Title of the Invention: Polymer

Abstract Title: Polyethylene with multi-modal molecular weight distribution

The present invention provides a polyethylene having a multimodal molecular weight distribution comprising:

(i) 20-70% wt of a lower molecular weight ethylene polymer;

(ii) 20-70% wt of a first higher molecular weight ethylene copolymer, and

(iii) 0.5-9.5% wt of a second higher molecular weight ethylene copolymer.

Another embodiment has component (iii) at 0.5-30% wt, where component (i) is polymerized in a first reactor, component (ii) is polymerized in a second reactor and component (iii) is polymerized in a third reactor, and optionally where component (i) is present in the second reactor during polymerization.
Figure 1
INTRODUCTION

The present invention concerns a polyethylene having a multimodal molecular weight distribution comprising: (i) 20-70% wt of a lower molecular weight ethylene polymer; (ii) 20-70% wt of a first higher molecular weight ethylene copolymer; and (iii) 0.5-9.5% wt of a second higher molecular weight ethylene copolymer. The invention is also concerned with a process for the preparation of the polyethylene, a composition comprising the polyethylene and methods of preparing articles using the polyethylene or its composition. The articles per se, particularly pipes, are a further aspect of the invention.

BACKGROUND

Polyethylene (PE) is the mostly commonly used material for the manufacture of pipes that are used for water and gas distribution, often under pressure. A major area of interest is polyethylene for HDPE pipes. These employ polyethylene polymerised at moderate pressures, using coordination catalysts.

Polyethylene used for the manufacture of HDPE pipes must meet certain requirements. They are often used at high inner pressure and subjected to external mechanical forces. Although the overall pressure is usually well below the yield stress of the polymer, mechanical failure almost always occurs before the polymer is chemically degraded. It is generally accepted that this is due to the existence of local heterogeneities of micrometer size in the polyethylene causing a strong localized stress distribution around the flaws that exceeds the yield stress. Such a stress concentration induces the formation and growth of a craze by rupture of the craze fibrils. This apparently brittle failure mode, so called slow crack growth (SCG), is therefore observed and limits the lifetime of the polyethylene pipes.

Polyethylene pipes are particularly suited for non-conventional pipe installation due to their flexibility, deformability and availability in long lengths. The widespread use of modern relining techniques and fast pipe installation practices call for high material requirements and guarantees of performance, particularly with respect to the effect of scratches, notches, nicks and impingements that are inherent to these techniques and facilitates SCG. When installing pipes by modern no-dig or trenchless installation methods (e.g. pipe bursting, horizontal direction drilling) the pipe is dragged horizontally through the ground. While often highly advantageous in that the surface of
the ground, e.g. roads and other installations, need not be disturbed and the installation
cost significantly reduced, on the other hand, the no-dig methods give the
disadvantage of a high tendency for protruding stones, rocks etc to scratch the outer
surface of the pipe in the longitudinal direction. Furthermore, at the bottom of such
longitudinal scratches, there will be a very high local tangential stress when pressure is
applied inside the pipe. Thus, unfortunately, such scratches are very harmful since they
often start cracks propagating through the wall that would otherwise never even have
started.

A polyethylene with superior resistance both to initiation of cracks as well as
propagation by SCG of any cracks initiated will permit better and longer lasting pipes
and polyethylene volumes used in pipe production to increase even more.

There are several important properties that polyethylene should possess for
pressure pipe applications;

1) Slow crack growth (SCG) resistance
2) Rapid crack propagation (RCP) resistance
3) Processability to enable pipe extrusion (e.g. as indicated by MFR$_s$)
4) Resistance to scratches/depressions (e.g. as indicated by hardness and
abrasion resistance)

SCG and RCP resistance means that a crack is less likely to propagate from an
existing defect whilst resistance to scratches and depressions means that defects that
can induce cracks are less likely to occur.

The literature states that improvements in SCG usually cause concomitant
worsening in the RCP. This is because an increased level of comonomer (usually
corresponding to decreased density) is beneficial for SCG while a decreased level of
comonomer is usually said to be beneficial for RCP. Moreover it is known that if MFR$_s$
is decreased, this increases FNCT. However, this would not be acceptable since in
order to extrude the polymer to pipe, the MFR$_s$ must be maintained in the range
typically used for processability. The abrasion resistance to scratches must also be
kept at a maximum so that defects increasing the propensity for cracks to develop are
minimised. For the same reason the hardness of the polymer should be maximised.
The hardness of a polyethylene generally increases with increasing crystallinity and
increasing lamellar thickness. On the other hand, resistance to SCG is known to
increase with decreasing crystallinity.

These counteracting factors make it very challenging to develop polyethylene
for the manufacture of pipes with the necessary balance of properties, e.g. improved
SCG without detrimentally affecting RCP, hardness, abrasion resistance as well as processability.

The polymers currently employed in HDPE pipes are mainly of two types:

1) Monomodal Cr HDPE, made in a single reactor, with a Cr (Phillips) catalyst. This technology gives a relatively poor property profile with respect to demanding pressure pipe applications.

2) Bimodal Ziegler HDPE made with two reactors operating in series; one reactor making a lower molecular weight homopolymer and one reactor making a higher molecular weight polymer containing comonomer. This technology gives a better property profile compared to monomodal Cr HDPE.

The prior art has also suggested some new polyethylenes for the production of pipes. US2009/0105422, for example, discloses a polyethylene moulding composition having a multimodal molecular mass distribution and comprising 45-55 % wt of a low molecular weight ethylene homopolymer, 20-40 % wt of a high molecular weight copolymer comprising ethylene and another olefin having from 4 to 8 carbons and 15-30 % wt of an ultrahigh molecular weight ethylene copolymer. The polyethylene is said to have an improved combination of environmental stress crack resistance, mechanical strength and processing behaviours. The examples of US’422 show that a trimodal polyethylene comprising 50 % wt low molecular weight ethylene homopolymer, 32 % wt high molecular weight ethylene/1-butene copolymer and 18 % wt ultrahigh molecular weight ethylene/1-butene copolymer has improved ESCR compared to a comparative bimodal polyethylene. The examples also show that its mechanical performance, specifically notched impact toughness and tensile creep, of the trimodal polyethylene is similar to that of the bimodal comparative example.

US 6,713,561 discloses a similar polyethylene moulding composition and teaches that it provides a better ratio of stiffness to stress cracking resistance as well as a high swelling rate of its melt. The latter is particularly advantageous in the preparation of articles such as bottles and canisters by blow moulding. The examples of US’561 show that compared to a corresponding bimodal composition, the polyethylene moulding composition has improved stress cracking resistance and swelling rate as well as a comparable flexural creep resistance, which indicates stiffness.

Neither of the prior art documents, however, disclose a polyethylene for the production of pipes that provides an improved SCG compared to a bimodal polyethylene without impacting negatively on RCP and at the same time maintaining or
improving hardness and/or abrasion resistance. Such polyethylenes are particularly attractive since the properties of hardness and abrasion resistance minimise the production of detents, notches and imperfections that can subsequently initiate a crack whilst an improved SCG performance means that if a crack does develop it does so over a longer period of time thereby improving the service lifetime of a pipe.

Hence there is still a need for polyethylene for the manufacture of pipes that exhibits improved SCG without a concomitant reduction in RCP. Polyethylenes additionally showing comparable or increased abrasion resistance and/or hardness to current bimodal polyethylene pipes, and therefore reduced probability for an SCG-initiating scratch to occur, would be particularly attractive. Of course any newly developed polyethylene must also be processable as indicated by a MFR$_s$ in the accepted range for pipe applications, e.g. 0.2-1.4 g/10 min.

It has now been surprisingly found that a polyethylene having a multimodal, preferably trimodal, molecular weight distribution and comprising a relatively small amount (e.g. 0.5-9.5 % wt of polyethylene) of a relatively high molecular weight ethylene copolymer exhibits this highly desirably combination of properties. Given the small amount of the relatively high molecular weight ethylene copolymer present, the degree to which the SCG is improved without deleterious effect on the other key properties (e.g. RCP, hardness, abrasion resistance and processability) is astonishing.

**SUMMARY OF INVENTION**

Viewed from a first aspect, the present invention provides a polyethylene having a multimodal molecular weight distribution comprising:

(i) 20-70% wt of a lower molecular weight ethylene polymer;

(ii) 20-70% wt of a first higher molecular weight ethylene copolymer; and

(iii) 0.5-9.5% wt of a second higher molecular weight ethylene copolymer.

