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(54) Title: METHOD FOR PRODUCING ALPHA-OLEFIN POLYMER RESIN

(57) Abstract: The invention provides a method for producing alpha-olefin polymer resins with improved fouling and sheeting properties including at least one slurry-phase polymerisation step, wherein the catalyst particles are contacted with a catalyst poisoning agent before contacting alpha-olefin monomers in said slurry phase polymerisation step.

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Method for producing alpha-olefin polymer resin

The present invention relates to a process for producing alpha-olefin polymer resins in a polymerisation process comprising at least one slurry reactor. Especially the invention relates to a polymerisation process,
5 where fouling and sheeting problems are decreased.

One problem, which frequently is found especially in slurry phase reactors such as loop reactors, is the adhering of the polymer particles onto the reactor walls. Even slight amounts of polymer in the walls cause that the smoothness of the reactor inside surface disappears, where after
10 the adhering starts to accelerate and causes in the worst case the blocking of the reactor and further conduits of the system. A polymer layer on the reactor surface increases the flow resistance of the polymer suspension and the pumping power required. At the same time the heat transfer efficiency of the reactor decreases and makes the temperature control
15 more difficult. If high polymerisation temperatures are used, the undesired result can be melting of the polymer.

Also in gas phase reactors similar problems can be found. The polymer particles tend to adhere to the reactor surfaces and reactor internals and also polymer particles tend to adhere to each other and form lumps. This
20 will cause flow disturbances in the fluidized bed and local overheating because polymerisation heat cannot be effectively removed from larger polymer lumps. Especially polymer sheets adhering on reactor walls and later detaching cause severe problems in the product quality.

The harmful fouling phenomena described above has been tried to be
25 avoided by adding into the polymerisation reactor antistatic agents, which make the diluent more conductive and thereby prevent at least somewhat the formation of static electric charges. However these kind of antistatic agents are usually harmful for polymerisation catalyst, because they often act at least in some degree as catalyst poisons and thereby decrease

catalyst activity and therefore, the productivity. Therefore, the amounts of known fouling preventive agents must generally be rather low, which in turn decreases the effect of the antistatic agent. Similarly various antistatic compounds or fouling or sheeting preventive agents have been added also into the gas phase reactors to decrease fouling and sheeting problems there. Because the polymerisation environments in loop reactors and in gas phase reactors are quite different, it would be often necessary to use different types of antistatic agents in loop and gas phase reactors. Also, higher amounts of antistatic agents are usually necessary in gas phase reactors.

EP 1 183 285 A1 discloses an at least two stage process for the polymerisation of alpha-olefins, especially propylene block copolymers with ethylene, in which process the fouling is reduced in the gas phase reactor and any equipments thereafter. The first stage of the process comprises the forming of the alpha-olefin polymer matrix in at least one bulk reactor and optionally in at least one gas phase reactor and the second stage comprises copolymerisation of alpha-olefins and ethylene in the presence of said polymer matrix of the first stage in at least one gas phase reactor, which acts as a so called rubber phase reactor. According to this EP publication an antifouling composition is fed into said rubber phase reactor. As the antifouling composition a combination of an antistatic agent component and a catalyst killer component is proposed. By the method disclosed in this patent some problems relating to the stickiness problems originating from the use of ethylene as comonomer in said second stage (rubber phase) and post reactor handling steps of the polymer are solved.

However, this method cannot avoid the fouling and sheeting occurring in the first stage reactor, i.e. in a slurry reactor, such as a bulk reactor. If fouling phenomena occurs in the slurry reactor, in addition to the operation problems in the reactor the carrying over of the polymerisation

product from the loop reactor into the second stage reactor, i.e. into the gas phase reactor, may undermine the effect provided by providing the anti-fouling composition into the gas phase reactor.

EP 0 820 474 A1 discloses a method for preventing fouling and sheeting
5 in gas phase reactors in the polymerisation or copolymerisation of alpha-olefins in a multistage process comprising one or more loop reactors, by adding the whole amount of certain fouling preventive agents into a loop reactor(s), where at least 30 % of the whole amount of polymer
10 polymerized in the whole process is produced. The core idea of this patent is to use fouling preventive agents, which eliminate the need to add catalyst retarding agents into the gas phase reactor. Thus, as fouling preventive agent is used a composition of alpha-olefin acrylonitrile copolymers and polymeric polyamines or Cr or Ca organic salts stabilized
15 with polymers. Because the used agents do not affect negatively on the catalyst activity, the amount of the fouling agent added into the loop reactor can be reasonable high. Thus, these agents are transferred with the product from the first reactor also to the gas phase reactor, where the desired antifouling effect can be seen.

However, there are restrictions relating to the amounts and types of
20 antistatic agents to be used in many product fields, like in food packaging and in medical field. E.g. FDA regulations set limits to many additives.

EP 0 453 116 A1 relates to a process for the gas phase polymerisation of alpha-olefins which involves a pre-polymerisation step and the use of an alpha-olefin pre-polymer, wherein the pre-polymer introduced into the
25 gas phase (co-)polymerisation comprises an antistatic agent. The antistatic agent may be a composition or a mixture containing at least one metal salt of an organic carboxylic acid, optionally substituted with a sulfonic acid. The essential feature of this patent is that the used antistatic

agents do not decrease the catalytic activity, or the activity can even be increased.

