention. Among these catalysts, particular preference is given to those described in the patent applications WO-01/18069, WO-01/17675, WO-01/17676 and WO-01/90204. It has been determined that, surprisingly, that these catalysts make it possible to achieve very high solids concentrations in the reactor, even without the reactor tube of the loop reactor having a varying tube diameter.

10 The process of the present invention has numerous advantages over processes in which the solids concentration in the reactor is lower: the consumption of suspension medium is lower, the catalyst productivity is greater, the reactor throughput is greater, the space-time yield is greater, without significant additional capital investment being necessary. Since the process also makes it
15 possible to obtain products having a particularly high molecular weight (i.e. low melt flow rates), a higher activation temperature can be utilized for preparing products having an intermediate molecular weight when using Phillips catalysts. Activation at a higher activation temperature generally leads in turn to more active catalysts, so that the resulting polymers have a lower proportion of catalyst residues.

20 The products resulting from the process of the present invention also display a number of advantages. Compared to conventionally produced products, they display a lower level of catalyst residues (ash), a higher powder density, lower proportions of very fine particles and therefore better handleability. The low proportion of catalyst residues usually also results in more
25 homogeneous products having fewer specks.

The examples which follow illustrate the process of the invention:

Examples

30 Preparation of catalyst A:

The preparation of the catalyst up to the activation step was carried out by the method described in WO 01/90204. Activation was then carried out at 520°C in the presence of air in a fluidized-bed
35 activator. Fluoride doping was carried out by use of a mixture of the catalyst precursor with 2.5% by weight of ammonium hexafluorosilicate (resulted in a fluoride content of about 1% by weight, based on the total mass of the catalyst) in the activation. For activation, this mixture was heated to 350°C over a period of 1 hour, maintained at this temperature for 1 hour, subsequently heated to

the desired activation temperature of 520°C, maintained at this temperature for 2 hours and subsequently cooled, with cooling below 350°C being carried out under N₂.

Polymerization:

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Ethylene was copolymerized with 1-hexene at 104°C and a pressure of 39 bar using the above-described catalyst in a loop reactor having a reactor volume of 0.18 m³ and an impeller pump as axial pump. Ethylene was fed into the reactor at two points, one shortly before the impeller.

Isobutane was used as suspension medium. The isobutane was fed into the reactor at 6 points, including in the region of the impeller pump shaft and the place where the catalyst was introduced. The impeller pump was operated at 1700-1900 revolutions per minute. The product was discharged discontinuously via customary sedimentation legs. Polymerizations were carried out at slightly different ethylene/isobutane ratios, but the resulting product always had a density of about 0.949 g/ccm and a high-load melt index (21.6/190) of about 2.0.

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Further polymerization parameters are listed in Table A below:

Table A: Polymerizations using the chromium catalyst A

20	Experiment No.	1-A	2-A	3-A	4-A	5-A	6-A	7-A
	Ethene addition (kg/h)	33	35	34	33	33	33	33
	Isobutane addition (kg/h)	34	31	28	24	19	13	10
25	Ethene/isobutane	0.97	1.12	1.21	1.38	1.74	2.54	3.24
	Ethene fraction in suspension medium (mol%)	9.6	11.4	12.5	14.7	16.1	16.0	15.7
30	Solids concentration in reactor (% by weight)	48.0	55.2	58.8	61.2	64.8	66.9	68.8
	Productivity (g polymer/g catalyst)	4300	6900	7634	7752	9174	9259	10989
35	Powder density (kg/m ³)	480	500	506	513	515	522	516
	Fine dust (% by weight of particles < 125 µm)	1.3	n.d.	n.d.	n.d.	0.4.	n.d.	n.d.

Preparation of catalyst B:

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The preparation was carried out like that of catalyst A, but activation was carried out at 600°C for 10 hours without fluoride doping.

Polymerization:

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Ethylene was polymerized with 1-hexene at 102°C and under conditions indicated in Table B using the catalyst B in a loop reactor having a reactor volume of 32 m³. Isobutane addition and circulation were carried out as in Example A. The conditions were chosen so that a polymer having a density of 0.946 g/cm³ and a high-load melt index (21.6/190) of about 6.0 is formed. It can clearly be seen from the experiments at different pressures that an increase in the pressure has a significant influence on the solids concentration in the reactor.