Viewed from a further aspect, the present invention provides a process for the preparation of a polyethylene as hereinbefore defined comprising polymerising ethylene and, as required, at least one other α-olefin to yield said polyethylene, wherein said polymerisation is carried out in at least three steps.

Viewed from a further aspect, the present invention provides a polyethylene obtainable by a process as hereinbefore defined.

Viewed from a further aspect, the present invention provides a composition comprising a polyethylene as hereinbefore defined.
Viewed from a further aspect, the present invention provides an article comprising a polyethylene as hereinbefore defined or a composition as hereinbefore defined.

In a preferred embodiment, the article is a pipe.

Viewed from a further aspect, the present invention provides a process for the preparation of an article as hereinbefore defined comprising moulding, e.g. blow moulding, a polyethylene as hereinbefore defined or a composition as hereinbefore defined.

Viewed from a further aspect, the present invention provides the use of a polyethylene as hereinbefore defined or a composition as hereinbefore defined in the manufacture of a pipe.

Viewed from a further aspect, the present invention provides a process for the preparation of a polyethylene having a multimodal molecular weight distribution comprising:

(i) 20-70% wt of a lower molecular weight ethylene polymer;
(ii) 20-70% wt of a first higher molecular weight ethylene polymer; and
(iii) 0.5-30% wt of a second higher molecular weight ethylene polymer, wherein said process comprises the sequential steps (a)-(c):

(a) polymerising ethylene and optionally an α-olefin comonomer in a first reactor to produce a lower molecular weight ethylene polymer;
(b) polymerising ethylene and optionally an α-olefin comonomer in a second reactor to produce a second higher molecular weight ethylene polymer; and
(c) polymerising ethylene and optionally an α-olefin comonomer in a third reactor to produce a first higher molecular weight ethylene polymer.

DETAILED DESCRIPTION OF THE INVENTION

Definitions

As used herein the term “polyethylene” refers to a polymer that comprises at least 50 % wt, still more preferably at least 75 % wt, still more preferably at least 85 % wt and yet more preferably at least 90 % wt units derived from ethylene.

As used herein the term “ethylene homopolymer” refers to a polymer which consists essentially of repeat units deriving from ethylene. Homopolymers may, for example, comprise at least 99 %, e.g. 100 %, by weight of repeat units deriving from ethylene.
As used herein the term “ethylene copolymer” refers to a polymer comprising repeat units from ethylene and at least one other monomer. In typical copolymers at least 0.1 %, more preferably at least 0.4 % by weight of repeat units derive from at least one monomer other than ethylene. Typically ethylene copolymers will not comprise more than 15 % by weight of repeat units deriving from monomers other than ethylene.

As used herein %wt is expressed relative to the weight of polyethylene unless otherwise specified.

As used herein the terms “lower” and “higher” are used relatively. Thus a lower molecular weight ethylene polymer has a lesser molecular weight than a higher molecular weight polymer.

Whenever the term “molecular weight” is used, the weight average molecular weight is meant unless otherwise specified.

As used herein the term “multimodal” refers to a polymer comprising a plurality of components or fractions, which have been produced under different polymerisation conditions and/or by using a multisite catalyst system in one stage and/or by using two or more different catalysts in a polymerisation stage resulting in different weight average molecular weights and molecular weight distributions for the components. The prefix “multi” refers to the number of different components present in the polymer. Thus, for example, a polymer consisting of three components only is called “trimodal”.

The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as a function of its molecular weight, of a multimodal polyethylene can show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual components. In addition, multimodality may show as a difference in melting or crystallisation temperature of components. In contrast a polymer comprising one component produced under constant polymerisation conditions is referred to herein as unimodal.

As used herein the term catalyst system refers to the total active entity that catalyses the polymerisation reaction. Typically the catalyst system is a coordination catalyst system comprising a transition metal compound (the active site precursor) and an activator (sometimes referred to as a cocatalyst) that is able to activate the transition metal compound.

As used herein the term “Ziegler Natta (ZN)” catalyst refers to a catalyst that preferably comprises a transition metal component (e.g. Ti) which is sigma bonded to
its ligands and an activator (e.g. an Al containing organometallic compound). Preferred Ziegler Natta catalysts optionally comprise a particle building material.

As used herein the term “slurry polymerisation” refers to a polymerisation wherein the polymer forms as a solid in a liquid. The liquid may be a monomer of the polymer. In the latter case the polymerisation is sometimes referred to as a bulk polymerisation. The term slurry polymerisation encompasses what is sometimes referred to in the art as supercritical polymerisation, i.e. a polymerisation wherein the polymer is a solid suspended in a fluid that is relatively close to its critical point, or if the fluid is a mixture, its pseudocritical point. A fluid may be considered relatively close to its critical point if its compressibility factor is less than double its critical compressibility factor or, in the case of a mixture, its pseudocritical compressibility factor.

As used herein, the term “multistage polymerisation” refers to a polymerisation which is carried out in two or more stages. Generally each stage is carried out in a separate reactor. The term multistage polymerisation is used interchangeably with multistep polymerisation.

Polyethylene

The overall amount of ethylene monomer present in the polyethylene of the present invention is preferably 50-99.5 % wt, still more preferably 75-99.0 % wt, e.g. 85 to 97 % wt.

The total comonomer content of the polyethylene of the present invention is preferably 0.1-10 % wt, still more preferably 0.2-5 % wt and yet more preferably 0.3-3 % wt. When it is stated herein that the amount of a given monomer present in a polymer is a certain amount, it is to be understood that the monomer is present in the polymer in the form of a repeat unit. The skilled man can readily determine what is the repeat unit for any given monomer. The comonomer is preferably one or more (e.g. one) α-olefin selected from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. Preferably, however, the α-olefin is 1-butene.

The polyethylene of the present invention is preferably a high density polyethylene (HDPE). HDPE has the advantage of having a relatively low inherent weight, yet high mechanical strength, corrosion and chemical resistance and long-term stability. Preferably the polyethylene of the present invention has a density of 935-970 kg/m³, still more preferably 940-965 kg/m³ and yet more preferably 945-962 kg/m³.

The polyethylene of the present invention preferably has a MFR₆ of 0.05-1.0, still more preferably 0.1 to 0.75 and yet more preferably 0.15 to 0.6 g/10min. This is
an acceptable range of pipe applications, i.e. it ensures that the polyethylene may be extrusion moulded.

The polyethylene of the present invention preferably has a FRR (MFRs/MFRg) of 2.6-10, more preferably 2.9-8 and still more preferably 3-6.

The polyethylene of the present invention preferably has a melting temperature of 100-140 °C, still more preferably 110-138 °C and yet more preferably 120-135 °C.

The Mn of the polyethylene of the present invention is preferably 1,000-50,000 g/mol, still more preferably 3,000-40,000 g/mol and yet more preferably 5,000-30,000 g/mol. The weight average molecular weight (Mw) of the polyethylene of the invention is preferably 100,000-1,000,000 g/mol, still more preferably 150,000-750,000 g/mol and yet more preferably 200,000-500,000 g/mol.

The polyethylene of the present invention is multimodal. Particularly preferably the polyethylene of the present invention is trimodal. Preferably the molecular weight distribution (Mw/Mn) of the polyethylene is 5-100, more preferably 10-50.

The trimodality and broad molecular weight distribution of the polyethylene of the present invention ensures that an attractive balance of polymer properties can be achieved. In particular the presence of a small amount, e.g. 0.5-9.5 % wt of a second higher molecular weight ethylene copolymer, and especially an ultra high weight ethylene copolymer, yields polyethylene with excellent SCG resistance as well as high resistance to RCP.

Lower molecular weight polymer

The lower molecular weight polymer present in the polyethylene of the present invention may be an ethylene homopolymer or ethylene copolymer. Preferred copolymers comprise one or more (e.g. one) α-olefin comonomers selected from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. Preferably the α-olefin is 1-butene. Preferably, however, the lower molecular weight ethylene polymer is an ethylene homopolymer.

Preferably the lower molecular weight ethylene polymer has a density of 920-970 kg/m³, still more preferably 930-965 kg/m³ and yet more preferably 940-960 kg/m³.

Preferably the lower molecular weight ethylene polymer has a MFRs of 10-5000 g/10min, still more preferably 20-2000 g/10min and yet more preferably 50-1500 g/10min.

