(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 137 516 B1**

(12) **EUROPEAN PATENT SPECIFICATION**

(45) Date of publication and mention of the grant of the patent:
25.04.2018 Bulletin 2018/17

(21) Application number: **16711821.5**

(22) Date of filing: **23.03.2016**

(51) Int Cl.:
C08F 10/02 $^{(2006.01)}$

(86) International application number:
PCT/EP2016/056338

(87) International publication number:
WO 2016/150996 (29.09.2016 Gazette 2016/39)

(54) CONTINUOUS GAS-PHASE POLYMERIZATION PROCESSES

POLYMERISATIONSVERFAHREN MIT KONTINUIERLICHER GASPHASE

PROCÉDÉS CONTINUS DE POLYMÉRISATION EN PHASE GAZEUSE

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **25.03.2015 US 201562137883 P**

(43) Date of publication of application:
08.03.2017 Bulletin 2017/10

(73) Proprietor: **Basell Polyolefine GmbH**
50389 Wesseling (DE)

(72) Inventors:
- **FRAAIJE, Volker**
  60325 Frankfurt (DE)
- **LYNCH, Michael**
  Houston, TX 77010 (US)
- **MIHAN, Shahram**
  65812 Bad Soden (DE)
- **MEIER, Gerhardus**
  60320 Frankfurt (DE)
- **SCHUELLER, Ulf**
  64331 Weiterstadt (DE)

(74) Representative: **Seelert, Stefan et al**
Basell Polyolefine GmbH
Intellectual Property
Bldg. B852, 5th floor
Industriepark Hoechst
65926 Frankfurt (DE)

(56) References cited:
EP-A1- 2 722 347 **US-A1- 2010 167 058**

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present disclosure relates to a continuous process for the preparation of ethylene homopolymers or ethylene copolymers comprising polymerizing ethylene or copolymerizing ethylene and one or more other olefins in the presence of a chromium catalyst in a gas-phase polymerization reactor, which contains a reactor bed of particulate polymer and which is equipped with a cycle gas line for withdrawing reactor gas from the reactor, leading the reactor gas through a heat-exchanger for cooling and feeding the reactor gas back to the reactor.

BACKGROUND OF THE INVENTION

[0002] Gas-phase polymerization processes are economical processes for the polymerization or copolymerization of olefins. Such gas-phase polymerization processes can be carried out either as gas-phase fluidized-bed processes or as stirred gas-phase processes. A characteristic of gas-phase fluidized-bed processes is that the bed comprising polymerizing polymer particles is kept in the fluidized state by introduction of a gas mixture from below. This gas mixture also removes the heat of polymerization from the reactor. The reaction gas is cooled in a heat exchanger located outside the reactor and is recirculated back into the reactor through a gas distributor plate (cycle gas).

[0003] However, the cycle gas also entrains a certain amount of finely divided polymer and carries it from the reactor and into the cycle gas system. These polymer particles comprise active catalyst and can thus polymerize further in the cycle gas system. If these particles deposit in the cycle gas system, deposits and fouling can occur in these places. These deposits can lead to malfunctions (blockage of the cooler, conglutination in the compressor) and parts of these deposits can become detached again. The detached deposits can block the holes of the gas distributor plate of the reactor and thus necessitate system shutdown and costly cleaning. If pieces of detached deposits get through the gas distributor plate into the reactor, the product quality is adversely affected by these particles by the formation of so-called specks or gels. Particularly in the case of products for film applications, out-of-specification material may thus be obtained.

[0004] For reducing the proportion of fine polymer dust in the cycle gas system, it is possible to install in the cycle gas line a cyclone downstream of the reactor outlet. However, complete precipitation cannot be achieved by means of a cyclone, as fine dust containing active catalyst may pass the cyclone.

[0005] Another option for avoiding fouling and the formation of polymer deposits in the cycle gas system is feeding a catalyst poison into the cycle gas line.

[0006] EP 0 431 626 A1 discloses a method for inhibiting polymer build-up in a heat exchanger during the gas phase polymerization of alpha-olefins which comprises introducing para-ethylethoxybenzoate upstream of the heat exchanger in amounts sufficient to inhibit polymer build-up. The prepared polyolefin is preferably a propylene impact copolymer.

[0007] US 5,625,012 describes a method for inhibiting polymer build-up in a recycle line and a heat exchanger during a polymerization of one or more alpha olefins in the presence of a transition metal catalyst, which comprises introducing as an antifouling agent an alcohol having 1 to 10 carbon atoms, an alkyl or cycloalkyl ether having 2 to 20 carbon atoms, or a mixture thereof at one or more locations in the recycle gas line in an amount sufficient to inhibit polymer build-up, and discloses the preparation of EPDM rubbers while feeding isopropanol into the cycle gas line.

[0008] EP-A-0 927 724 and WO 03/042253 A1 disclose gas-phase polymerization processes in which a catalyst poison having a boiling point above the maximum temperature within the cycle gas line is fed into this cycle gas line to prevent polymer deposits in the cycle gas line. The catalyst poison is preferably an alkylamino ethoxylate.

[0009] WO 2006/107373 A1 describes a process for reducing the ultra-high molecular weight polymeric material content of a high density polyethylene produced with a bis-triarylsilyl chromate catalyst system in which a catalyst deactivator, which has a boiling point lower than the maximum temperature within the cycle gas line, is introduced into the recycle gas line.

[0010] EP 2 722 347 A1 discloses a multistage process for the gas-phase polymerization of olefins which is carried out in the presence of a hydroxyester having at least one free hydroxyl group, obtained from reacting a polyalcohol with a carboxylic acid having from 4 to 22 carbon atoms. US 2010/167058 A1 discloses a process for producing a heterophasic copolymer in a combination of two polymerization reactors which includes adding a multicomponent antifoulant to the second polymerization reactor.

[0011] However, feeding catalyst poisons to ethylene polymerizations carried out in the presence of chromium catalysts may adversely affect the mechanical properties of the resulting polyethylenes and sometimes an increased tendency to yellowing of the obtained polymers is observed. Moreover, adding catalyst poisons can result in an increased content of ultra-high molecular weight polymeric material in the produced polyethylene which is also detrimental to the optical properties and which may further increase the gel level. Consequently, there is still a need for a process for the preparation of ethylene homopolymers or ethylene copolymers in the presence of a chromium catalyst, which process allows preparing ethylene polymers having outstanding optical, mechanical and processing properties and a low gel content and which can be carried out with high catalyst productivity and without operational problems.

SUMMARY OF THE INVENTION

[0012] The present disclosure provides a continuous process for the preparation of ethylene homopolymers or ethylene copolymers comprising polymerizing ethylene or copolymerizing ethylene and one or more other olefins in the presence of a chromium catalyst in a gas-phase polymerization reactor, which contains a reactor bed of particulate polymer and which is equipped with a cycle gas line for withdrawing reactor gas from the reactor, leading the reactor gas through a heat-exchanger for cooling and feeding the reactor gas back to the reactor, wherein the polymerization is carried out at a temperature from 30°C to 130°C and a pressure of from 0.1 to 10 MPa and an aliphatic carboxylic acid ester having from 8 to 24 carbon atoms, which has a melting point of less than 20°C, is added.