Further, WO2003/033543 discloses use of antistatic agent in gas phase polymerisation process. As antistatic agent is used e.g. sorbitan mono
5 oleate type compounds in combination of water, peroxide and/or salt and is added directly to the gas phase reactor.

Problems, as is evident from prior art documents, relating to the sheeting and blocking problems due to the static electricity, are tried to be solved by adding antistatic agents into the actual polymerisation reactors, or in
10 case of a gas phase one stage polymerisation into the prepolymerisation reactor or directly to the gas phase reactor. According to the prior art catalyst activity should not be decreased, if antistatic agent is fed to the prepolymerisation reactor or into the first actual polymerisation step of a multistage polymerisation process. A relevant problem relates also to the
15 used of antistatic or antifouling agents. However, the type or amount needed is often not allowed to be used in food and medical applications.

An additional reason for fouling problems can, however, be a too active catalyst, which results in sticky material, agglomerations and thus blocking problems. Especially by polymerising ethylene as such or as a
20 comonomer with other alpha-olefins, e.g. propylene, fouling problems of this type can occur. Especially polymerisations run in a multistage process comprising a slurry reactor as a first actual polymerisation reactor suffer from these problems. These fouling problems can even restrict the amount of ethylene used as comonomer at the first stage. Use of antistatic
25 agents as such does not solve this problem as a whole, but other solutions have to be found. The problem can be seen, when high activity catalysts of any type, like high activity heterogeneous Ziegler-Natta or single-site catalyst are used.

Therefore, it is the object underlying the present invention to provide an improved process for the preparation of alpha-olefin polymer resin which provides counter-measures for effectively and securely preventing fouling and sheeting in each of the polymerisation steps of a single or multi-stage
5 alpha-olefin polymerisation process, comprising at least one slurry reactor.

A further object of the invention is to minimize the amount of additives, i.e. fouling preventive agents in the process and in the final product.

Still an additional beneficial object of the invention is the possibility to
10 use fouling preventive agents, which are allowed to use also in food and medical applications.

Further, one desired object of the invention is to produce alpha-olefin copolymers, especially propylene copolymers with ethylene, where a polymer matrix is produced at the first stage of the multistage process,
15 and which matrix has a reasonable high amount of ethylene. By higher ethylene content in the polymer matrix of propylene copolymer some special polymer properties can be achieved. Due to the fouling and stickiness problems of prior art ethylene content in the polymer produced in the slurry reactor of the first stage has been kept usually at a
20 reasonable low level.

The above objects have been now surprisingly and effectively solved by the process according to claim 1. Preferred embodiments are defined in the dependent claims.

Accordingly, the present invention resides in the finding of a method for
25 producing alpha-olefin polymer resin in the presence of a particulate alpha-olefin polymerisation catalyst in a polymerisation process comprising at least one slurry phase polymerisation step,

wherein the catalyst particles are contacted with a catalyst poisoning agent before contacting alpha-olefin monomers in said slurry phase polymerisation step.

It has now been surprisingly found by the present inventors that
5 contacting a catalyst activity retarding agent or catalyst poisoning agent, which terms can be used exchangeable in this application, with the catalyst particles before contacting the particles with the alpha-olefin monomers in the first actual polymerisation step being a slurry phase polymerisation step, is highly advantageous for avoiding fouling and/or
10 sheeting in a single stage polymerisation process or in all stages of multi-stage polymerisation process used for the preparation of the alpha-olefin polymer resins.

Further, it has been noted that the catalyst particles should be contacted with the catalyst poisoning agent preferably before essentially any
15 reaction with a cocatalyst and the catalyst particles takes place.

In a preferred mode the contact between the catalyst poisoning agent and catalyst particles is carried out before or during a prepolymerisation step, which precedes the first actual polymerisation step.

In the present invention it is preferred to feed the catalyst poisoning
20 agent to the pre-polymerisation step together with the particulate catalyst component and after that to add to this feed alpha-olefin monomer(s) or to add monomers separately to the prepolymerisation reactor. Further, it is preferred that the catalyst poisoning agent can react with the surfaces of catalyst particles before they are contacted and reacted with any
25 cocatalyst used during the prepolymerisation step. However, presence of small amounts of cocatalysts at this step are in practice not detrimental to the effect desired, if the above reaction can happen.

The catalyst poisoning agent can be used as such, optionally dissolved in a suitable solvent, or it can be a part of an antifouling composition, or it is possible to add the catalyst poisoning agent together with an additional antifouling agent.

- 5 Special benefits achieved by the invention can especially be seen, when propylene random copolymers with ethylene are produced, and especially, if reasonable high amount of ethylene is copolymerized with propylene at the first polymerisation stage comprising a slurry step.

10 In the pre-polymerisation stage the alpha-olefin monomers may be propylene, ethylene or other alpha-olefin monomers, preferable propylene and/or ethylene.