The lower molecular weight ethylene polymer preferably has a FRR (MFRs/MFRg) of 2.6-10, still more preferably 2.9-8 and yet more preferably 3-6.
The lower molecular weight ethylene polymer preferably has a melting temperature of 120-140 °C, still more preferably 125-138 °C and yet more preferably 127-135 °C.

The Mn of the lower molecular weight ethylene polymer is preferably 1,000-100,000 g/mol, still more preferably 1,500-80,000 g/mol and yet more preferably 2,000-60,000 g/mol. The weight average molecular weight (Mw) of the lower molecular weight ethylene polymer is preferably 5,000-150,000 g/mol, still more preferably 10,000-100,000 g/mol and yet more preferably 15,000-80,000 g/mol.

The Mw/Mn of the lower molecular weight ethylene polymer is preferably 3-18, still more preferably 4-15 and yet more preferably 5-13.

The amount of the lower molecular weight ethylene polymer present in the polyethylene of the present invention is preferably 30-70 % wt, more preferably 35-65 % wt, still more preferably 40-60 % wt and yet more preferably 45-55 % wt, wherein % wt is based on the weight of the polyethylene.

First higher molecular weight polymer

The first higher molecular weight polymer present in the polyethylene of the present invention is an ethylene copolymer. Preferred copolymers comprise one or more (e.g. one) α-olefin comonomers selected from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. Preferably the comonomer is 1-butene, i.e. preferably the first higher molecular weight polymer is an ethylene 1-butene copolymer.

The amount of ethylene monomer present in the first higher molecular weight polymer is preferably 50-99.5 % wt, still more preferably 75-99.0 % wt, e.g. 85 to 97 % wt based on weight of the copolymer. The total comonomer content of the first higher molecular weight polymer is preferably 0.1-9.5 % wt, still more preferably 0.2-4.5 % wt and yet more preferably 0.3-2.5 % wt based on the weight of the copolymer.

Preferably the first higher molecular weight ethylene copolymer has a density of 880-940 kg/m³, still more preferably 890-930 kg/m³ and yet more preferably 890-920 kg/m³.

Preferably the first higher molecular weight ethylene copolymer has a MFR\textsubscript{21} of 0.1-10 g/10min, still more preferably a MFR\textsubscript{21} of 0.2-5 g/10min and yet more preferably a MFR\textsubscript{21} of 0.3-4 g/10min.

The first higher molecular weight ethylene copolymer preferably has a FRR (MFR\textsubscript{6}/MFR\textsubscript{2}) of 2.6-10, more preferably 2.8-8 and yet more preferably 3-6.
The Mn of the first higher molecular weight ethylene copolymer is preferably 10,000-150,000 g/mol, still more preferably 20,000-125,000 g/mol and yet more preferably 30,000-100,000 g/mol.

The weight average molecular weight (Mw) of the first higher molecular weight ethylene copolymer is preferably higher than the Mw of the lower molecular weight ethylene polymer. The weight average molecular weight (Mw) of the first higher molecular weight ethylene copolymer is preferably 100,000-1,000,000 g/mol, still more preferably 150,000-800,000 g/mol and yet more preferably 200,000-700,000 g/mol.

The Mw/Mn of the first higher molecular weight ethylene copolymer is preferably 3-25, more preferably 4-20 and yet more preferably 5-18.

The amount of the first higher molecular weight ethylene polymer present in the polyethylene of the present invention is preferably in the range 30-70 % wt, more preferably 35-65 % wt, still more preferably 40-60 % wt and still more preferably 40 to 50 % wt, wherein % wt is based on the weight of the polyethylene.

Second higher molecular weight polymer

The second higher molecular weight polymer present in the polyethylene of the present invention is an ethylene copolymer. Preferred copolymers comprise one or more (e.g. one) α-olefin comonomers selected from propylene, 1-butene, 1-pentene, 4-methyl-1-pentene, 1-hexene and 1-octene. Preferably the comonomer is 1-butene, i.e. preferably the second higher molecular weight polymer is an ethylene 1-butene copolymer.

The amount of ethylene monomer present in the second higher molecular weight polymer is preferably 50-99.5 % wt, still more preferably 75-99.0 % wt, e.g. 85 to 97 % wt based on the weight of the copolymer. The total comonomer content of the second higher molecular weight polymer is preferably 0.1-30 % wt, still more preferably 0.5-25 % wt and yet more preferably 1-20 % wt based on the weight of the copolymer.

Preferably the second higher molecular weight ethylene copolymer has a density of 875-935 kg/m³, still more preferably 885-920 kg/m³ and yet more preferably 890-915 kg/m³.

Preferably the second higher molecular weight ethylene copolymer has a MFR₁ of 0.001-40 g/10min, still more preferably 0.005-30 g/10min and yet more preferably 0.006-20 g/10min.

Preferably the second higher molecular weight ethylene copolymer has a FRR (MFR₁/MFR₅) of 4.4-20, more preferably 6-18 and still more preferably 7-15.
The Mn of the second higher molecular weight ethylene copolymer is preferably 20,000-500,000 g/mol, still more preferably 30,000-400,000 g/mol and yet more preferably 40,000-300,000 g/mol.

The weight average molecular weight (Mw) of the second higher molecular weight ethylene copolymer is preferably greater than the Mw of the first higher molecular ethylene copolymer. Still more preferably the Mw of the second higher molecular weight ethylene copolymer is 5-1250%, still more preferably 10-1000 % and yet more preferably 15-750 % greater than the Mw of the first higher molecular weight ethylene copolymer. The weight average molecular weight (Mw) of the second higher molecular weight ethylene copolymer is preferably in the range 100,000-3,000,000 g/mol, still more preferably 150,000-2,500,000 g/mol, yet more preferably 200,000-2,000,000 g/mol and especially preferably 500,000-1,500,000. This polymer may be considered to be an ultra high molecular weight ethylene copolymer.

The Mw/Mn of the second higher molecular weight ethylene copolymer is preferably 3-30, more preferably 4-25 and still more preferably 5-23.

The amount of the second molecular weight ethylene copolymer present in the polyethylene of the present invention is preferably in the range 0.5-9.5 % wt, more preferably 1.0-7.5 % wt, still more preferably 1.5-6.0 % wt and yet more preferably 3-6 % wt, wherein % wt is based on the weight of the polyethylene.

Without wishing to be bound by theory, it is hypothesised that the introduction of a relatively high amount of comonomer to the ethylene copolymer that is only present in a small amount means that the comonomer is incorporated into the longer chains present in the copolymer as well as its shorter chains. This means that the level of side chains present in the copolymer is increased and correspondingly that chain entanglement is also increased. These effects are both believed to contribute to the improved SCG performance. At the same time, however, because only a small amount of the polyethylene is modified in this way, there is little, if any, deleterious effect on RCP as generally observed in the prior art.

Process

The polyethylene of the present invention may be prepared by blending ethylene polymers (i), (ii) and (iii) as defined herein. More preferably, however, the polyethylene of the present invention is prepared in a multistage polymerisation process. When a polymer is produced in a multistage process, the reactors may be in parallel or in series but arrangement in series is preferred. If the polymer components
are produced in a parallel arrangement, the powders are preferably mixed and extruded for homogenisation.

Catalyst system

The polyethylene of the present invention may be prepared using a Ziegler-Natta catalyst, a single site catalyst system or a hybrid of the afore-going catalysts. Preferably, however, the polyethylene is prepared using one or more Ziegler Natta catalyst system. Preferably the polyethylene of the present invention is prepared using one Ziegler Natta catalyst system, e.g. in each stage of multistage polymerisation.

The Ziegler Natta catalyst system preferably comprises a transition metal component and an activator. Preferably, the transition metal component, when added to the polymerisation reaction is contained within solid particles. Preferably, at least some activator, sometimes referred to as cocatalyst, is added to the polymerisation reaction in the form of a liquid or solution.

Ziegler Natta catalyst system

Transition metal component

The active site of the catalyst system is a transition metal. Group 4 or 5 transition metals are preferred, particularly Group 4 metals, and especially Ti. In particularly preferred Ziegler Natta catalysts only Group 4 transition metals (e.g. Ti) are present.

During preparation of the catalyst system it is preferred to use transition metals in the form of alkoxy or halide compounds, especially chlorides. Particularly preferably Ti, at the stage of its introduction into the catalyst system preparation process, is provided as TiCl₄.