[0013] In some embodiments, the aliphatic carboxylic acid ester is fed into the cycle gas system at a position upstream of the heat-exchanger.

[0014] In some embodiments, the cycle gas line is equipped with a cyclone upstream of the heat-exchanger and the aliphatic carboxylic acid ester is fed into the cycle gas system at a position between the reactor and the cyclone.

[0015] In some embodiments, the mixture of fine dust and aliphatic carboxylic acid ester which has been separated off in the cyclone is added to the polymerization product discharged from the polymerization reactor.

[0016] In some embodiments, the aliphatic carboxylic acid ester is added in an amount of from 0.05 ppm to 2 ppm, with respect to the weight of the prepared ethylene polymer.

[0017] In some embodiments, the aliphatic carboxylic acid ester is selected from the group consisting of isopropyl myristate, isopropyl laurate, isopropyl palmitate, isopropyl stearate, octylacetate, ethyloleate, laurylacetate, isobutyl myristate, butyl myristate, 2-ethylhexyl myristate, ethyl myristate and mixtures thereof.

[0018] In some embodiments, the aliphatic carboxylic acid ester is added together with another polymerization process additive.

[0019] In some embodiments, ethylene is copolymerized with 1-butene and/or with 1-hexene.

[0020] In some embodiments, the chromium catalyst is a Phillips-type chromium catalyst which has been activated at a temperature of from 350°C to 1000°C.

[0021] In some embodiments, the reactor gas comprises one or more C_3-C_6 alkanes.

[0022] In some embodiments, the content of C_3-C_6 alkanes in the reactor gas is from 1 vol.% to 10 vol.%.

[0023] In some embodiments, the polymerization is carried out in the presence of an aluminum alkyl.

[0024] In some embodiments, the ethylene polymer has a density determined according to DIN EN ISO 1183-1:2004, Method A at 23°C of from 0.918 g/cm^3 to 0.970 g/cm^3.

[0025] In some embodiments, the ethylene polymer has a melt flow rate MFR_{21}, determined according to DIN EN ISO 1133:2005 at a temperature of 190°C under a load of 21.6 kg from 0.1 g/10 min to 100 g/10 min.

DETAILED DESCRIPTION OF THE INVENTION

[0026] The present disclosure provides a continuous process for the preparation of ethylene homopolymers or ethylene copolymers comprising polymerizing ethylene or copolymerizing ethylene and one or more other olefins in the presence of a chromium catalyst. Suitable olefins for copolymerization with ethylene are especially 1-olefins, i.e. hydrocarbons having terminal double bonds. Suitable olefins can also be functionalized olefinically unsaturated compounds. Preference is given to linear or branched C_3-C_{12}-1-alkenes, in particular linear C_3-C_{10}-1-alkenes such as propylene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene or branched C_2-C_{10}-1-alkenes such as 4-methyl-1-pentene or conjugated and nonconjugated dienes such as 1,3-butadiene, 1,4-hexadiene or 1,7-octadiene. Suitable olefins also include ones in which the double bond is part of a cyclic structure which can have one or more ring systems. Examples are cyclopentene, norbornene, tetracyclododecene or methylnorbornene or dienes such as 5-ethylidene-2-norbornene, norbornadiene or ethylnorbornadiene. It is also possible to polymerize mixtures of two or more olefins.

[0027] The process is suitable for the homopolymerization or copolymerization of ethylene. Preferred comonomers are up to 20 wt.%, more preferably from 0.01 wt.% to 15 wt.% and especially from 0.05 wt.% to 12 wt.%, of C_3-C_8-1-alkenes, in particular 1-butene, 1-pentene, 1-hexene and/or 1-octene. In a preferred embodiment of the present disclosure, ethylene is copolymerized with 1-butene and/or with 1-hexene. Particular preference is given to a process in which ethylene is copolymerized with from 0.1 wt.% to 12 wt.% of 1-hexene and/or 1-butene.

[0028] The process of the present disclosure is carried out using a chromium catalyst, preferably a Phillips-type chromium catalyst. Phillips-type chromium catalysts are preferably prepared by applying a chromium compound to an inorganic support and subsequently activating the obtained catalyst precursor, preferably in the presence of oxygen or air, at temperatures in the range from 350°C to 1000°C, resulting in chromium present in valences lower than six being converted into the hexavalent state. Apart from chromium, further elements such as magnesium, calcium, boron, aluminum, phosphorus, titanium, vanadium, zirconium or zinc can also be used. Particular preference is given to the use of titanium, zirconium or zinc in combination with chromium. Combinations of the above mentioned elements are also possible. The catalyst precursor can be doped with fluoride prior to or during activation. As supports for Phillips-type catalysts, which are also known to those skilled in the art, aluminum oxide, silicon dioxide (silica gel), titanium dioxide, zirconium dioxide or their mixed oxides or cogels, or aluminum phosphate may be used. Further suitable support materials can be obtained by modifying the pore surface area, e.g. by means of compounds of the elements boron, aluminum, silicon or phosphorus. Preference is given to using a silica gel. Preference is given to spherical or granular silica gels, with the former also being able to be spray dried. Further suitable support materials can be obtained by chemical modification of inorganic support materials e.g. by means of compounds of the elements boron, aluminium, silicon or phosphorus. The activated chromium catalysts can subsequently be prepolymerized or prereduced. The prereduction can, for example, be carried out by means of carbonmonoxide, hydrogen, ethylene, 1-olefins or metal alkyls.

[0029] The process of the present disclosure is carried out as gas-phase polymerization, i.e. as process in which the solid polymers are obtained from a gas-phase of the monomer or the monomers in a gas-phase polymerization reactor containing a reactor bed of particulate polymer. The gas-phase polymerization reactor is equipped with at least one cycle gas line for withdrawing reactor gas from the reactor, leading the reactor gas through a heat-exchanger for cooling and feeding the reactor gas back to the reactor. Suitable reactors are, for example, stirred gas-phase reactors, multizone circulating gas-phase reactors, or fluidized-bed gas-phase reactors. Reactors of these types are generally known to those skilled in the art.

[0030] Stirred gas-phase reactors, in which the reaction bed of polymer particles is kept in motion by means of a stirrer, can for example be horizontally or vertically stirred gas-phase reactors. The cooling of the polymerization usually occurs by withdrawing reactor gas from the reactor, leading the reactor gas through a heat-exchanger and feeding the reactor gas back to the reactor.