By "alpha-olefin monomer" in this connection is meant a compound having the structure $\text{CH}_2=\text{CHR}$, wherein R is hydrogen or a linear, branched or cyclic alkyl group. In particular R is hydrogen or a linear or
15 branched alkyl group having 1 to 19 carbon atoms, preferably 1 to 11 carbon atoms or a cyclic alkyl group having 4 to 8 carbon atoms. Typical alpha-olefin monomers used in the present invention are ethylene, propylene, 1-butene, 4-methylpentene, 1-hexene and octene. Preferably alpha-olefin is ethylene or propylene. Preferably, propylene is
20 copolymerised with ethylene and optionally with other alpha-olefins, such as butene or hexene.

In a more preferred mode of the present invention random propylene copolymerisation is carried out. Propylene and one or more other C_2 to C_{14} alpha-olefins, e.g. ethylene, 1-butene, 4-methyl-1-pentene, 1-hexene,
25 dienes, or cyclic alpha-olefins, are subjected to polymerisation and copolymerisation, respectively, in a plurality of polymerisation reactors connected in series.

Especially preferred mode is to polymerise propylene with ethylene and optionally other alpha-olefins selected from C₄- to C₈-olefins in a multistage process comprising at least two polymerisation stages and before the first actual polymerisation stage a prepolymerisation step, and
5 where propylene-ethylene random polymer is produced at the first stage comprising at least one slurry reactor and optionally a gas phase reactor, and polymerisation is continued at the second stage comprising at least one gas phase polymerisation reactor with or without additional monomer feed. Different amounts of hydrogen can be used as a molar mass
10 modifier or regulator in any or every reactor.

Benefits of the invention can also be seen in polymerising ethylene, optionally with comonomers as defined above.

The present invention in a especially preferred embodiment provides a process for producing a propylene random copolymer with ethylene and
15 the total comonomer content being 1 to 10 wt-%, preferably 2 to 9 wt-%, more preferably 3 to 8 wt-%. Polymer produced at the first slurry polymerisation stage, e.g. in a bulk reactor, comprises 1 to 6 wt-%, preferably 2 to 5 wt-% and more preferably 3 to 5 wt-% of ethylene.

It should be noted that in addition to the polymerisation reactors
20 producing propylene random polymers, the process configuration can further comprise additional polymerisation steps for producing propylene block copolymers. Such configuration can contain e.g. additional gas phase reactors, so called "rubber" phase reactors.

In case propylene copolymers are produced in a process comprising in
25 addition to the polymerisation steps a prepolymerisation step, the amount of ethylene in the prepolymerisation step can be up to 5 wt-%.

Other multistage polymerisation process alternatives include a process comprising at least two slurry reactors for actual polymerisation, which can optionally be followed by one or more gas phase reactors, and where preferably a prepolymerisation step precedes the first polymerisation step.

- 5 A single stage polymerisation process according to the invention can comprise in addition to a slurry phase reactor a prepolymerisation step.

Prepolymerisation can be carried out in a separate prepolymerisation reactor (used in a continuous process) or in the actual polymerisation reactor before the actual polymerisation starts, if the process is run
10 batchwise. During the prepolymerisation step the temperature is usually lower than in polymerisation step, and only a few wt-% of the total amount of polymer is produced in the prepolymerisation step.

Catalyst and catalyst systems used in the present invention are any catalyst systems being able to polymerise alpha-olefins. The preferred
15 catalyst system used comprises a heterogeneous high yield Ziegler-Natta catalyst system including a solid catalyst component, a co-catalyst component, and optionally an external donor (used in propylene polymerisation). Another preferred catalyst system is a heterogeneous single site-based catalyst system, the catalyst component having e.g. a
20 bridged ligand structure giving high stereoselectivity and being suitable for polymerising the desired alpha-olefins into polymers.

Said catalysts comprise a catalyst component comprising a compound of a transition metal belonging to groups 4 to 10, preferably to groups 4 to 6, of the Periodic Table of Elements (IUPAC 1990), or lanthanide or
25 actinide, and a co-catalyst based on an organic compound of a metal belonging to any of groups 1 to 3 and 13 of said Table.

In Ziegler-Natta type catalysts typical compounds of transition metals are halides, preferably chlorides, especially the tetrachloride of titanium. Typical organometallic co-catalysts are organoaluminium compounds such as alkyl aluminium compounds, typically trialkyl aluminium compounds with alkyl groups having 1 to 10 C-atoms, preferably 1 to 6 C-atoms. Typical cocatalyst used is triethyl aluminium.

Catalysts can be supported on external carrier materials, as typical examples being inorganic oxides, like silica, and magnesium dichloride. In addition it is known to use e.g. polymeric support materials. An other alternative to prepare solid catalysts components, both of Ziegler-Natta and single site type is based on an liquid/liquid at least two phase emulsion method, where liquid droplets forming the dispersed phase contain catalyst compounds. After solidifying the droplets of the dispersed phase solid catalyst particles with uniform and compact morphology are formed, however without using any external support material. This type of catalyst preparation is described e.g. in patent publications WO 03/000757, WO 03/000754, WO 2004/029112, WO 03/106510 and WO 03/051934 which are mentioned here as references.

External electron donors, which form part of the Ziegler-Natta catalyst system for propylene polymerisation, are well known in the art and include ethers, esters, polysilanes, polysiloxanes and alkoxysilanes, typically alkyl alkoxy silanes compounds, such as cyclohexyl methylmethoxy silanes or dicyclopentyl dimethoxy silanes. External donors are typically added separately to the actual polymerisation step or can be added at least partly also to the prepolymerisation step.