The content of transition metal in the final solid catalyst based on the weight of dry, solid, catalyst component is preferably 0.1–5 mmol/g.

Preferably the final solid catalyst particles also comprise a group 2 metal, preferably a magnesium compound, still more preferably a Mg-Cl compound, e.g. MgCl₂.

The magnesium compound may be introduced into the catalyst preparation as the Mg-Cl (e.g. MgCl₂ compound itself), but it is preferred to make it in situ within the catalyst preparation procedure to endure a high degree of dispersion, contact with the
transition metal and porosity. The skilled man is aware of how to carry out such an in situ reaction.

The content of Mg in the final solid catalyst based on the weight of dry, solid, catalyst component is preferably 1–25 % wt.

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Particle building material

The particle building material present in the catalyst system comprising a Ziegler Natta catalyst may be an inorganic oxide support such as silica, alumina, titania, silica-alumina and silica-titania or it may be Mg or Ca compounds such as chlorides, oxychlorides, alkyls or alkoxides or metal salts with organic anions. Preferably, however, the material is silica or MgCl₂ with optional other components. Still more preferably the material is MgCl₂. This is particularly advantageous in the polymerisation to produce the second higher molecular weight ethylene copolymer.

When present, the particle building material preferably comprises 30 – 90 % wt of the final, dry, solid catalyst. If the particle building material comprises Mg-Cl compounds, then typically the building material will also function as the magnesium compound hereinbefore described. If the particle building material is a metal oxide, the metal oxide particles typically define the final catalyst system outer morphology and the other components of the catalyst system will be synthesised inside its pores.

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Activator and additional components

The activator is a compound that is capable of activating the transition metal component. It is sometimes referred to as a cocatalyst. Useful activators are, amongst others, aluminium alkyls and aluminium alkoxy compounds. Especially preferred activators are aluminium alkyls, in particular, aluminium trialkyls (e.g. trimethyl aluminium, triethyl aluminium and tri-isobutyl aluminium). The activator is preferably used in excess to the transition metal component. For instance, when an aluminium alkyl is used as an activator, the molar ratio of the aluminium in the activator to the transition metal in the transition metal component is preferably from 1 to 500 mol/mol, preferably 2 to 100 mol/mol, e.g. 5 to 50 mol/mol. The activator is typically not part of the solid, particulate catalyst but added to the polymerisation reactor as a liquid.

The catalyst system comprising a Ziegler Natta catalyst may additionally comprise co-activators and/or modifiers. Thus, for example, two or more alkyl aluminium compounds as described above may be used and/or the catalyst system
components may be combined with different types of ethers, esters, silicon ethers etc to modify the activity and/or selectivity of the catalyst system as is known in the art.

Catalyst system preparation

The catalyst system comprising a Ziegler Natta catalyst may be prepared by procedures known in the art, e.g. as disclosed in US6828267, US4081674 and US4792588.

The solid catalyst system particles may optionally be washed prior to use to remove non bonded transition metal. In the final catalyst system particle added to the polymerisation, only very minor amounts of transition metal should be extractable in alkanes at 80 °C.

The average particle size of the catalyst system particles is preferably in the range 1 to 250 μm, more preferably 4 to 100 μm, still more preferably 6 to 30 μm, e.g. 10 to 25 μm. The particles are preferably spherical.

The surface area of the catalyst system particles is preferably in the range 1-500 m²/g, more preferably 2-300 m²/g. The pore volume of the catalyst system particles is preferably in the range 0.1-5 cm³/g, preferably 0.2-1.5 cm³/g.

Single site catalyst system

General single site catalyst

The catalyst system comprising a single site catalyst that may be used in the process of the present invention is preferably a metalloocene-containing catalyst system. Such catalyst systems are well known in the art, e.g. from WO98/02246, the contents of which are hereby incorporated herein by reference.

The catalyst system may be supported or unsupported, but is preferably supported. Supported catalyst systems may be prepared by impregnating the active site precursors into it. Alternatively the catalyst system may be synthesised by producing the solid particles from liquid starting material components directly, without a separate impregnation step. Preferred catalyst systems comprising a single site catalyst comprise a carrier.

The catalyst system comprising a single site catalyst preferably comprises a carrier, an activator and at least one transition metal active site precursor (e.g. a metalloocene). The activator may be aluminoxane, borane or borate but preferably is aluminoxane. Preferably the active site precursor is a metalloocene.
Catalyst morphology and carrier

The catalyst system comprising a single site catalyst is preferably in particulate form. Preferably the catalyst system is in the form of particles having a weight average particle size of 1 to 250 microns, preferably 4 to 150 microns. Preferably the catalyst system is in the form of a free-flowing powder.

Suitable carrier materials for use in the catalyst system comprising a single site catalyst are well known in the art. The carrier material is preferably an inorganic material, e.g. an oxide of silicon and/or of aluminium or MgCl₂. Preferably the carrier is an oxide of silicon and/or aluminium. Still more preferably the carrier is silica.

Preferably the carrier particles have an average particle size of 1 to 500 microns, preferably 3 to 250 microns, e.g. 10 to 150 microns. Particles of appropriate size can be obtained by sieving to eliminate oversized particles. Sieving can be carried out before, during or after the preparation of the catalyst system. Preferably the particles are spherical. The surface area of the carrier is preferably in the range 5 to 1200 m²/g, more preferably 50 to 600 m²/g. The pore volume of the carrier is preferably in the range 0.1 to 5 cm³/g, preferably 0.5-3.5 cm³/g.

Preferably the carrier is dehydrated prior to use. Particularly preferably the carrier is heated at 100 to 800 °C, more preferably 150 to 700 °C, e.g. at about 250 °C prior to use. Preferably dehydration is carried out for 0.5-12 hours.

Carriers that are suitable for the preparation of the catalyst systems herein described are commercially available, e.g. from Grace and PQ Corporation.

Activator

Aluminoxane is preferably present in the catalyst system as activator. The aluminoxane is preferably oligomeric. Still more preferably the aluminoxane is a cage-like (e.g. multicyclic) molecule, e.g. with an approximate formula (Al₄₆R₆₈O₉₆), where n is 10-60 and R is an alkyl group, e.g. a C₁₂₋₂₀ alkyl group. In preferred aluminoxanes R is a C₆₋₈ alkyl group, e.g. methyl. Methylaluminoxane (MAO) is a mixture of oligomers with a distribution of molecular weights, preferably with an average molecular weight of 700 to 1500. MAO is a preferred aluminoxane for use in the catalyst system.

The aluminoxane may be modified with an aluminium alkyl or aluminium alkoxy compound. Especially preferred modifying compounds are aluminium alkyls, in
particular, aluminium trialkyls such as trimethyl aluminium, triethyl aluminium and triisobutyl aluminium. Trimethyl aluminium is particularly preferred.

Aluminoxanes, such as MAO, that are suitable for the preparation of the catalyst systems herein described are commercially available, e.g. from Albemarle and Chemtura.

It is also possible to generate the activator in situ, e.g. by slow hydrolysis of trimethylaluminium inside the pores of a carrier. This process is well known in the art.

Alternatively, activators based on boron may be used. Preferred boron based activators are those wherein the boron is attached to at least 3 fluorinated phenyl rings as described in EP520732.

Alternatively, an activating, solid surface as described in US 7312283 may be used as a carrier. These are solid, particulate inorganic oxides of high porosity which exhibit Lewis acid or Brønsted acidic behaviour and which have been treated with an electron-withdrawing component, typically an anion, and which have then been calcined.

Transition metal active site precursor

Generally the metal of the transition metal precursors are 16-electron complexes, although they may sometimes comprise fewer electrons, e.g. complexes of Ti, Zr or Hf.

The active site transition metal precursor is preferably a metalloocene.

The metalloocene preferably comprises a metal coordinated by one or more \( \eta \)-bonding ligands. The metal is preferably Zr, Hf or Ti, especially Zr or Hf. The \( \eta \)-bonding ligand is preferably a \( \eta^5 \)-cyclic ligand, i.e. a homo or heterocyclic cyclopentadienyl group optionally with fused or pendant substituents. Two of the \( \eta \) – bonding ligands may be bridged.

The preparation of metalloenes can be carried out according to, or analogously to, the methods known from the literature and is within the skills of a polymer chemist.