[0031] Multizone circulating reactors are gas-phase reactors in which two polymerization zones are linked to one another and the polymer is passed alternately a plurality of times through these two zones. Such reactors are, for example, described in WO 97/04015 A1 and WO 00/02929 A1 and have two interconnected polymerization zones, a riser, in which the growing polymer particles flow upward under fast fluidization or transport conditions, and a downcomer, in which the growing polymer particles flow in a densified form under the action of gravity. The polymer particles leaving the riser enter the downcomer and the polymer particles leaving the downcomer are reintroduced into the riser, thus establishing a circulation of polymer between the two polymerization zones, and the polymer is passed alternately a plurality of times through these two zones. It is also possible to operate the two polymerization zones of one multizone circulating reactor with different polymerization conditions by establishing different polymerization conditions in its riser and its downcomer. For this purpose, the gas mixture leaving the riser and entraining the polymer particles can be partially or totally prevented from entering the downcomer. This can for example be achieved by feeding a barrier fluid in the form of a gas and/or a liquid mixture into the downcomer, preferably in the upper part of the downcomer. The barrier fluid should have a suitable composition, different from that of the gas mixture present in the riser. The amount of added barrier fluid can be adjusted in a way that an upward flow of gas countercurrent to the flow of the polymer particles is generated, particularly at the top, acting as a barrier to the gas mixture entrained among the particles coming from the riser. In this manner it is possible to obtain two different gas composition zones in one multizone circulating reactor. Furthermore, it is possible to introduce make-up monomers, comonomers, molecular weight regulators such as hydrogen and/or inert fluids at any point of the downcomer, preferably below the barrier feeding point. Thus, it is also possible to create varying monomer, comonomer and/or hydrogen concentrations along the downcomer, resulting in a further differentiation of the polymerization conditions. The cooling of the polymerization usually occurs by withdrawing reactor gas leaving the riser, leading the reactor gas through a heat-exchanger and feeding the cooled reactor gas back to the reactor at a position before the riser for fast-fluidizing the polymer particles in the riser.

[0032] The process of the present disclosure is preferably carried out in a fluidized-bed gas-phase reactor. Fluidized-bed polymerization reactors are reactors in which the polymerization takes place in a bed of polymer particles which is maintained in a fluidized state by feeding in gas at the lower end of the reactor, usually below a gas distribution grid having the function of dispensing the gas flow, and taking off the gas again at the upper end of the reactor. The reactor gas is then returned to the lower end to the reactor via a cycle gas line equipped with a compressor and a heat exchanger.

[0033] The velocity of the reactor gas within the fluidized-bed reactor has to be sufficiently high to fluidize the bed of particulate polymer present in the tube serving as polymerization zone and to remove the heat of polymerization effectively. The velocity of the reactor gas velocity is generally specified as superficial velocity. To prevent the unintended transfer of small particles being carried from the polymerization zone into the cycle gas system, the gas-phase fluidized-bed reactor used for the process of the present disclosure preferably has a calming zone with an increased diameter at its upper end so as to reduce the velocity of the circulating gas. Preferably, the gas velocity in the calming zone is from one-third to one-sixth of the gas velocity in the polymerization zone.

[0034] For removing entrained polymer particles from the reactor gas withdrawn from the reactor, the cycle gas line can be equipped with a cyclone which is preferably located in the cycle gas line upstream of the heat-exchanger for cooling the cycle gas.

[0035] The circulated reactor gas is usually a mixture of the olefins to be polymerized and inert gases such as nitrogen and/or lower alkanes. The process for the preparation of an ethylene polymer according to the present disclosure is preferably conducted in the presence of nitrogen or a C_2-C_5 alkane as inert gas and more preferably in the presence of nitrogen or propane. The circulated reactor gas may further include a C_3-C_6 alkane to raise the molecular weight or specific heat of the gas in order to promote condensation. Examples of such condensing agents are propane, isobutane, cyclobutane isopentane, neopentane, n-hexane or iso-hexane. The content of C_3-C_6 alkanes in the reactor gas is preferably from 1 vol.% to 10 vol.%.

[0036] Furthermore, hydrogen may be added to the polymerization reactor. Hydrogen is then preferably added in an amount that the content of hydrogen in the reactor gas composition is from 1 vol.% to 10 vol.%.

[0037] Oxygen may also be added to the polymerization reactor. Oxygen is then preferably added in an amount that the content of oxygen in the reactor gas composition is from 0.1 ppm to 0.5 ppm by volume.

[0038] In the process of the present disclosure, an aliphatic carboxylic acid ester having from 8 to 24 carbon atoms, preferably from 10 to 20 carbon atoms and more preferably from 12 to 18 carbon atoms is added to the polymerization. The carboxylic acid ester acts as a catalyst poison and is thus able to prevent polymer deposits in the cycle line. The aliphatic carboxylic acid ester has a melting point, at atmospheric pressure, of less than 20°C, preferably of less than 10°C.

[0039] The carboxylic acid ester of the present disclosure can be any combination of one or more aliphatic monocarboxylic acids, dicarboxylic acids or tricarboxylic acids and one or more aliphatic mono-alcohols, diols or triols as long as the total number carbon atoms is from 8 to 24. Preferably the carboxylic acid ester is a mono ester, i.e.an ester of an aliphatic mono-alcohol and an aliphatic monocarboxylic acid, of formula R^1-C(O)OR^2 in which R^1 and R^2 are a straight chain or branched C_1-C_{22}-alkyl or C_2-C_{22}-alkenyl group or a C_3-C_{22}-cycloalkyl or a C_3-C_{22}-cycloalkenyl group. In a preferred embodiment of the present disclosure, R^1 has from 1 to 5 carbon atoms, more preferably from 2 to 5 carbon atoms, and R^2 has from 7 to 23 carbon atoms, more preferably from 8 to 18 carbon atoms and especially preferably from 10 to 16 carbon atoms. In another preferred embodiment of the present disclosure, R^1 has from 7 to 23 carbon atoms, more preferably from 8 to 18 carbon atoms and especially preferably from 10 to 16 carbon atoms and R^2 has from 1 to 5 carbon atoms and more preferably from 2 to 5 carbon atoms. The aliphatic acid ester may also comprise one or more additional heteroatoms of Groups 14, 15 or 16 of the Periodic Table of the Elements as long as the total number carbon atoms is from 8 to 24. Non-limiting examples of suitable catalyst poisons are isopropyl myristate, isopropyl laurate, isopropyl palmitate, isopropyl stearate, octylacetate, ethyloleate, laurylacetate, isobutyl myristate, butyl myristate, 2-ethylhexyl myristate or ethyl myristate. Most preferably, the carboxylic acid ester of the present disclosure is isopropyl myristate. It is also possible to use mixtures of carboxylic acid esters.

[0040] Preferably, the aliphatic carboxylic acid ester is added to the polymerization in an amount of from 0.05 ppm to 2 ppm, more preferably from 0.1 ppm to 1 ppm, most preferably from 0.2 ppm to 0.7 ppm with respect to the weight of the prepared ethylene polymer.