In the present invention the multistage process is defined to be a polymerisation process in which a polymer comprising two or more fractions is produced by producing each or at least two polymer

fraction(s) in a separate reaction stage, in the presence of the reaction product of the previous stages which comprises a polymerisation catalyst.

The first reaction stage of such a multistage process, after the prepolymerization step, comprises a slurry phase polymerisation step and optionally a gas phase polymerisation step, and the subsequent reaction stage may comprise another slurry phase polymerisation step or one or more gas-phase polymerisation steps. The slurry phase polymerisation step may advantageously be carried out in a so-called slurry reactor.

For the purpose of the present invention, "slurry reactor" designates any reactor, such as a continuous or simple batch stirred tank reactor or loop reactor, operating in bulk or slurry and in which the polymer forms in particulate form. "Bulk" means a polymerisation in a reaction medium that comprises at least 60 wt-% monomer. According to a preferred embodiment the slurry reactor comprises a bulk loop reactor.

The bulk loop reactor can be of conventional design, which includes means for feeding various feed components to the reactor, means for circulating the polymer suspension through the reactor, heat transfer means for removing heat of polymerisation and means for discharging polymer slurry from the reactor.

After carrying out the first step polymerisation, the reaction mixture is usually discharged from the first, preferably loop reactor and the polymer may be transferred into a second loop reactor or one or more gas-phase reactors, where the polymerisation can be completed in the presence of the polymer produced in the previous step, optionally additional α -olefin monomer and optionally hydrogen and/or other comonomers. The reaction mixture may be removed from the loop reactor either continuously or intermittently by conventional means and transferred to the subsequent reactor(s).

By "gas phase reactor" is meant any mechanically mixed or fluid bed reactor. Preferably the gas phase reactor comprises a mechanically agitated fluid bed reactor with gas velocities of at least 0.2 m/sec.

The gas phase reactor can be a conventional fluidized-bed reactor, although other types of gas-phase reactors can also be used. In the fluid-bed reactor the bed may comprise formed and growing polymer particles as well as catalyst components. The bed is preferably kept in fluidized state by introducing gaseous components, such as propylene, ethylene and/or other alpha monomer(s) at a velocity sufficient to cause the particles to act as a fluid. The fluidizing gas can include also inert carrier gases, such as nitrogen and also hydrogen, if desired as a modifying component.

It is common knowledge that the polymer matrix, which may comprise random, homo/random or random/random (co)polymers with a comonomer content needed to obtain the desired properties, can preferably be prepared at the first stage of the polymerisation process. The first stage comprises bulk reactor, preferably loop reactor(s) and optionally gas phase reactor(s).

Advanced heterophasic propylene copolymers can be obtained, if one or more additional gas phase reactors, which are often called rubber phase reactors, are used, combined in series with the first stage reactor(s). Copolymerisation of propylene monomer and alpha-olefins in the presence of the polymer matrix from the previous stage may be carried out in the rubber phase reactor(s).

The above multistage polymerisation process is preferably preceded according to the present invention by a pre-polymerisation step. In such a step the catalyst can be pre-polymerised prior to feeding into the first polymerisation reactor of the series. During pre-polymerisation the

catalyst components are contacted with the monomer, e.g. propylene and/or ethylene, before feeding into the reactor.

According to the present invention, in the pre-polymerisation step alpha-olefin monomers are polymerised in the presence of a catalyst in an amount of at most 10 wt.-% of the total amount of polymer produced in the whole process. Preferably the amount of polymer produced in the prepolymerisation step is 0.1 to 7 wt.-%, more preferably 1 to 5 wt.-% and very often only 1 to 3 wt.-% of the total polymer amount produced by the process.

- 10 In one specific embodiment, the catalyst component used in the process is the heterogeneous Ziegler-Natta type catalyst, which however, does not contain any external carrier, but is prepared using an emulsion method as described above.

The polymer produced in the pre-polymerisation step may be transferred directly to the first polymerisation step, together with the catalyst used in the pre-polymerisation step.

According to the present invention the catalyst retarding or poisoning agent is contacted with the catalyst particles before contacting the catalyst particles with the alpha-olefin monomers in the first polymerisation step, i.e. in the slurry phase polymerisation step. Preferably, contacting with the catalyst poisoning agent is carried out during or before the pre-polymerisation step. As a result it is possible to avoid fouling and/or sheeting of the polymer particles in the actual polymerisation process comprising at least one slurry reactor. In order to achieve the best results, it is beneficial to contact the catalyst poisoning agent with the catalyst particles before catalyst particles are reacted with the cocatalyst. In one embodiment the catalyst poisoning agent should be contacted the catalyst particles before the prepolymerisation step, e.g. in the feed line of the

catalyst and poisoning agent, where after monomers and cocatalyst can be added separately to the prepolymerisation reactor or combined into the same feed with the catalyst.

While pre-polymerisation is generally known in the polymerisation of alpha-olefin polymers, it was standard knowledge in the art that in the use of a multi-stage polymerisation process, the addition of anti-static agents needs to be done at least in one of the bulk and gas phase reactors to avoid the above fouling and/or sheeting phenomenon in each of the separate reactor dependent on separate conditions in each of the reactors. However, according to the present invention the above advantages can be achieved by adding the catalyst retarding or catalyst poisoning agent before any actual polymerisation step.