Other types of single site precursor compounds are described in:


Dupont-Brookhart type active site precursors are disclosed in US5880241.
Catalyst system preparation

The preparation of single site catalyst systems can be carried out according to methods known in the art. For example, methods of supporting single site catalysts via a preformed carrier and aluminoxide are given in EP279863, WO93/23439, EP 793678, WO96/00245, WO 97/29134. Alternative methods of supporting single site catalysts via preformed carriers and boron activators are given inWO91/09882 and WO 97/31038. Methods of obtaining particulate catalyst systems without employing preformed carriers are given in EP 810344 and EP 792297.

Multistep polymerisation processes

Preferably the polyethylene of the present invention is prepared in a multistage polymerisation process. Preferably the polyethylene is prepared in three stages or steps, still more preferably in three different reactors. Preferably the process is semi-continuous or continuous.

The polyethylene of the present invention is preferably prepared by slurry polymerisation reactions. The polymerisation is preferably carried out in conventional circulating loop or stirred tank reactors, preferably in stirred tank reactors. The diluent is preferably a hydrocarbon of 3 – 10 carbon atoms. Preferably, it is n-hexane or isobutane. Most preferably, it is n-hexane.

When present, the comonomer is preferably an alpha olefin of 3 – 10 carbon atoms. Preferably, it is propylene, n-butene, n-pentene, 4-methyl-pentene-1, n-hexene or n-octene. If the diluent is n-hexane, then preferably the comonomer is propylene, n-butene, n-pentene or 4-methyl-pentene-1. More preferably, the comonomer is n-butene or n-pentene and most preferably it is n-butene. If the diluent is isobutane, then preferably the comonomer is n-butene, n-pentene, 4-methyl-pentene-1, hexene or 1-octene. More preferably, the comonomer is n-butene, n-pentene, n-hexene or n-octene, and most preferably it is n-hexane.

General slurry polymerisation conditions

The conditions for carrying out slurry polymerisations are well established in the art. The reaction temperature is preferably in the range 30 to 120 °C, e.g. 50 to 100 °C. The reaction pressure will preferably be in the range 1 to 100 bar, e.g. 10 to 70 bar. The total residence time in the reactors is preferably in the range 0.5 to 6 hours, e.g. 1 to 4 hours. The diluent used will generally be an aliphatic hydrocarbon having a boiling
point in the range −70 to 100 °C. Preferred diluents include n-hexane, isobutane and propane, especially n-hexane.

Hydrogen is also preferably fed into at least one of the reactors to function as a molecular weight regulator. When used, the ratio of partial pressures in the reactors between hydrogen and is 0.001-5.

Preferably the polymerisation reactions are carried out as a continuous or semi-continuous process. Thus monomers, diluent and hydrogen are preferably fed continuously or semi-continuously into the reactor. Preferably the catalyst system is also fed continuously or semi-continuously into the reactor. Still more preferably polymer slurry is continuously or semi-continuously removed from the reactor. By semi-continuously is meant that addition and/or removal is controlled so they occur at relatively short time intervals compared to the polymer residence time in the reactor, e.g. between 20 seconds to 2 minutes, for at least 75 % (e.g. 100 %) of the duration of the polymerisation.

Preferably the concentration of polymer present in the reactor during polymerisation is in the range 15 to 55 % wt based on total slurry, more preferably 25 to 50 % wt based on total slurry. Such a concentration can be maintained by controlling the rate of addition of monomer, the rate of addition of diluent and catalyst system and, to some extent, the rate of removal of polymer slurry from the slurry reactor.

First preferred process

In a first preferred process of the invention, the multimodal polyethylene is prepared by preparing its ethylene polymer components in sequence from lowest molecular weight to highest molecular weight.

One preferred process comprises the sequential steps (i)-(iii):

(i) polymerising ethylene and optionally an α-olefin comonomer in a first (LMW) reactor to produce a lower molecular weight ethylene polymer;

(ii) polymerising ethylene and an α-olefin comonomer in a second (HMW1) reactor to produce a first higher molecular weight ethylene copolymer; and

(iii) polymerising ethylene and an α-olefin comonomer in a third (HMW2) reactor to produce a second higher molecular weight ethylene copolymer.

In a preferred process, during said polymerisation to produce a first higher molecular weight ethylene copolymer, at some of said lower molecular weight ethylene polymer is present in said second reactor. In a particularly preferred process, during
said polymerisation to produce a second higher molecular weight ethylene copolymer, said lower molecular weight ethylene polymer and said first higher molecular weight ethylene copolymer, are present in said third reactor.

In this preferred process essentially all of the catalyst used in the reactors is preferably fed to first (LMW) reactor. The first reactor is also preferably fed with ethylene, hydrogen and diluent. Preferably the conditions for carrying out the polymerisation in the first reactor are as follows:

Temperature: 50 to 100 °C, preferably 70 to 90 °C
Pressure: 1 to 20 bar, preferably 5 to 15 bar
Partial pressure of ethylene: 1-10 bar
Residence time: 0.5 to 4 hours, preferably 1-2 hours
Diluent: hexane

Partial pressure ratio of H₂:ethylene: 5:1 to 0.5:1, preferably 3:1 to 1:1
Comonomer in reactor: 0-1 % wt, preferably 0 % wt

Preferably the optional comonomer is 1-butene.

The polymerisation in the first reactor preferably produces 30 – 70 % wt of the total polyethylene, more preferably 35 – 65 % wt, still more preferably 40-60 % wt and most preferably 45 – 55 % wt.

The flow out of first (LMW) reactor is preferably directed to the second reactor.

Preferably 100 % of flow goes to the second reactor. The most volatile components are preferably removed from the outgoing flow of the first reactor such that more than 80 % of the hydrogen, more preferably at least 90 % of the hydrogen, is removed before the flow enters the second reactor.

The second reactor is fed with ethylene, comonomer, diluent and optionally hydrogen. The pressure is preferably lower in the second reactor than in the first reactor. Preferably the conditions for carrying out the polymerisation in the second reactor are as follows:

Temperature: 50 to 100 °C, preferably 70 to 90 °C
Pressure: 1 to 15 bar, preferably 2 to 10 bar
Partial pressure of ethylene: 0.5-6 bar
Residence time: 0.5 to 4 hours, preferably 1-2 hours
Diluent: hexane

Partial pressure ratio of H₂:ethylene: 0.01:1 to 0.5:1, preferably 0.02:1 to 0.2:1

Ratio % wt comonomer/% wt ethylene in reactor: 0.05-1%, preferably 0.1 to 0.5 %

Preferably the optional comonomer is 1-butene.
In the second reactor, 30 – 70 % wt of the total polyethylene is preferably made, more preferably 35 – 65 % wt, still more preferably 40-60 % wt and most preferably 40 – 50 % wt.

Essentially all of the flow out of second reactor is preferably fed into the third reactor. The hydrogen is preferably removed. To the third reactor is fed ethylene, diluent and comonomer. Preferably the conditions for carrying out the polymerisation in the third reactor are as follows:

Temperature: 50 to 100 °C, preferably 70 to 90 °C
Pressure: 1 to 10 bar, preferably 1.5 to 7 bar
Partial pressure of ethylene: 0.3-4 bar
Residence time: 2 minutes to 1 hour, preferably 5 to 30 minutes
Diluent: hexane

Partial pressure ratio of $\text{H}_2$:ethylene: 0.000:1 to 0.05:1, preferably 0.000:1 to 0.01:1
Ratio % wt comonomer/% wt ethylene in reactor: 0.5-10, preferably 1 to 6 %, e.g. 2-5 %

Preferably the optional comonomer is 1-butene.

The molar ratio between comonomer and ethylene in the third reactor is preferably 1.5-20 times, more preferably 2-15 times, and still more preferably 3-10 times higher, than the molar ratio between comonomer and ethylene in the second reactor.

In the third reactor, 0.5 – 9.5 % wt of the total polyethylene is preferably made, more preferably 1.0 – 7.5 % wt, still more preferably 1.5-6 % wt and most preferably 3 – 6 % wt.

Second preferred process

In a second preferred process of the invention the polyethylene is prepared by preparing its ethylene polymer components in the sequence lower molecular weight ethylene polymer, second higher molecular weight ethylene copolymer and then first higher molecular weight ethylene copolymer.