[0041] According to the present disclosure, the aliphatic carboxylic acid ester may be added at any position of the gas-phase polymerization reactor. Preferably, the aliphatic carboxylic acid ester is fed into the cycle gas system at a position up-stream the heat-exchanger and, more preferably, the aliphatic carboxylic acid ester is fed into the cycle gas system at a position between the reactor and the cyclone (if present). The aliphatic carboxylic acid ester thus may have the opportunity of wetting the highly catalytically active fine dust particles. These wetted fine dust particles may then be removed from the cycle gas in the cyclone (if present). This process step may make it possible to remove the fine dust and also the aliphatic carboxylic acid ester from the circulating reactor gas, or at least to achieve a reduction in its concentration in the cycle gas. Preferably, the mixture of fine dust and aliphatic carboxylic acid ester which has been separated off in the cyclone is added to the polymerization product discharged from the polymerization reactor. As a result, less aliphatic carboxylic acid ester may reach the reactor where it can have an adverse effect on the polymerization reaction. Alternatively, it may be possible to add larger amounts of the aliphatic carboxylic acid ester to achieve more effective deactivation of the polymerization-active fine dust particles. In addition, fine dust which is not precipitated in the cyclone may be also wetted by the aliphatic carboxylic acid ester, wherein polymerization and deposit formation in the cycle gas system may be avoided or reduced.

[0042] In an alternative embodiment, the circulated reactor gas is not passed through a cyclone. Instead, in this embodiment, the aliphatic carboxylic acid ester is preferably fed at a point after the reactor up-stream the heat-exchanger, and the circulating gas is then passed to a compressor and the heat-exchanger; these equipment items may be present in either order. Optionally, the catalyst poison is fed after the reactor and after the equipment (cycle gas compressor or cycle gas cooler) and before re-circulation. The cooled and compressed cycle gas may be then introduced back into the well-mixed particle bed of the gas-phase fluidized-bed reactor via a customary gas distributor plate. This may result in homogeneous gas distribution, which ensures good mixing of the particle bed.

[0043] In a preferred embodiment of the process of the present disclosure, the cooling of the reactor gas in the heat-exchanger located in the cycle gas line is carried out in a way that the reactor gas is partly condensed by cooling below the dew point and the amount of liquid in the reactor gas returned to the polymerization reactor is from 0.5 wt.% to 10 wt.%, preferably from 1 wt.% to 8 wt.%, and more preferably from 2 wt.% to 6 wt.%. The liquefied part of the reactor gas may be returned to the reactor together with the remaining gas as a two-phase mixture. It is however also possible to separate the liquid and the gaseous phase and return both portions separately to the reactor.

[0044] The polymerization of the present disclosure is carried out at a temperature from 30°C to 130°C, preferably from 108°C to 125°C, more preferably from 110°C to 120°C, and especially preferred from 108°C to 116°C.

[0045] According to the process of the present disclosure, the polymerization is carried out at a pressure from 0.1 MPa to 20 MPa, more preferably from 0.5 MPa to 10 MPa and in particular from 1.0 MPa to 5 MPa.

[0046] Preferably, the polymerization is carried out in the presence of an aluminum alkyl of formula AlR_3 or of formula $AlR_nR'_m$, in which R is, independently of each other, a C_4-C_{12}-alkyl, preferably a C_6-C_{10}-alkyl, R' is, independently of each other, a C_4-C_{24}-alkanediyl group which is bridging two aluminum atoms, and n + m = 3. Examples of suitable aluminum alkyls of formula AlR_3 are tri-isobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum, tri-n-decylaluminum, or tridodecylaluminum. An example for an aluminum alkyl of formula $AlR_nR'_m$ is isoprenylaluminum which has the formula $(i\text{-}C_4H_9)_mAl(C_5H\text{-}_{10})_n$ with n/m ≥ 3,5. Preferred aluminum alkyls for the process of the present disclosure are tri-isobutylaluminum, tri-n-hexylaluminum, tri-n-octylaluminum and especially tri-n-hexylaluminum. It is also possible to conduct the process of the present disclosure in the presence of a mixture of such aluminum alkyls.

[0047] The aluminum alkyl compound can bed fed to the polymerization reactor as such. Preferably, the aluminum alkyl is fed as a solution, preferably as a solution in a hydrocarbon solvent like n-hexane or iso-hexane or as a solution in a mineral oil. The concentration of aluminum alkyl in a solution to be fed to the polymerization reactor is preferably from 0.5 wt.% to 5 wt.%, more preferably from 1 wt.% to 3 wt.%

[0048] Preferably, the aluminum alkyl is fed into the polymerization reactor in an amount which is in the range of from 0.0025 to 0.1 mole per ton of ethylene dosed into the polymerization reactor. Preferably, the amount of aluminum alkyl fed into the polymerization reactor is from 0.005 to 0.05 mole per ton of prepared ethylene polymer and more preferably from 0.01 to 0.04 mole per ton of prepared ethylene polymer.

[0049] The aluminum alkyl can be fed to polymerization process by introducing the aluminum alkyl into the polymerization reactor at any point of the reactor. However, preferably the aluminum alkyl is introduced into the polymerization reactor at a position where the reactor bed is present or the aluminum alkyl is introduced into the cycle gas line.

[0050] The gas-phase polymerization reactor, in which the process of the present disclosure is conducted, may be a single polymerization reactor. The gas-phase polymerization reactor may also be part of a reactor cascade of two or more polymerization reactors. Preferably, all polymerization reactors of the cascade are gas-phase reactors. In a preferred embodiment of the present disclosure, the reactor cascade is a series of two fluidized-bed reactors or a reactor cascade comprising a fluidized-bed reactor and a multizone circulating reactor in which preferably the fluidized-bed reactor is arranged upstream of the multizone circulating reactor. Such a reactor cascade of gas-phase reactors may further comprise additional polymerization reactors. Further reactors of such a reactor cascade can however also be of any kind of low-pressure polymerization reactors such as suspension reactors and may include a pre-polymerization stage.

[0051] The process of the present disclosure is preferably carried out in the presence of an antistatic agent. All the antistatic agents conventionally known in the art, which are able to avoid electrostatic charging, may be used in the process of the present disclosure. Common antistatic agents comprise antistatically acting compounds which have polar functional groups such as acid or ester groups, amine or amide groups or hydroxyl or ether groups. Examples of antistatically acting compounds are polysulfone copoly-mers, polymeric polyamines, oil-soluble sulfonic acids, polysiloxanes, alkoxyamines, polyglycol ethers, etc. Quite efficient as antistatic agents are further compositions which comprise more than one antistatically acting compound. An overview of antistatic agents suitable for polymerization processes is given in EP 0 107 127 A1. Examples of suitable antistatic agents are Statsafe™ 3000 and Statsafe™ 6000 commercially available from Innospec Speciality Chemicals