As disclosed, said catalyst retarding agents can be added as such or together with commonly used antifouling agents or they can be part of an antifouling agent composition. If needed, additional antifouling agents without any catalyst poisoning agent can be added also at actual polymerisation stages. However, the effect of the catalyst poisoning agent added according to the invention i.e. before contacting the catalyst particles with the monomers in the slurry reactor, e.g. during or before a prepolymerisation step, is usually so efficient that no later antifouling agent addition is needed.

A special advantage achieved by adding the catalyst poisoning agent before or during the prepolymerisation step is that higher comonomer amounts are possible to be incorporated into the alpha-olefin copolymer in the first stage, preferably loop reactor, because agglomeration/stickiness problems are essentially reduced.

It is well known that a large variety of compounds can be used as catalyst poisoning agents. Well known catalyst poisons are organic compounds containing polar functional groups. Typical examples of such groups include e.g. -OH, -O-, -OR, -COOH, -SO₂ (OH), -(C=O)-NH- groups etc., i.e., water and alcohol, ester, ether, acid and amide compounds etc. are typical catalyst poisoning agents. It can be noted that inert gases and unpolar organic compounds do not act as poisons for catalysts. In the present invention, any compound or mixture of compounds or agent that act as a poison for alpha-olefin polymerisation catalysts can be used to achieve the objects of the invention. Due to practical reasons (handling and controllability) it is advantageous to use such compounds that do not react too fast with the catalyst. Suitable compounds to be used in the present invention are e.g. the above listed alcohol, ester, ether, acid and amide compounds or mixtures thereof. Especially useful catalyst poisoning agents are alcohols with 1 to 6 C-atoms, especially 1 to 3 C-atoms, like methanol, ethanol and isopropanol. Alcohols, like the ones mentioned above can suitably be combined with other polar compounds, like acidic compounds, such as alkyl sulphonic acids, especially dinonyl naphthyl sulphonic acid. These compounds can be used alone or in combination. If needed, the catalyst poisoning agent can be dissolved into a suitable solvent.

As disclosed above the catalyst poisoning agent can be used as a separate agent or it can be a part of an antifouling or antistatic agent or composition. Catalyst poisoning agent can also be used in combination with other antistatic agents, if desired.

However, essential is, that catalyst retarding or poisoning agent is added into the process, preferably into the pre-polymerisation reactor in an amount sufficient to prevent fouling and/or sheeting in each of the reactors as used. It is specifically preferred to add the poisoning agent in or before the pre-polymerization step as described above in an amount of

from 0.1 to 10.0 wt- ppm, preferably 0.1 to 5.0 wt-ppm, more preferably 0.2 to 3.0 wt-ppm calculated from the total alpha-olefin feed to the pre-polymerisation and slurry, preferably loop reactor. The most suitable amount depends on the poisoning effect of the poisoning agent. The higher the poisoning effect on the catalyst used is, the smaller amount of the agent can be used. Thus, the most suitable amount of poisoning agent is dependent on the type of poisoning agent, on the catalyst used and on the desired effect level.

As one example of antistatic compositions, which comprises components acting as catalyst poison, is e.g. a composition sold under the name Octastat[®]. This composition contains e.g. aromatic solvents, like petroleum, C₁₋₆ alkyl alcohols and sulfonic acids. This type of composition is known to be used in polymerisation process, where it is added to the actual polymerisation step.

There are also other well known antistatic agents, such as sorbitan mono-oleate type antistatics, used in the polymerisation processes, which can be used in combination with catalyst poisoning agent according to the invention.

As a preferred embodiment of the present invention, the method is used for producing random propylene copolymers having a reasonable high C₂ content. Very often viscosity increase, friction increase, resistance of flow and velocity drop causing stickiness and fouling problems occur. These problems and deficiencies can now be overcome by using the catalyst poisoning agent according to the present invention in the alpha-olefin copolymer preparation, especially random propylene copolymer preparation in a multistage process comprising at least one slurry phase polymerisation step.

With the present invention it is thus possible to get high comonomer content in the polypropylene with usual equipment. Moreover, very high comonomer contents may be produced in the first loop reactor. Preferably, the comonomer, like ethylene, content of such a random
5 alpha-olefin copolymer is about 1 to about 7 wt-%, more preferably about 2 to 5 wt-%, of the total alpha-olefin, like propylene copolymer produced in the loop reactor without any fouling problems. As regards operability it is beneficial that e.g. decreased power consumption of the pumps is needed in the system, specifically in the loop recycling pumps, and
10 further, less other operability problems will arise.

In the following, the present invention will be illustrated by specifically preferred Examples, representing the invention compared to Comparative Examples being outside the present invention.

Methods

15 a. Melt flow rate

The melt flow rate is determined according to ISO 1133 and it is indicated in g/10min. The MFR is an indication of the flowability and thus the processability of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer. The MFR of the propylene copolymer
20 polymer is measured with a load of 2.16 kg at 230°C.

b. Xylene solubles

Xylene solubles (XS) values are measured according to the following method:

2.0 g of polymer are dissolved in 250 ml p-xylene at 135 °C under
25 agitation. After 30 ± 2 minutes the solution is allowed to cool for 15

minutes at ambient temperature and then allowed to settle for 30 minutes at 25 ± 0.5 °C . The solution is filtered with filter paper into two 100 ml flasks.