This preferred process comprises the sequential steps (i)-(iii):

(i) polymerising ethylene and optionally an $\alpha$-olefin comonomer in a first (LMW) reactor to produce a lower molecular weight ethylene polymer;
(ii) polymerising ethylene and an $\alpha$-olefin comonomer in a second (HMW2) reactor to produce a second higher molecular weight ethylene copolymer; and
(iii) polymerising ethylene and an α-olefin comonomer in a third (HMW1) reactor to produce a first higher molecular weight ethylene copolymer.

This preferred process is shown in Figure 1 which is discussed in more detail below.

In a preferred process, during said polymerisation to produce a second higher molecular weight ethylene copolymer, at least some said lower molecular weight ethylene polymer is present in the second reactor. In a further preferred process, during said polymerisation to produce a first higher molecular weight ethylene copolymer, said lower molecular weight ethylene polymer and said second higher molecular weight ethylene copolymer, are present in the third reactor.

In this preferred process essentially all of the catalyst used in the reactors is preferably fed to the first (LMW) reactor. To first reactor is also preferably fed ethylene, hydrogen and diluent. Preferably the conditions for carrying out the polymerisation in the first reactor are as follows:

- Temperature: 50 to 100 °C, preferably 70 to 90 °C
- Pressure: 1 to 20 bar, preferably 5 to 15 bar
- Partial pressure of ethylene: 1-10 bar
- Residence time: 0.5 to 4 hours, preferably 1-2 hours
- Diluent: hexane
- Partial pressure ratio of H₂:ethylene: 5:1 to 0.5:1, preferably 3:1 to 1:1
- Comonomer in reactor: 0-1 % wt, preferably 0 % wt

Preferably the optional comonomer is 1-butene.

The polymerisation in the first reactor preferably produces 30 – 70 % wt of the total polyethylene, more preferably 35 – 65 % wt, still more preferably 40-60 % wt and most preferably 45 – 55 % wt.

The flow out of first reactor is preferably split between going directly to the third (HWM2) reactor and going via the second (HMW1) reactor. Preferably 5 – 100 % of flow goes via the second reactor, more preferably 10 – 70 %, most preferably 15 – 50 %, for example 20 – 40%. The most volatile components are preferably removed from the outgoing flow of the first reactor such that more than 96 % of the hydrogen is removed before the flow enters the second reactor and more than 80 % of the hydrogen is removed before flow enters third reactor directly.

To the second reactor (HMW2) is fed ethylene, comonomer and diluent and optionally hydrogen. Preferably the conditions for carrying out polymerisation in the second reactor are as follows:
Temperature: 50 to 100 °C, preferably 70 to 90 °C
Pressure: 1 to 16 bar, preferably 5 to 11 bar
Partial pressure of ethylene: 0.3-4 bar
Partial pressure ratio of H₂:ethylene: 0.000:1 to 0.05:1, preferably 0.000:1 to 0.01:1
Residence time: 1 minute to 1 hour, preferably 2 to 20 minutes
Diluent: hexane

Ratio % wt comonomer/% wt ethylene in reactor: 0.5-10, preferably 1 to 6 %, e.g. 2-5 %

Preferably the optional comonomer is 1-butene.

In the second reactor, 0.5 – 9.5 % wt of the total polymer is preferably made, more preferably 1.0 – 7.5 % wt, still more preferably 1.5-6 % wt and most preferably 3 – 6 % wt.

Essentially all of the polymer flow out of second reactor is preferably fed into the third reactor. Any polymer flow out of the first reactor that does not enter the second reactor is also preferably fed into the third reactor.

To the third reactor is fed ethylene, hydrogen, diluent and comonomer. Preferably the conditions for carrying out the polymerisation in the third reactor are as follows:

Temperature: 50 to 100 °C, preferably 70 to 90 °C
Pressure: 1 to 15 bar, preferably 2 to 10 bar
Partial pressure of ethylene: 0.5-6 bar
Residence time: 0.5 to 4 hours, preferably 1-2 hours
Diluent: hexane

Partial pressure ratio of H₂:ethylene: 0.01:1 to 0.5:1, preferably 0.02:1 to 0.2:1

Ratio % wt comonomer/% wt ethylene in reactor: 0.05-1%, preferably 0.1 to 0.5 %

Preferably the optional comonomer is 1-butene.

The molar ratio comonomer/ethylene is preferably 5-90 % of that in the second reactor, more preferably 10-40 % of that in the second reactor. The pressure is preferably lower in the third reactor than in the second reactor.

In the third reactor, 30 – 70 % wt of the total polymer is preferably made, more preferably 35 – 65 % wt, still more preferably 40-60 %wt and most preferably 40 – 50 % wt.

This polymerisation is generally applicable to the preparation of trimodal polyethylene. Thus viewed from a further aspect, the present invention provides a
process for the preparation of a polyethylene having a multimodal molecular weight
distribution comprising:
(i) 20-70 % wt of a lower molecular weight ethylene polymer;
(ii) 20-70 % wt of a first higher molecular weight ethylene polymer; and
(iii) 0.5-30 % wt of a second higher molecular weight ethylene polymer,
wherein said process comprises the sequential steps (a)-(c):
(a) polymerising ethylene and optionally an \( \alpha \)-olefin comonomer in a first (LMW) reactor
to produce a lower molecular weight ethylene polymer;
(b) polymerising ethylene and optionally an \( \alpha \)-olefin comonomer in a second (HMW2)
reactor to produce a second higher molecular weight ethylene polymer; and
(c) polymerising ethylene and optionally an \( \alpha \)-olefin comonomer in a third (HMW1)
reactor to produce a first higher molecular weight ethylene polymer.

In a preferred process, during said polymerisation to produce a second higher
molecular weight ethylene copolymer, at least some said lower molecular weight
ethylene polymer is present in said second reactor. In a further preferred process,
during said polymerisation to produce a first higher molecular weight ethylene
copolymer, said lower molecular weight ethylene polymer and said second higher
molecular weight ethylene copolymer, are present in said third reactor. Thus any lower
molecular weight ethylene polymer that is not present in said second reactor preferably
passes directly to the third reactor.

In such processes, the lower molecular weight ethylene polymer is an ethylene
homopolymer. Preferably the first higher molecular weight ethylene polymer is an
ethylene copolymer. Preferably the second higher molecular weight ethylene polymer
is an ethylene copolymer. Preferably the amount of said second higher molecular
weight ethylene polymer is 0.5 to 30 % wt, more preferably 1 to 15 % wt and still more
preferably 1.5 to 9.5 % wt. Preferably the second higher molecular weight ethylene
polymer has a higher comonomer content than the first higher molecular weight
ethylene polymer.

The preferred characteristics of each polymer component are as described
above. Additionally the preferred conditions for carrying out each polymerisation stage
are as described above.

The process described above is shown schematically in Figure 1. Figure 1
shows how the flow from the first (LMW) reactor is split between the second (HMW2)
reactor and the third (HMW1) reactor. Figure 1 also shows how this process
advantageously enables diluent and/or comonomer to be recycled. The dashed lines
in Figure 1 illustrate recycling of comonomer separated from polyethylene product into each of the reactors. The thin solid lines in Figure 1 illustrate recycling of diluent, either in purified or non-purified form. As used herein, non-purified diluent refers to diluent wherein wax (PE fraction soluble in hexane) has not been removed and comonomer has not been completely removed. Correspondingly, by purified diluent is meant diluent which is essentially free of wax and comonomer.

In preferred processes purified diluent comprises 30 -100 % of the total diluent recycled. Preferably the first (LMW) reactor is fed with purified diluent. Preferably the second (HMW2) reactor is fed with non-purified and/or purified diluent. Preferably the third (HMW1) reactor is fed with non-purified and/or purified diluent. Additionally, an amount of fresh diluent is preferably added to the reactor system.

In a further preferred process the first (LMW), second (HMW2) and third (HMW1) reactors are fed fresh comonomer and/or recycled comonomer. Preferably comonomer is not fed to the first (LMW) reactor.

Advantages of the process shown in Figure 1 over a conventional process wherein polymers of increasing molecular weight are made in sequence include:

- Total mass flow of comonomer from the separation is reduced, since the comonomer concentration is typically lower in the third and final reactor.
- The HMW2 reactor volume may be much lower, both since the catalyst concentration is much higher there, and since the pressure typically would be higher that early in the process.
- A high fraction of the recycled diluent may be utilised as non-purified diluent

Regardless of the process used, there may optionally be a reactor subsequent to the third reactor. This preferably produces a copolymer. In this reactor would be produced 1 – 30 % wt of the total polymer, more preferably 2 – 9.5 % wt.