[0052] According to a preferred embodiment of the present disclosure, the antistatic agent is a mixture comprising an oil-soluble surfactant, water, and optionally an alcohol. For utilizing such mixtures, preferably a mixture of the oil-soluble surfactant, the water, optionally the alcohol, and one or more aliphatic hydrocarbons is prepared and then the mixture is introduced into the polymerization reactor. Preferred mixtures comprise from 10 to 69.9 wt.% of oil-soluble surfactant, from 0.1 to 2 wt.% of water, from 0 to 15 wt.% of alcohol and from 30 to 89.9 wt.% of aliphatic hydrocarbon and especially preferred mixtures comprise from 20 to 50 wt.% of oil-soluble surfactant, from 0.2 to 1 wt.% of water, from 2 to 10 wt.% of alcohol and from 40 to 77.8 wt.% of aliphatic hydrocarbon. The oil-soluble surfactant is preferably an ionic oil-soluble surfactant and is more preferably a strong organic acid comprising a hydrocarbyl group of from 6 to 40 carbon atoms. Suitable classes of organic acids are organic sulfonic acids, organic sulfinic acids or organic phosphonic acids. Preferably, the organic acid is a sulfonic acid. Especially preferred representatives of such oil-soluble surfactants are dinonylnaphthylsulfonic acids and dodecylbenzenesulfonic acids. Preferred alcohols are linear or branched C_1-C_{12} alcohols, which can be mono alcohols, diols or triols. More preferably such alcohols are mono-alcohols having from 1 to 4 carbon atoms. Most preferably the alcohol is methanol, ethanol or isopropanol. Preferred hydrocarbons for a preparing the antistatic mixtures are propane, isobutane, n-hexane, isohexane, EXXOL® grades obtainable from ExxonMobil Chemical or white mineral oils. The amount of oil-soluble surfactant introduced into the polymerization reactor is preferably from 0.025 to 50 ppm per weight, with respect to the weight of the prepared ethylene polymer, and the amount of water introduced into the polymerization reactor is preferably from 0.005 to 0.5 ppm per weight with respect to the weight of the prepared ethylene polymer. Preferably, the amount of alcohol introduced into the polymerization reactor is from 0.05 ppm to 5 ppm per weight, with respect to the weight of the prepared polyethylene. Such antistatic agents are described in WO 2014/198693 A1.

[0053] The aliphatic carboxylic acid ester may be added to the polymerization together with another polymerization process additive. Suitable polymerization process additives, which can be fed into the polymerization reactor together with the aliphatic carboxylic acid ester, may be, for example, antistatic agents or aluminum alkyls.

[0054] The residence time of the mixture of reactants including gaseous and liquid reactants, catalyst, and polymer particles in the polymerization reactor is preferably in the range from 1 to about 6 hours and more preferably in the range from 1.5 to about 4 hours.

[0055] The process of the present disclosure allows efficiently preparing ethylene homopolymers or ethylene copolymers in the presence of a chromium catalyst with high catalyst productivity without operational problems such as fouling or sheeting in the cycle gas line or formation of fines and which results in ethylene polymers with outstanding optical, mechanical and processing properties and a low gel content.

[0056] The process of the present disclosure is especially suitable for the preparation of polyethylenes having a relatively high molecular weight. Preferably, the polyethylenes have a $MFR_{21.6}$ at a temperature of 190°C under a load of 21.6 kg, determined according to DIN EN ISO 1133:2005, condition G, of from 0.1 to 100 g/10 min, more preferably of from 1 to 20 g/10 min, and especially of from 1.2 to 12 g/10 min. The ratio of $MFR_{21.6}$ and MFR_5, determined according to DIN EN ISO 1133:2005, condition T, at a temperature of 190°C under a load of 5 kg, is preferably from 10 to 40, more preferably from 12 to 30 and especially from 15 to 25.

[0057] Polyethylenes obtained by the process of the present disclosure have preferably a density according to DIN EN ISO 1183-1:2004, Method A at 23°C in the range of from 0.918 g/cm^3 to 0.970 g/cm^3, more preferably in the range of from 0.935 g/cm^3 to 0.968 g/cm^3 and especially preferred in the range of from 0.940 g/cm^3 to 0.960 g/cm^3.

[0058] Preferred polyethylenes obtained by the process of the present application have a content of vinyl groups/1000 carbon atoms, determined by means of IR in accordance with ASTM D 6248 98, of not more than 1.2 and more preferably a content of vinyl groups/1000 carbon atoms in the range from 0.5 to 1.0.

[0059] The polyethylenes obtained by the process of the present disclosure process are characterized by a low level of polymer gels. In a preferred embodiment of the present disclosure, the number of gels, determined by preparing a 50 μm cast film, analyzing the film defects by means of an optical scanning device and classifying and counting the film defects according to their size, is not more than 1000/m^2, more preferably not more than 800/m^2 and especially not more than 500/m^2.

[0060] The polyethylenes obtained by the process of the present disclosure process are further characterized by a low content of catalyst residues. Preferably the ash content of the obtained polyethylene, determined according to DIN EN ISO 3451-1:2008-11, is not more than 250 ppm, more preferably not more than 200 ppm and especially not more than 150 ppm.

[0061] The processes of the present disclosure are distinguished in that the utilized Phillips-type catalysts achieve high productivity, i.e. produce a high amount of polymer per amount of employed catalysts and the polymerization results in a low amount of fines and low electrostatics.

[0062] The technology is illustrated below with the aid of examples, without being restricted thereto.

EXAMPLES

[0063] The melt flow rate $MFR_{21.6}$ was determined according to DIN EN ISO 1133-1:2005, condition G at a temperature of 190°C under a load of 21.6 kg.

[0064] The density was determined according to DIN EN ISO 1183-1:2004, Method A (Immersion) with compression molded plaques of 2 mm thickness. The compression molded plaques were prepared with a defined thermal history: Pressed at 180°C, 20MPa for 8 min with subsequent crystallization in boiling water for 30 min.

[0065] The tensile-impact strength was determined according to ISO 8256:2004 using type 1 double notched specimens according to method A. The test specimens (4 x 10 x 80 mm) were cut from a compression molded sheet which had been prepared according ISO 1872-2 requirements (average cooling rate 15 K/min and high pressure during cooling phase). The test specimens were notched on two sides with a 45° V-notch. The depth was 2±0.1 mm and curvature radius on notch dip was 1.0±0.05 mm. The free length between grips was 30±2 mm. Before the measurements were taken, all test specimens had been conditioned at a constant temperature of -30°C over a period of 2 to 3 hours. The procedure for measuring the tensile impact strength including energy correction following method A is described in ISO 8256:2004.

[0066] The environmental stress cracking resistance was determined by a full notch creep test (FNCT) in accordance with international standard ISO 16770:2004 in aqueous surfactant solution. From the polymer sample, a compression molded 10 mm thick sheet was prepared. The bars with squared cross sections (10x10x100 mm) were notched using a razor blade on four sides perpendicularly to the stress direction. A notching device as described in M. Fleissner in Kunststoffe 77 (1987), pp. 45 was used for the sharp notch with a depth of 1.6 mm. The load applied was calculated from tensile force divided by the initial ligament area. Ligament area was the remaining area = total cross-section area of specimen minus the notch area. For FNCT specimen: 10x10 mm^2 - 4 times of trapezoid notch area = 46.24 mm^2 (the remaining cross-section for the failure process/crack propagation). The test specimen was loaded using standard conditions as suggested by the ISO 16770 with constant load of 6 MPa at 50°C in an aqueous solution of 2% by weight of ARKOPAL N100. The elapsed time until the rupture of the test specimen was detected.