- 5 The solution from the first 100 ml vessel is evaporated in nitrogen flow and the residue is dried under vacuum at 90 °C until constant weight is reached.

$$XS\% = (100 \times m_1 \times v_0) / (m_0 \times v_1)$$

- 10 m_0 = initial polymer amount (g)
 m_1 = weight of residue (g)
 v_0 = initial volume (ml)
 v_1 volume of analysed sample (ml)

c. Bulk density (BD)

- 15 Bulk density of the polymer is measured according to ASTM D 1895

Examples

Example 1

Catalyst

A highly active propylene polymerisation catalyst of Ziegler-Natta (ZN)
5 type prepared by emulsion method according to WO2004/029112,
example 8 with the exception that instead of triethyl aluminium as Al
compound diethyl aluminium chloride was used in catalyst preparation.

Catalyst Feeding

Catalyst was fed continuously to the polymerisation in oil slurry. The
10 method is described in patent application EP1489110.

Co-catalyst and Donor

Triethylaluminium (TEAL) was used as a co-catalyst with constant feed
ratio of 150 g TEAL / ton propylene. Dicyclopentyl dimethoxy silane (D)
was used as an external donor with Al/D mol ratio 10 mol/mol. Actual
15 donor feed was about 30 g/ton propylene.

Prepolymerisation stage

The catalyst was flushed with propylene to the prepolymerisation reactor
in which also TEAL and donor were fed. Prepolymerisation reactor,
CSTR (continuous stirred tank reactor) was operated at 30°C and 55 barg
20 pressure. The residence time of the particles in propylene slurry was
about 0.5 h.

Hydrogen / propylene feed ratio to the prepolymerisation reactor was 2.6
mol/kmol.

Catalyst poisoning agent feed

Catalyst poisoning agent was fed to the prepolymerisation reactor together with catalyst in order to prevent stickiness of the polymer and fouling of the loop reactor.

- 5 As poisoning agent was used a mixture of isopropanol (25 wt-%), and dinonylnaphthyl sulphonic acid (75 wt-%). It was used as dissolved in toluene.

The catalyst was contacted with the catalyst poisoning agent in the pipeline. The residence time was 1.5 – 3 minutes in this pipeline. The
10 catalyst poisoning agent feed was 0.88 wt-ppm calculated from the total propylene feed to the prepolymerisation and loop reactor (155 kg).

Liquid phase polymerisation stage (Loop Reactor)

The prepolymerised catalyst component was used in loop reactor and gas phase reactor (GPR) connected in series.

- 15 The loop reactor was operated at 70 °C and in 55 bar pressure.

Propylene feed to pre-polymerisation and loop reactor was in total 155 kg/h. Polymer residence time in loop reactor was around 0.5-0.75 h and the production rate was 20-30 kg/h.

Ethylene was used as a co-monomer.

- 20 *Gas phase polymerisation stage (Gase phase reactor)*

Polymer slurry was fed from loop to the gas phase reactor (GPR) as a direct feed without flash. The GPR was operated at 80°C temperature and the pressure was 30 bar. Propylene concentration was about 75 mol-%.

Ethylene was used as co-monomer. The ethylene / propylene molar ratio was 22-30 mol/kmol.

Polymer residence time in GPR was about 3 - 4 hours.

Product Control

- 5 Random propylene copolymer was produced in both reactors. Ethylene content of the product was controlled by ethylene feed.

The production split between loop and GPR was controlled to be close to 50/50%.

- 10 The MFR (2,16 kg / 230°C) was controlled to be about 2 in both reactors (loop and GPR) by hydrogen feed.

Results

Ethylene content in the loop product was 4.3 wt-%, Measured XS values were 6.5 - 9 wt-%.

- 15 No fouling was observed in loop after 5 days running. No stickiness of the polymer was found.

Power consumption of the loop circulation pump was on normal level.

Polymerisation conditions and product characteristics are shown in Table 1.

Example 2

The procedure was the same as in Example 1 but the catalyst poisoning agent feed was 1.75 wt-ppm calculated from total propylene feed to prepolymerisation and loop reactor (155 kg).

5 Results

The results are equivalent to those described in Example 1.

No effect on catalyst productivity was observed when catalyst poisoning agent feed was doubled.

10 Ethylene content in the loop product was 4.2 wt-%. Measured XS values were 6.7 – 9.2 wt-%

No fouling was observed in loop after 3 days running.

No stickiness of the polymer was found.

Power consumption of the loop circulation pump was on normal level.

15 Polymerisation conditions and product characteristics are shown in Table 1.

Comparative Example 1

The procedure was the same as in Example 1 but no catalyst poisoning agent was fed to the pre-polymerisation reactor.

Results

Stability of the loop process was poor. Even if the XS content (5.2 – 6.1 wt-%) and loop product ethylene content (2.85 wt-%) were lower compared to Example 1 and 2.

- 5 Stickiness of the polymer was observed in loop product sampling system.