Downstream processing

When the final polyethylene is obtained from a slurry reactor, the polymer is removed therefrom and the diluent preferably separated from it by flashing or filtration. The major part of the diluent and unconverted comonomer is preferably recycled back to the polymerisation reactor(s). Preferably the polymer is then dried (e.g. to remove residues of liquids and gases from the reactor). Optionally the polymer is subjected to a deashing step, i.e. to washing with an alcohol, optionally mixed with a hydrocarbon liquid, or water. Preferably there is no deashing step.
In order that the polyethylene can be handled without difficulty, both within and downstream of the polymerisation process, the polyethylene from the reactors is preferably in a free-flowing state, preferably by having relatively large particles of high bulk density, e.g. less than 20 % wt of the polymer powder being smaller than 100 μm size, and the loose bulk density being higher than 300 kg/m³.

Preferably the processes from the polymerisation until the pelletisation extruder outlet are carried out under an inert (e.g. N₂) gas atmosphere.

Antioxidants are preferably added (process stabilisers and long term antioxidants) to the polyethylene. As antioxidant, all types of compounds known for this purpose may be used, such as sterically hindered or semi-hindered phenols, aromatic amines, aliphatic sterically hindered amines, organic phosphates and sulphur-containing compounds (e.g. thioethers). Other additives (antiblock, colour masterbatches, antistatics, slip agents, fillers, UV absorbers, lubricants, acid neutralisers and fluoroelastomer and other polymer processing agents) may optionally be added to the polymer.

If the polyethylene is to be used for the manufacture of pipe, a pigment (e.g. carbon black) is preferably added before extrusion. Pigments are preferably added in the form of a master batch.

The polyethylene is preferably extruded and granulated into pellets. Preferred pellets have a loose bulk density of greater than 400 kg/m³ and less than 10 % wt of pellets smaller than 2 mm in size.

Further additives (e.g. polymer processing agents or antiblock) may be added after pelletisation of the polyethylene. In this case the additives are preferably used as masterbatches and pellets mixed therewith before being, e.g. moulded into articles.

Polyethylene composition

The polyethylene composition of the present invention preferably has at least one of the following properties.

The polyethylene preferably has a FNCT time to failure of greater than 10 hours, more preferably greater than 15 hours and still more preferably greater than 20 hours, e.g. under the conditions specified in the examples below. The maximum FNCT time to failure may be, e.g. 50 hours.

The polyethylene preferably has a Charpy Impact of greater than 5 kJ/m², more preferably greater than 10 kJ/m² and still more preferably greater than 12 hours, e.g.
under the conditions specified in the examples below. The maximum Charpy Impact may be, e.g. 50 kJ/m².

The polyethylene preferably has a Shore hardness of at least 30, more preferably at least 40 and still more preferably at least 50, e.g. under the conditions specified in the examples below. The maximum Shore hardness may be 90.

The polyethylene preferably has an Abrasion resistance of at least 5%, more preferably at least 7% and still more preferably at least 10%, e.g. under the conditions specified in the examples below. The maximum Abrasion resistance may be 35%.

An advantage of the polyethylene composition of the present invention is the combination of properties that may be achieved. Preferred polyethylene compositions of the invention possess at least two, more preferably at least three and still more preferably all four of the following properties, e.g. as determined under the conditions specified in the examples below:

- FNCT time to failure: >10 hours
- Charpy Impact: >5 kJ/m²
- Shore hardness: >30
- Abrasion resistance: >5%

Still more preferably the polyethylene composition of the invention possesses at least two, more preferably at least three and still more preferably all four of the following properties, e.g. as determined under the conditions specified in the examples below:

- FNCT time to failure: >20 hours
- Charpy Impact: >12 kJ/m²
- Shore hardness: >50
- Abrasion resistance: >10%

Applications

The polyethylene of the present invention may be used in any moulding application or in the preparation of film. Preferably, however, the polyethylene is used in moulding, e.g. extrusion moulding.

The polyethylene of the present invention is preferably used in pipe applications. Preferably it is used in HDPE pipes, e.g. according to PE80 or PE100 standards. The pipes may be used e.g. for water and gas distribution, sewer, wastewater, agricultural uses, slurries, chemicals etc.
The invention will now be described with reference to the following non-limiting examples and Figures wherein:

Figure 1 is a schematic of a preferred process of the present invention.
EXAMPLES
Determination methods for polymers

Unless otherwise stated, the following parameters were measured on polymer samples as indicated in the Tables below.

$MFR_{2}$, $MFR_{5}$ and $MFR_{21}$ were measured according to ISO 1133 at loads of 2.16, 5.0, and 21.6 kg respectively. The measurements were at 190 °C.

Molecular weights and molecular weight distribution, Mn, Mw and MWD were measured by Gel Permeation Chromatography (GPC) according to the following method: The weight average molecular weight Mw and the molecular weight distribution ($MWD = Mw/Mn$ wherein Mn is the number average molecular weight and Mw is the weight average molecular weight) is measured by a method based on ISO 16014-4:2003. A Waters Alliance GPCV2000 instrument, equipped with refractive index detector and online viscosimeter was used with 1 PLgel GUARD + 3 PLgel MIXED-B and 1,2,4-trichlorobenzene (TCB, stabilised with 250 mg/L 2,6-Di tert butyl-4-methyl-phenol) as solvent at 140 °C and at a constant flow rate of 1 mL/min. 200 μL of sample solution were injected per analysis. The column set was calibrated using universal calibration (according to ISO 16014-2:2003) with 15 narrow molecular weight distribution polystyrene (PS) standards in the range of 1.0 kg/mol to 12 000 kg/mol. These standards were from Polymer Labs and had Mw/Mn from 1.02 to 1.10. Mark Houwink constants were used for polystyrene and polyethylene ($K: 0.19 \times 10^{-5}$ dL/g and $a: 0.655$ for PS and $K: 3.9 \times 10^{-4}$ dL/g and $a: 0.725$ for PE). All samples were prepared by dissolving 0.5-3.5 mg of polymer in 4 mL (at 140 °C) of stabilised TCB (same as mobile phase) and keeping for 3 hours at 140 °C and for another 1 hour at 160 °C with occasional shaking prior to sampling into the GPC instrument.

Melting temperature was measured according to ISO 11357-1 on Perkin Elmer DSC-7 differential scanning calorimetry. Heating curves were taken from −10 °C to 200 °C at 10 °C/min. Hold for 10 min at 200 °C. Cooling curves were taken from 200 °C to −10 °C at 10 °C per min. Melting temperature was taken as the peak of the endotherm of the second heating. The degree of crystallinity was calculated by dividing the observed melting peak with the heat of melting of a perfectly crystalline polyethylene, generally taken to be 290 J/g.
Coomonomer content (% wt) was determined based on Fourier transform infrared spectroscopy (FTIR) determination calibrated with C13-NMR.

Density of materials is measured according to ISO 1183:1987 (E), method D, with isopropanol-water as gradient liquid. The cooling rate of the plaques when crystallising the samples was 15 C/min. Conditioning time was 16 hours.

Rheology of the polymers was determined by frequency sweep at 190 °C under nitrogen atmosphere according to ISO 6721-10, using Rheometrics RDA II Dynamic Rheometer with parallel plate geometry, 25 mm diameter plate and 1.2 mm gap. The measurements gave storage modulus (G'), loss modulus (G'') and complex modulus (G*) together with the complex viscosity (η*), all as a function of frequency (ω). These parameters are related as follows: For any frequency ω: The complex modulus: G* = (G''^2 + G'^2)^(1/2). The complex viscosity: η* = G*/ω. The denomination used for modulus is Pa (or kPa) and for viscosity is Pa s and frequency (1/s). η*0.05 is the complex viscosity at a frequency of 0.05 s⁻¹ and η*300 is the complex viscosity at 300 s⁻¹. According to the empirical Cox-Merz rule, for a given polymer and temperature, the complex viscosity as a function of frequency measured by this dynamic method is the same as the viscosity as a function of shear rate for steady state flow (e.g. a capillary).

The activity coefficient for the bench scale polymerisation runs is calculated by the following equation:

\[ \text{Activity coefficient (kg.h/ (g.bar,h))} = \frac{\text{Yield of polymer (kg)}}{\text{(Catalyst amount (g)) × (Partial pressure of ethylene (bar)) × (Polymerisation time – (h))}} \]

Polydispersity Index, PI, is the crossoverpoint in a RDA frequency sweep where G' equals G'', and given by: PI = 10^5 Pa/G'.