[0067] The swell ratio was measured in a high-pressure capillary rheometer (Rheograph25, Göttfert Werkstoff-Prüfmaschinen GmbH, Buchen, Germany) at a shear rate of 1440 s^{-1} in a 30/2/2/20 round-perforation die with conical inlet (angle = 20°, D = 2mm, L = 2mm, total length = 30 mm) at a temperature of 190°C, using a laser-diode placed at a distance of 78 mm from the die exit. The extrudate was cut (by an automatic cutting device from Göttfert) at a distance of 150 mm from the die-exit, at the moment the piston reaches a position of 96 mm from the die-inlet. Swell ratio (SR) [%] is defined as difference (d_{max} - d_d) x 100 divided by d_d with d_{max} being the maximum diameter of the strand and d_d being the diameter of the die; $SR°=°(d_{max}-d_d)°100\%°/ d_d$.

[0068] The number of gels was determined by preparing a 50 μm cast film, analyzing the film defects by means of an optical scanning device and classifying and counting the film defects according to their size (circle diameter). The films were prepared by an extruder (type ME20) equipped with a chill roll and winder, model CR-9, and analyzed by an optical film surface analyzer with flash camera system, model FTA100 (all components produced by OCS Optical Control Systems GmbH, Witten, Germany). The apparatus had the following characteristics

- screw diameter: 20 mm;
- screw length: 25 D;
- compression ratio: 3:1;
- screw layout 25 D: 10 D feeding, 3 D compression, 12 D metering;
- dimensions: 1360x 650 x1778 mm^3 (L x W x H; without die);
- die width (slit die): 150 mm;
- resolution: 26 μm x 26 μm;

and was operated under the following conditions

- T 1: 230°C;
- T 2: 230°C;
- T 3: 230°C;
- T 4 (adapter): 230°C;
- T 5 (die): 230°C;
- die: slit die 150 mm;
- take off speed: 3.0 m/min;
- screw speed: to be adjusted to film thickness 50 μm;
- throughput: 1.0 to 1.5 kg/h (target 1.15 kg/h);
- air shower: on - 5 m^3/h,
- chill roll temperature: 50°C;
- vab chill roll: 4 N;
- winding tensile force: 4 N,
- draw off strength: 5 N;
- camera threshold threshold 1: 75% - threshold 2: 65%.

For starting the measurement, the extruder and take off unit were set to the specified conditions and started with a material having a known gel level. The film inspection software was started when the extruder showed steady conditions of temperature and melt pressure. After having operated the extruder with the starting material for at least half an hour or after the gel count reached the known gel level, the first sample to measure was fed to the extruder. After reaching a stable gel level for 45 minutes the counting process was started until the camera had inspected an area of at least 3 m^2 of film. Thereafter the next sample was fed to the extruder and after having again reached a stable gel count for 45 minutes the counting process for the next sample was started. The counting process was set for all samples in a way that the camera inspected an area of at least 3 m^2 of film and the number of measured defects per size-class was normalized to 1 m^2 of film.

Example 1

Preparation of Phillips-type catalyst

[0069] A Phillips-type catalyst was prepared as in Example 1 of WO 99/29736 A1 except that an amount of $Cr(NO_3)_39H_2O$ solution was used such that the resulting intermediate contained 0.3 wt.% of chromium and that the chromium-doped support was activated at 560°C.

Examples 2

Polymerization

[0070] A high-density polyethylene was prepared using the catalyst obtained in Example 1. The polymerization was carried out in a stainless steel fluidized bed reactor having an internal diameter of 500 mm equipped with a gas circulation system comprising a cycle gas line having a cyclone upstream of a heat exchanger, control systems for controlling temperature and pressure and feeding lines for ethylene, 1-hexene, nitrogen and n-hexane. The reactor pressure was controlled to be 2.2 MPa. 1-Hexene was introduced into the reactor at a rate of 9 kg per ton of prepared polyethylene. The feeding of the other compounds was controlled to obtain a reactor gas composition of 55 vol.% ethylene and 4 vol.% n-hexane, with the remainder being 1-hexene and nitrogen.

[0071] The catalyst was injected in a discontinuous way by means of a dosing valve with nitrogen. In addition, trihexylaluminum (THA; obtained from Chemtura Organometallics GmbH, Bergkamen, Germany) was added to the reactor in an amount of 10 ppm per weight THA with respect to the weight of the prepared polyethylene, and an antistatic agent was added to the reactor in an amount of 8 ppm per weight with respect to the weight of the prepared polyethylene. The antistatic agent was a mixture of 0.6 wt.% water, 6 wt.% isopropanol, 30 wt.% dodecylbenzenesulfonic acid and 63.4 wt.% n-heptane which had previously been prepared by shaking the components until a clear homogeneous stable formulation had been obtained.

[0072] Isopropyl myristate (IPM) was metered as a 0.04 wt.% solution in hexane via a nozzle into the cycle gas line at the midpoint of the distance from the entry of the reactor gas into the cycle gas line and the entry of the reactor gas into the cyclone. The amount of added isopropyl myristate was 0.7 ppm per weight with respect to the weight of the prepared polyethylene.

[0073] After three days of very smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of the polymerization reactor, cycle gas line, cyclone and heat-exchanger. No fouling or layer formation could be observed in the equipment parts.

[0074] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Example 3

[0075] The polymerization of Example 2 was repeated, except that the amount of added isopropyl myristate was reduced to 0.4 ppm per weight with respect to the weight of the prepared polyethylene.

[0076] After three days of very smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of polymerization reactor, cycle gas line, cyclone and heat-exchanger. No fouling or layer formation could be observed in the equipment parts.

[0077] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Example 4

[0078] The polymerization of Example 2 was repeated, except that the amount of added isopropyl myristate was reduced to 0.3 ppm per weight with respect to the weight of the prepared polyethylene.

[0079] After three days of very smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of polymerization reactor, cycle gas line, cyclone and heat-exchanger. No fouling or layer formation could be observed in the equipment parts.

[0080] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Comparative Example A

[0081] The polymerization of Example 2 was repeated, except that no catalyst poison was metered into the cycle gas line.

[0082] After three days of smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of polymerization reactor, cycle gas line, cyclone and heat-exchanger. Some fouling could be observed in the heat-exchanger.

[0083] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Comparative Example B

[0084] The polymerization of Example 2 was repeated, except that a 0.04 wt.% solution of Atmer 163 in hexane was metered into the cycle gas line.

[0085] After three days of very smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of polymerization reactor, cycle gas line, cyclone and heat-exchanger. A yellow sticky layer of polymer fines could be observed in the cycle gas line directly after the injection point of the Atmer 163.