Signs of increased friction and grown resistance of flow were seen in loop reactor. This was seen as increased power demand of recycling pump.

Polymerisation conditions and product characteristics are shown in Table 1.

10 **Example 3**

The procedure was the same as in Example 1 but the MFR (2.16 kg / 230°C) was controlled by hydrogen feed to be 14 -15 in the loop reactor and 10-12 in GPR.

- 15 Catalyst poisoning agent feed was 1.75 wt-ppm calculated from total propylene feed to pre-polymerisation and loop reactor (155 kg).

Results

Ethylene content in the loop product was 4.1 wt-%. Measured XS values were 8.7 – 11.6 wt-%.

No fouling was observed in loop after 5 days running.

- 20 No stickiness of the polymer was found.

Power consumption of the loop circulation pump was on low level.

Polymerisation conditions and product characteristics are shown in Table 1.

Comparative Example 2

The procedure was the same as in Example 1 but no catalyst poisoning
5 agent was fed to the pre-polymerisation reactor.

Higher ethylene content in loop product was tried to reach compared to the Example 2.

Results

There was a lot of operability problems in loop reactor when ethylene
10 content of 3.2-3.5 wt-% was reached in loop product. Stability of the loop process was bad.

Stickiness of the polymer was observed in loop product sampling system.

Friction increased and resistance of flow grew in loop reactor. This
resulted in increased power demand of recycling pump, which limited the
15 production.

Finally after 12 hours run loop reactor fouled badly and the outlet of the reactor plugged and the run had to be terminated. The reactor was opened and there was a considerable fouling layer on the reactor walls.

In the beginning the product was transferred to the GPR and samples
20 were managed to be taken. However there are no final product characteristics due to the fouling and plugging of the loop reactor.

Table 1. Polymerisation conditions and product characteristics.

	Example 1	Example 2	Compar. 1	Example 3	Compar. 2
Product type	Random PP	Random PP	Random PP	Random PP	Random PP
Catalyst feed (g/h)	0.97	0.93	0.92	0.77	1.16
Catalyst poisoning agent (wt-ppm)	0.88	1.75	0	1.75	0
Loop H ₂ /C ₃ ratio (mol/kmol)	0.80	0.77	0.55	7.39	0.73
Loop Residence time (h)	0.68	0.72	0.73	0.49	0.66
Loop Production rate (kg/h)	22	23.2	24.7	26.3	27.2
Loop Catalyst productivity (kg/g)	23	25	31	35	23
Loop Solid concentration (%)	21	23	24	25	24
Process stability in loop	GOOD	GOOD	POOR	GOOD	BAD
Loop Split %	56	48	52	54	46
Loop product MFR ₂ (g/10 min)	2.08	1.83	2.00	14.4	1.68
Loop product XS (wt-%)	6.5 - 9.0	6.7-9.2	5.2 - 6.1	8.7 - 11.6	5.6
Loop product C ₂ content (wt-%)	4.3	4.2	2.85	4.1	3.5
Loop product BD (kg/m ³)	368	367	236	361	357
GPR C ₃ = partial pressure (kPa)	2436	2428	2375	2412	2394
GPR H ₂ /C ₃ ratio (mol/kmol)	4.7	4.7	7.8	71	4.2
GPR C ₂ /C ₃ ratio (mol/kmol)	28.0	28.7	22.2	46.1	22.9
GPR Residence time (h)	4.11	3.3	3.85	3.97	3.11
GPR Production rate (kg/h)	24	26	23	22	32
Loop+GPR Cat productivity (kg/g)	46.7	50.6	53.8	56.2	55.5
Process stability in GPR	GOOD	GOOD	POOR	GOOD	POOR
GPR Split (%)	44	52	48	46	54
GPR product MFR ₂ (g/10 min)	1.49	1.35	1.51	10.19	1.24
GPR product XS (wt-%)	8.2	6.3	4.7	14.1	6.1
GPR product C ₂ content (wt-%)	4.01	4.08	2.97	5.09	3.54

Claims

1. A method for producing an alpha-olefin polymer in the presence of a particulate alpha-olefin polymerisation catalyst in a polymerisation process comprising at least one slurry phase polymerisation step,
5 wherein the catalyst particles are contacted with a catalyst poisoning agent before contacting alpha-olefin monomers in said slurry phase polymerisation step.
2. The method according to claim 1, wherein the alpha-olefin is selected from the group consisting of C₂ to C₂₀ alpha-olefins or mixtures thereof, preferably from C₂ to C₁₂ alpha-olefins.
10
3. The method according to claim 1 or 2, wherein polyethylene, polypropylene or copolymers thereof with C₂ to C₁₂ comonomers are produced.
- 15 4. The method according to any of claims 1 to 3, wherein a propylene copolymer comprising ethylene as a comonomer is produced.
5. The method according to any of the preceding claims, wherein the process is a multistage process comprising at least two polymerisation stages, the first of which comprising said at least one slurry phase polymerisation step and optionally a gas phase polymerisation step.
20
6. The method according to any of the preceding claims, wherein said slurry phase polymerisation step is carried out in bulk, and preferably in a loop reactor or a continuous stirred tank reactor (CSTR).
25