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Table B: Polymerizations using the chromium catalyst B

15	Experiment No.	1-B	2-B	3-B	4-B	5-B	6-B	7-B
	Reaction pressure (bar)	42.5	42.5	42.5	43.5	43.5	43.5	43.5
	Ethene addition (t/h)	7.1	7.1	7.2	7.0	7.0	7.0	6.7
	Isobutane addition (t/h)	5.3	5.5	5.5	4.7	4.7	4.7	4.5
	Ethene/isobutane	1.34	1.29	1.31	1.49	1.49	1.49	1.49
20	Ethene fraction in suspension medium (vol%)	12.0	11.7	11.7	12.4	13.5	13.5	14.4
	Solids concentration in reactor (% by weight)	50.1	50.7	50.8	55.4	55.7	56.1	56.2
25	Powder density (kg/m ³)	489	496	485	490	482	480	477
	Fine dust (% by weight of particles < 125 µm)	1.2	0.5	0.4	0.4	0.4	0.4	0.3
30	Ash residue (ppm)	230	240	235	200	200	200	180

Preparation of catalyst C:

The catalyst was prepared as in EP-B1-589350, example 2, but at an activation temperature of 520°C and an activation time of 5 hours.

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Polymerization:

Ethylene was polymerized with 1-hexene at 106°C in the presence of 0.13-0.14 ppm of carbon monoxide and under the conditions indicated in Table C using the catalyst C in a loop reactor

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having a reactor volume of 32 m³. Isobutane addition and circulation were carried out as in Example A. The conditions were chosen such that a polymer having a density of 0.954 g/cm³ and a high-load melt index (21.6/190) of about 2.0 is formed.

5 Table C: Polymerizations using the chromium catalyst C

	Experiment No.	1-C	2-C	3-C	4-C	5-C	6-C	7-C
	Reaction pressure (bar)	42.5	42.5	42.5	43.5	43.5	43.5	43.5
	Ethene addition (t/h)	5.1	5.1	5.0	5.0	5.0	5.0	6.0
10	Isobutane addition (t/h)	4.6	4.5	4.2	3.4	3.4	3.4	3.7
	Ethene/isobutane	1.11	1.13	1.19	1.47	1.47	1.47	1.62
15	Ethene fraction in suspension medium (vol%)	9.0	9.0	9.5	11.5	11.5	11.5	11.5
	Solids concentration in reactor (% by weight)	51.3	51.3	51.6	57.2	57.2	57.2	57.4
	Ash residue (ppm)	420	430	380	270	270	270	320
20	Fine dust (% by weight of particles < 125 µm)	0.9	1.0	1.0	0.6	0.2	0.2	0.4
	Powder density (kg/m ³)	490	486	495	503	500	501	500

Polymerization in the presence of catalyst D:

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Ethylene was polymerized with 1-hexene at 106.7°C and under the conditions indicated in Table C using the catalyst D (catalyst 967 BWFL from Grace) in a loop reactor having a reactor volume of 32 m³. Isobutane addition and circulation were carried out as in Example A. The conditions were chosen so that a polymer having a density of 0.954 g/cm³ and a high-load melt index

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Table D: Polymerizations using the chromium catalyst D

	Experiment No.	1-D	2-D
35	Reaction pressure (bar)	42.5	46.5
	Ethene addition (t/h)	6.0	6.0
	Isobutane addition (t/h)	5.1	3.7
40	Ethene/isobutane	1.18	1.62

5	Ethene fraction in suspension medium (vol%)	10.0	15.0
	Solids concentration in reactor (% by weight)	50.4	59.9
	Ashing residue (ppm)	310	220
	Powder density (kg/m ³)	475	500

Polymerization in the presence of catalyst E:

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Ethylene was polymerized with 1-hexene at 95°C and under the conditions indicated in Table C using the catalyst E (Ziegler catalyst Sylopol 5951 from Grace) in a loop reactor having a reactor volume of 32 m³. Isobutane addition and circulation were carried out as in Example A. The conditions were chosen so that a polymer having a density of 0.951 g/cm³ and a melt index (2.16/190) of about 6.0 is formed.

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Table E: Polymerizations using the Ziegler catalyst E.

20	Experiment No.	1-E	2-E	3-E	4-E	5-E	6-E
	Reaction pressure (bar)	42.5	42.5	43.5	43.5	43.5	43.5
	Ethene addition (t/h)	6.0	5.5	5.5	5.5	5.5	5.5
	Isobutane addition (t/h)	6.2	6.0	5.3	5.3	5.3	5.3
25	Ethene/isobutane	0.97	0.92	1.04	1.04	1.04	1.06
	Ethene fraction in suspension medium (vol%)	12.5	10.4	12.2	12.1	11.8	11.7
	Solids concentration in reactor (% by weight)	45.7	45.2	49.4	49.8	49.7	49.4
30	Powder density (kg/m ³)	408	406	415	404	411	415

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We claim:

1. A process for polymerizing at least one olefinic monomer in a loop reactor at from 20 to 150°C, but below the melting point of the polymer to be formed, and a pressure of from 5 to 100 bar, where the polymer formed is present in a suspension in a liquid or supercritical suspension medium and this suspension is circulated by means of an axial pump, wherein the polymerization is carried out at an average solids concentration in the reactor of more than 53% by weight, based on the total mass of the contents of the reactor, in the case of continuous product discharge and at an average solids concentration in the reactor of more than 45% by weight, based on the total mass of the contents of the reactor, in the case of discontinuous product discharge, and wherein the polymerization is carried out at an ethylene concentration of at least 10 mol%, based on the suspension medium.
2. A polymerization process as claimed in claim 1, wherein the loop reactor comprises a cyclic reactor tube whose diameter varies by at least 10%, based on the predominant reactor tube diameter, and in which there is at least one widening and narrowing in a region other than that of the axial pump.
3. A process as claimed in claim 1 or 2, wherein there is an additional widening and narrowing of the reactor tube in the region of the axial pump.
4. A process as claimed in any of the preceding claims, wherein the polymerization is carried out at pressure of from 43 to 80 bar.
5. A process as claimed in any of the preceding claims, wherein ethylene is used as monomer and at least one α -olefin having from 3 to 8 carbon atoms is used as comonomer.
6. A process as claimed in any of the preceding claims, wherein at least one olefinic monomer is fed in at at least 2 points along the reactor tube.
7. A process as claimed in any of the preceding claims, wherein the polymer formed is discharged continuously from the reactor.
8. A process for polymerizing at least one olefinic monomer in a loop reactor as claimed in any of the preceding claims, wherein the polymerization in this loop reactor is preceded or followed by at least one further polymerization step in a loop reactor or a gas-phase reactor.

INTERNATIONAL SEARCH REPORT

Inter: I Application No
PCT/EP2004/010376

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 B01J19/18 C08F2/01

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 B01J C08F

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 482 148 A (MONTEDISON SPA) 3 August 1977 (1977-08-03) page 1, line 36 - line 56 page 1, line 84 - page 2, line 7 page 2, line 8 - line 30; figure 1	2-8
A	WO 97/04015 A (MONTELL TECHNOLOGY COMPANY BV) 6 February 1997 (1997-02-06) abstract page 11, line 1 - line 8 page 11 - page 13; figure 1 page 14, paragraph 4 - page 15, paragraph 1 ----- -/--	2-8

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

° Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *G* document member of the same patent family

Date of the actual completion of the international search

3 December 2004

Date of mailing of the international search report

13/12/2004

Name and mailing address of the ISA

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Thomasson, P

INTERNATIONAL SEARCH REPORT

Inter:

Application No

PCT/EP2004/010376

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 6 239 235 B1 (FRANKLIN III ROBERT K ET AL) 29 May 2001 (2001-05-29) cited in the application abstract column 1, line 40 - line 53 column 2, line 60 - column 3, line 33 -----	2-8
P,X	WO 2004/026463 A (ATOFINA RES ; FOUARGE LOUIS (BE); LEWALLE ANDRE (BE)) 1 April 2004 (2004-04-01) abstract page 3, line 4 - line 30; figure 1 page 4, line 9 - line 11 claim 15 -----	2-8
A	DE 905 547 C (BATAAFSCHE PETROLEUM) 4 March 1954 (1954-03-04) page 1, line 1 - line 25 page 2, line 90 - line 100 page 3, line 10 - line 32; figure 4 -----	2-8

INTERNATIONAL SEARCH REPORT

In international application No.
PCT/EP2004/010376

Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☒ Claims Nos.: 1
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
see FURTHER INFORMATION sheet PCT/ISA/210
3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☐ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest.

☐ No protest accompanied the payment of additional search fees.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box II.2

Claims Nos.: 1

Claim 1 indicates a process defined by reference to a desirable characteristic, namely an average solids concentration of more than 53 % by weight (continuous discharge) or more than 45 % by weight (discontinuous discharge) and with an ethylene concentration of at least 10 mol %. Claim 1 lacks clarity (Article 6 PCT). An attempt is made to define the process by reference to a result to be achieved. The concentrations of solids and of ethylene indicated in claim 1 are achieved by only a limited number of methods, namely those using a loop reactor whose diameter varies by at least 10% and in which there is at least one widening and narrowing (see the description on page 2, lines 18-26; page 4, line 29-32; page 4, line 34 - page 5, line 17). In the present case, claim 1 so lacks support that a meaningful search over the whole of the claimed scope of claim 1 is impossible. Consequently, the search has been carried out for those parts of the claims which appear to be clear namely claim 2 and claims 3-8 restricted to the dependency of claim 2.

The applicant's attention is drawn to the fact that claims relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure. If the application proceeds into the regional phase before the EPO, the applicant is reminded that a search may be carried out during examination before the EPO (see EPO Guideline C-VI, 8.5), should the problems which led to the Article 17(2) declaration be overcome.

INTERNATIONAL SEARCH REPORT

Information on patent family members

Intern

Application No

PCT/EP2004/010376

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INTERNATIONAL SEARCH REPORT

Information on patent family members

Interr Application No
PCT/EP2004/010376

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