[0086] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Comparative Example C

[0087] The polymerization of Example 4 was repeated, except that a 0.04 wt.% solution of isopropanol in hexane was metered into the cycle gas line.

[0088] After three days of very smooth polymerization without chunk formation or any disruption of the discharge system, the operation was stopped for inspection of polymerization reactor, cycle gas line, cyclone and heat-exchanger. No fouling or layer formation could be observed in the equipment parts.

[0089] The reaction conditions in the polymerization reactor and the properties of the obtained polyethylene are reported in Table 1.

Table 1

	Example 2	Example 3	Example 4	Comparative Example A	Comparative Example B	Comparative Example C
Catalyst poison	IPM	IPM	IPM	-	Atmer 163	i-propanol
Amount of catalyst poison [ppm]	0.7	0.4	0.3	-	0.7	0.3
Reactor temperature [°C]	115.7	116.0	116.2	116.3	116.2	115.0
Residence time [h]	2.9	3.0	3.0	2.9	2.8	3.1
Productivity [g of PE/g of solid catalyst]	8880	9880	10675	10760	10640	8720
$MFR_{21.6}$ [g/10 min]	5.9	5.6	5.9	5.8	5.8	5.9
Density [g/cm^3]	0.9448	0.9446	0.9444	0.9446	0.944	0.9445
Tensile impact strength [kJ/m^2]	164	177	172	170	167	161
FNCT [h]	33	29	29	29	23	27
Swell ratio [%]	199	197	199	200	201	197
Gel count						
450 - 600 μm [1/m^2]	82	71	67	478	110	116
600 - 700 μm [1/m^2]	16	12	9	134	18	22

(continued)

	Example 2	Example 3	Example 4	Comparative Example A	Comparative Example B	Comparative Example C
700 - 1500 μm [1/m^2]	9	7	10	16	13	15
1500 - 10000 μm [1/m^2]	0	0	0	0	0	0
>10000 μm [1/m^2]	0	0	0	0	0	0
Total number of gels						
>450μm [1/m^2]	107	90	86	628	141	153

Claims

1. A continuous process for the preparation of ethylene homopolymers or ethylene copolymers comprising polymerizing ethylene or copolymerizing ethylene and one or more other olefins in the presence of a chromium catalyst in a gas-phase polymerization reactor, which contains a reactor bed of particulate polymer and which is equipped with a cycle gas line for withdrawing reactor gas from the reactor, leading the reactor gas through a heat-exchanger for cooling and feeding the reactor gas back to the reactor, wherein the polymerization is carried out at a temperature from 30°C to 130°C and a pressure of from 0.1 to 10 MPa and an aliphatic carboxylic acid ester having from 8 to 24 carbon atoms, which has a melting point of less than 20°C, is added.

2. The process according to claim 1, wherein the aliphatic carboxylic acid ester is fed into the cycle gas system at a position upstream of the heat-exchanger.

3. The process according to claim 1 or 2, wherein the cycle gas line is equipped with a cyclone upstream of the heat-exchanger and the aliphatic carboxylic acid ester is fed into the cycle gas system at a position between the reactor and the cyclone.

4. The process according to claim 3, wherein the mixture of fine dust and aliphatic carboxylic acid ester which has been separated off in the cyclone is added to the polymerization product discharged from the polymerization reactor.

5. The process according to any of claims 1 to 4, wherein the aliphatic carboxylic acid ester is added in an amount of from 0.05 ppm to 2 ppm with respect to the weight of the prepared ethylene polymer.

6. The process according to any of claims 1 to 5, wherein the aliphatic carboxylic acid ester is selected from the group consisting of isopropyl myristate, isopropyl laurate, isopropyl palmitate, isopropyl stearate, octylacetate, ethyloleate, laurylacetate, isobutyl myristate, butyl myristate, 2-ethylhexyl myristate, ethyl myristate and mixtures thereof.

7. The process according to any of claims 1 to 6, wherein the aliphatic carboxylic acid ester is added together with another polymerization process additive.

8. The process according to any of claims 1 to 7, wherein ethylene is copolymerized with 1-butene or with 1-hexene or with mixtures thereof.

9. The process according to any of claims 1 to 8, wherein the chromium catalyst is a Phillips-type chromium catalyst which has been activated at a temperature of from 350°C to 1000°C.

10. The process according to any of claims 1 to 9, wherein the reactor gas comprises one or more C_3-C_6 alkanes.

11. The process according to claim 10, wherein the content of C_3-C_6 alkanes in the reactor gas is from 1 vol.% to 10 vol.%.

12. The process according to any of claims 1 to 11, wherein the polymerization is carried out in the presence of an aluminum alkyl.

13. The process according to any of claims 1 to 12, wherein the ethylene polymer has a density determined according to DIN EN ISO 1183-1:2004, Method A at 23°C of from 0.918 g/cm^3 to 0.970 g/cm^3.

14. The process according to any of claims 1 to 13, wherein the ethylene polymer has a melt flow rate MFR$_{21}$, determined according to DIN EN ISO 1133:2005 at a temperature of 190°C under a load of 21.6 kg from 0.1 g/10 min to 100 g/10 min.

Patentansprüche

1. Kontinuierliches Verfahren zur Herstellung von Ethylenhomopolymeren oder Ethylencopolymeren, umfassend Polymerisieren von Ethylen oder Copolymerisieren von Ethylen und einem oder mehreren anderen Olefinen in Gegenwart eines Chromkatalysators in einem Gasphasenpolymerisationsreaktor, der ein Reaktorbett aus teilchenförmigem Polymer enthält und mit einer Kreisgasleitung zum Abziehen von Reaktorgas aus dem Reaktor, Führen des Reaktorgases durch einen Wärmetauscher zur Kühlung und Rückspeisen des Reaktorgases in den Reaktor ausgestattet ist, wobei die Polymerisation bei einer Temperatur von 30 °C bis 130 °C und einem Druck von 0,1 bis 10 MPa durchgeführt wird, und wobei ein aliphatischer Carbonsäureester mit 8 bis 24 Kohlenstoffatomen zugegeben wird, der einen Schmelzpunkt kleiner als 20 °C aufweist.

2. Verfahren nach Anspruch 1, wobei der aliphatische Carbonsäureester an einer dem Wärmetauscher vorgeschalteten Stelle in das Kreisggassystem eingespeist wird.

3. Verfahren nach Anspruch 1 oder 2, wobei die Kreisggasleitung mit einem dem Wärmetauscher vorgeschalteten Zyklon ausgestattet ist und der aliphatische Carbonsäureester an einer Stelle zwischen dem Reaktor und dem Zyklon in das Kreisggassystem eingespeist wird.

4. Verfahren nach Anspruch 3, wobei die Mischung aus Feinstaub und aliphatischem Carbonsäureester, die in dem Zyklon abgetrennt worden ist, dem Polymerisationsprodukt zugegeben wird, welches aus dem Polymerisationsreaktor abgezogen wird.