7. The method according to any of the preceding claims, wherein a second stage polymerisation is carried out in at least one gas phase reactor.
8. The method according to any of the preceding claims, wherein the polymerisation process comprises a pre-polymerisation step preceding said first slurry phase polymerisation step.
9. The method according to any of the preceding claims, wherein the catalyst poisoning agent is an agent capable of poisoning the surface of the catalyst particles.
10. The method according to any of the preceding claims, wherein the catalyst poisoning agent is selected from organic compounds or mixtures thereof having at least one polar functional group, such as -OH, -O-, -OR, -COOH, -SO₂ (OH), or -(C=O)-NH- group.
11. The method according to any of the preceding claims, wherein the catalyst poisoning agent is selected from an acidic compound and an alcohol having 1 to 6 carbon atoms, preferably an alcohol having 1 to 3 carbon atoms, or mixtures thereof.
12. A method according to any of claims 8 to 11, wherein the catalyst particles are contacted with the catalyst poisoning agent during or before the prepolymerisation step.
13. The method according to any of the preceding claims, wherein the alpha-olefin polymerisation catalyst is a Ziegler-Natta or single site catalyst.

14. The method according to claim 13, wherein the catalyst comprises a catalyst component in particle form, a co-catalyst component and optionally an external donor.
- 5 15. The method according to claim 14, wherein the catalyst poisoning agent is contacted with the catalyst particles essentially before a reaction between the cocatalyst component and catalyst particles takes place.
- 10 16. The method according to any of the preceding claims, wherein the amount of the catalyst poisoning agent to be contacted with catalyst particles is 0.1 to 10.0 wt.-ppm, preferably 0.1 to 5 wt.-ppm, more preferably 0.2 to 3 wt.-ppm, calculated from the total alpha-olefin feed into the prepolymerisation and first slurry polymerisation reactor.
- 15 17. The method according to any of the preceding claim, wherein the catalyst poisoning agent is included as one component of an antifouling composition.
- 20 18. The method according to any of the preceding claims, wherein propylene is copolymerised with ethylene in the first polymerisation stage comprising at least one bulk reactor and polymerisation is continued in the second stage in a gas phase reactor.
- 25 19. A method for reducing fouling in an alpha-olefin polymerisation process comprising polymerisation of one or more alpha-olefins in at least one slurry phase polymerisation step in the presence of a particulate alpha-olefin polymerisation catalyst by contacting polymerisation catalyst particles with a catalyst poisoning agent

before contacting catalyst particles with said alpha-olefin monomer(s) in said slurry phase polymerisation step.

INTERNATIONAL SEARCH REPORT

International application No

PCT/EP2008/004002

A. CLASSIFICATION OF SUBJECT MATTER

INV. C08F10/00 C08F2/40 C08F2/00

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)

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)

EPO-Internal, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	EP 0 549 252 A (BP CHEM INT LTD [GB]; BP CHEMICALS SNC [FR]) 30 June 1993 (1993-06-30) column 5, line 19 - line 26 column 8, line 40 - line 43 column 1, line 53; claims	1-19
X	US 4 634 747 A (BEST STEVEN A [US]) 6 January 1987 (1987-01-06)	1-7,9-19
Y	column 3, line 28 column 6, line 30 - line 64 claims	1-19
X	US 4 558 025 A (BEST STEVEN A [US]) 10 December 1985 (1985-12-10)	1-7,9-19
Y	column 3, line 30 column 6, line 30 - line 64 claims	1-19
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Further documents are listed in the continuation of Box C.



See patent family annex.

* Special categories of cited documents:

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- * & * document member of the same patent family

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INTERNATIONAL SEARCH REPORT

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C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 108 432 A (SOLVAY [BE]) 16 May 1984 (1984-05-16) claims	1-9, 12-19
A	----- EP 1 183 285 B1 (BOREALIS TECH OY [FI]) 30 June 2004 (2004-06-30) cited in the application the whole document -----	1-19

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2008/004002

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0549252	A	30-06-1993	JP 5239109 A	17-09-1993
US 4634747	A	06-01-1987	NONE	
US 4558025	A	10-12-1985	AU 588160 B2	07-09-1989
			AU 4578185 A	13-02-1986
			CA 1248509 A1	10-01-1989
			DE 3569545 D1	24-05-1989
			EP 0174102 A1	12-03-1986
			JP 61087705 A	06-05-1986
EP 0108432	A	16-05-1984	BR 8305432 A	15-05-1984
			CA 1217000 A1	20-01-1987
			DE 3365151 D1	11-09-1986
			FR 2533932 A1	06-04-1984
			JP 1745408 C	25-03-1993
			JP 4030406 B	21-05-1992
			JP 59086608 A	18-05-1984
EP 1183285	B1	30-06-2004	AT 270309 T	15-07-2004
			AU 769562 B2	29-01-2004
			AU 4569800 A	17-11-2000
			BR 0010301 A	13-02-2002
			CA 2372574 A1	09-11-2000
			CN 1359397 A	17-07-2002
			DE 60011897 D1	05-08-2004
			DE 60011897 T2	25-08-2005
			EP 1183285 A1	06-03-2002
			ES 2223513 T3	01-03-2005
			WO 0066640 A1	09-11-2000
			US 6689846 B1	10-02-2004