5. Verfahren nach einem der Ansprüche 1 bis 4, wobei der aliphatische Carbonsäureester in einer Menge von 0,05 ppm bis 2 ppm, bezogen auf das Gewicht des hergestellten Ethylenpolymers, zugegeben wird.

6. Verfahren nach einem der Ansprüche 1 bis 5, wobei der aliphatische Carbonsäureester ausgewählt ist aus der Gruppe bestehend aus Isopropylmyristat, Isopropyllaurat, Isopropylpalmitat, Isopropylstearat, Octylacetat, Ethyloleat, Laurylacetat, Isobutylmyristat, Butylmyristat, 2-Ethylhexylmyristat, Ethylmyristat und Mischungen davon.

7. Verfahren nach einem der Ansprüche 1 bis 6, wobei der aliphatische Carbonsäureester zusammen mit einem anderen Additiv für das Polymerisationsverfahren zugegeben wird.

8. Verfahren nach einem der Ansprüche 1 bis 7, wobei Ethylen mit 1-Buten oder mit 1-Hexen oder mit Mischungen davon copolymerisiert wird.

9. Verfahren nach einem der Ansprüche 1 bis 8, wobei der Chromkatalysator ein Chromkatalysator vom Phillips-Typ ist, der bei einer Temperatur von 350 °C bis 1000 °C aktiviert worden ist.

10. Verfahren nach einem der Ansprüche 1 bis 9, wobei das Reaktorgas ein oder mehrere C$_3$- bis C$_6$-Alkane umfasst.

11. Verfahren nach Anspruch 10, wobei der Gehalt an C$_3$- bis C$_6$-Alkanen in dem Reaktorgas 1 Vol.% bis 10 Vol.% beträgt.

12. Verfahren nach einem der Ansprüche 1 bis 11, wobei die Polymerisation in Gegenwart von Aluminiumalkyl durchgeführt wird.

13. Verfahren nach einem der Ansprüche 1 bis 12, wobei das Ethylenpolymer eine gemäß DIN EN ISO 1183-1:2004, Methode A, bei 23 °C bestimmte Dichte von 0,918 g/cm^3 bis 0,970 g/cm^3 aufweist.

14. Verfahren nach einem der Ansprüche 1 bis 13, wobei das Ethylenpolymer eine gemäß DIN EN ISO 1133:2005 bei

einer Temperatur von 190 °C unter einer Last von 21,6 kg bestimmte Schmelzflussrate MFR_{21} von 0,1 g/10 min bis 100 g/10 min aufweist.

Revendications

1. Procédé continu pour la préparation d'homopolymères d'éthylène ou de copolymères d'éthylène comprenant la polymérisation d'éthylène ou la copolymérisation d'éthylène et d'une ou plusieurs autres oléfines en présence d'un catalyseur au chrome dans un réacteur de polymérisation en phase gazeuse, qui contient un lit de réacteur de polymère particulaire et qui est équipé d'une conduite de gaz de cycle pour soutirer le gaz de réacteur du réacteur, conduire le gaz de réacteur à travers un échangeur de chaleur pour refroidir gaz de réacteur et l'alimenter dans le réacteur, la polymérisation étant réalisée à une température de 30° C à 130° C et à une pression de 0,1 à 10 MPa et un ester d'acide carboxylique aliphatique comprenant 8 à 24 atomes de carbone, qui présente un point de fusion inférieur à 20° C, étant ajouté.

2. Procédé selon la revendication 1, l'ester d'acide carboxylique aliphatique étant introduit dans le système de gaz de cycle en une position en amont de l'échangeur de chaleur.

3. Procédé selon la revendication 1 ou 2, la conduite de gaz de cycle étant équipée d'un cyclone en amont de l'échangeur de chaleur et l'ester d'acide carboxylique aliphatique étant introduit dans le système de gaz de cycle en une position entre le réacteur et le cyclone.

4. Procédé selon la revendication 3, le mélange de poussières fines et d'ester d'acide carboxylique aliphatique qui a été séparé dans le cyclone étant ajouté au produit de polymérisation évacué du réacteur de polymérisation.

5. Procédé selon l'une quelconque des revendications 1 à 4, l'ester d'acide carboxylique aliphatique étant ajouté en une quantité de 0,05 ppm à 2 ppm par rapport au poids du polymère d'éthylène préparé.

6. Procédé selon l'une quelconque des revendications 1 à 5, l'ester d'acide carboxylique aliphatique étant choisi dans le groupe constitué par le myristate d'isopropyle, le laurate d'isopropyle, le palmitate d'isopropyle, le stéarate d'isopropyle, l'acétate d'octyle, l'oléate d'éthyle, l'acétate de lauryle, le myristate d'isobutyle, le myristate de butyle, le myristate de 2-éthylhexyle, le myristate d'éthyle et leurs mélanges.

7. Procédé selon l'une quelconque des revendications 1 à 6, l'ester d'acide carboxylique aliphatique étant ajouté conjointement avec un autre additif de procédé de polymérisation.

8. Procédé selon l'une quelconque des revendications 1 à 7, l'éthylène étant copolymérisé avec du 1-butène ou avec du 1-hexène ou avec des mélanges de ceux-ci.

9. Procédé selon l'une quelconque des revendications 1 à 8, le catalyseur au chrome étant un catalyseur au chrome de type Phillips qui a été activé à une température de 350° C à 1000° C.

10. Procédé selon l'une quelconque des revendications 1 à 9, le gaz de réacteur comprenant un ou plusieurs alcanes en C_3-C_6.

11. Procédé selon la revendication 10, la teneur en alcanes en C_3-C_6 dans le gaz de réacteur étant de 1 % en volume à 10 % en volume.

12. Procédé selon l'une quelconque des revendications 1 à 11, la polymérisation étant réalisée en présence d'un alkylaluminium.

13. Procédé selon l'une quelconque des revendications 1 à 12, le polymère d'éthylène présentant une densité, déterminée selon la norme DIN EN ISO 1183-1 :2004, procédé A, à 23° C, de 0,918 g/cm^3 à 0,970 g/cm^3.

14. Procédé selon l'une quelconque des revendications 1 à 13, le polymère d'éthylène présentant un indice de fluidité à chaud MFR_{21}, déterminé selon la norme DIN EN ISO 1133 :2005, à une température de 190° C sous une charge de 21,6 kg, de 0,1 g/10 min à 100 g/10 min.

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- EP 0431626 A1 **[0006]**
- US 5625012 A **[0007]**
- EP 0927724 A **[0008]**
- WO 03042253 A1 **[0008]**
- WO 2006107373 A1 **[0009]**
- EP 2722347 A1 **[0010]**
- US 2010167058 A1 **[0010]**
- WO 9704015 A1 **[0031]**
- WO 0002929 A1 **[0031]**
- EP 0107127 A1 **[0051]**
- WO 2014198693 A1 **[0052]**
- WO 9929736 A1 **[0069]**