Determination methods for polymer composition

Unless otherwise stated, the following parameters were measured on 4mm plates that were compression molded on a Collin 300 P compression moulder with reference to ISO 293-186, ISO1872-2-1197 and ISO1873-2-1997;
FNCT time to failure is measured according to ISO16770 with 8.5MPa load at a
temperature of 80 °C in 2 wt% Arkopal N110 in deionised water on 10mm compression
molded dogbones, milled from compression molded plate, notch depth 1.6mm all round.
Charpy Impact is measured according to ISO179 on compression moulded specimens
at +23 °C.

Charpy Impact is measured according to ISO179-1/1eA on compression moulded specimens at +23 °C.

Shore Hardness: Shore D is measured on a digital shoremeter, Bareiss type HHP-2001
according to any cracks initiated. Sample conditioning is done according to

Abrasion resistance is measured according to ISO 4649, type B test (non-rotating
sample) with force 10 N.

For small scale experiments, for which no pipes can be made and tested, it is
conventional to use FNCT measurement on compound as a measure for SCG and to
use Charpy Impact on compound as a measure of RCP. Similarly Shore hardness D
measures the hardness of the sample and is a measure of the probability that
scratching can occur. Abrasion resistance according to ISO4649 measures volume
loss of the test material after being subjected to abrasion by an abrasive sheet which
will cause a reference compound to lose a defined mass under the same specified
conditions of test. Like the hardness test therefore, it provides a measure of the
likelihood that a scratch can occur.

Experimental
A conventional Ziegler-Natta catalyst with Ti as the transition metal was used. The
catalyst is described in US4792588. The titanium content was 3.4 % wt.

Polymerisation was carried out in a 8 litre flask fitted with a stirrer and a temperature
control system. The catalyst was added as a mud. TEA, triethyl aluminium was used
as activator. The same comonomer feeding system was used for all runs. The
procedure comprised the following steps:
Polymerization of lower molecular weight ethylene polymer:

The reactor was purged with nitrogen and heated to 110°C. Hydrogen was then loaded at 20°C to give a pressure of 3.05 bar. 3000 ml liquid hexane was then added to the reactor and stirring started; 300 rpm. The reactor temperature was 70°C. Cocatalyst and TEA were then pre-contacted in mud for 5 min and loaded with 800 ml of hexane. Ethylene was then fed to get a total pressure of 12.3 bar. Ethylene was then fed continuously. When sufficient amount of powder is made, the polymerization is stopped and the hexane is evaporated.

Polymerization of first higher molecular weight ethylene:

Hydrogen is loaded at 20°C to 0.16 bar. Stirring is then started at 300 rpm. The reactor is then heated to >70°C. When the temperature reaches 72°C, 35ml 1-butene is added and ethylene is fed to get a total pressure of 5.7 bar g. Ethylene and 1-butene are then fed continuously. When sufficient amount of powder is made, the polymerization is stopped and the hexane is evaporated.

Polymerization of second higher molecular weight ethylene polymer:

The reactor is heated to >70°C, 3000 ml hexane is loaded and stirring is started at 300 rpm. When the temperature reaches 72°C, ethylene and 180 ml 1-butene is fed to get a total pressure of 5.3 bar. Ethylene and 1-butene were then fed continuously. When sufficient amount of powder is made, the polymerization is stopped and the hexane is evaporated.

Two comparative polymerisations were also carried out. The first comparative polymerisation (C1) was carried out in the same manner as above except that no 1-butene was added on the polymerization of the second higher molecular weight ethylene polymer. The second comparative polymerisation (C2) was carried out in the same manner as above except that the polymerization was stopped after the polymerization of the first higher molecular weight ethylene.

Further details of the polymerisation procedure and details of the resulting polyethylene polymers are summarised in Table 1 below wherein RI refers to the polymerisation in and the product of the first reactor, RII refers to the polymerisation in the second reactor and the product of the first and second second reactor together and
RIII refers to the polymerisation in the third reactor and the product of the first, second and third reactor together, which is the final polyethylene product.
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|        | C1-RI| C1-RI| C1-RI| C1-RI| EX-1-RI| EX-1-RI| EX-1-RI| C2-RI| C2-RI
The polymers were compounded with 155ppm of Irganox B215 (antioxidant) on a Prism16 extruder with L/D=25. The extruder was run with an output rate of 1kg/h, 500rpm, no vacuum and with nitrogen flushing. The extruder temperature profile was 180-200x4-180(die). The resulting pellets were then pressed into 4mm plates following ISO293-1986, 1872-2 and 1873-2. Proper test specimens were then made from these plates.

The results are shown in Table 2 below.

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<th>Polyethylene</th>
<th>C1</th>
<th>Example 1</th>
<th>C2</th>
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<td>Density</td>
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<td>Shore hardness</td>
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<td>Abrasion resistance (ISO 4649) %</td>
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<td>16,6</td>
<td>18,7</td>
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*All samples showed brittle failure in FNCT

The final polymers of example 1, C1 and C2 have identical density values and very similar MFR5 values, which means that their stiffnesses are also very similar as are their practical extrusion processability. As a result, they can be compared fairly. Astonishingly, the polyethylene of the invention has more than double the FNCT result of the two comparative polymers. Even more surprisingly, the Charpy impact indicating RCP resistance, was not reduced, which as mentioned, usually occurs when a modification to a polymer is made that increases FNCT. Even Shore hardness was maintained in spite of the fact that the third component/fraction is a relative soft component due to its high comonomer content.
It is impressive that such a significant improvement in mechanical properties, specifically SCG and RCP, could be obtained by the incorporation of such a small amount of a second higher molecular weight copolymer. Even more desirably, the results (Shore hardness and abrasion resistance) show that the polyethylene of the invention is more resistant to becoming scratched, nicked or notched in the first place by the handling of the pipes in the field, which means that the number and size of defects that can propagate into cracks is also reduced. This combination of properties is highly desirable for the manufacture of pipes, particularly high pressure pipes.

It is hypothesised that the third polymer, having a relatively high molecular weight and a relatively high comonomer content increases the level of tie-chains and entanglements in the polyethylene composition. This increased level of tie-chains and entanglements will dissipate the energy associated with the stress field in an initiated crack and reduce the likeliness of a crack to propagate. Moreover the polymer of the present invention is also convenient to prepare. The relatively small amount of second high molecular weight copolymer, may be made in a relatively small reactor, with a short residence time or alternatively in a medium size reactor where very conservative reactor conditions are employed.
CLAIMS

1. A polyethylene having a multimodal molecular weight distribution comprising:
   (i) 20-70% wt of a lower molecular weight ethylene polymer;
   (ii) 20-70% wt of a first higher molecular weight ethylene copolymer; and
   (iii) 0.5-9.5% wt of a second higher molecular weight ethylene copolymer.

2. A polyethylene as claimed in claim 1 having a density of 945-962 kg/m³.

3. A polyethylene as claimed in claim 1 or 2 having a MFR₅ of 0.15-0.6 g/10min.

4. A polyethylene as claimed in any preceding claim, wherein said lower molecular
   weight ethylene polymer is an ethylene homopolymer.

5. A polyethylene as claimed in any preceding claim, wherein said lower molecular
   weight ethylene polymer has a MFR₂ of 50-1500 g/10min.

6. A polyethylene as claimed in any preceding claim, wherein said lower molecular
   weight ethylene polymer is present in an amount of 40-60 % wt.

7. A polyethylene as claimed in any preceding claim, wherein said first higher
   molecular weight copolymer is an ethylene 1-butene copolymer.

8. A polyethylene as claimed in any preceding claim, wherein said first higher
   molecular weight copolymer has a molecular weight of 200,000 to 700,000 g/mol.

9. A polyethylene as claimed in any preceding claim, wherein said first higher
   molecular weight copolymer is present in an amount of 40-60 % wt.

10. A polyethylene as claimed in any preceding claim, wherein said second higher
    molecular weight copolymer is an ethylene 1-butene copolymer.

11. A polyethylene as claimed in any preceding claim, wherein said second higher
    molecular weight copolymer has a greater molecular weight than said first higher
    molecular weight copolymer.
12. A polyethylene as claimed in any preceding claim, wherein said second higher molecular weight copolymer has a molecular weight of 200,000 to 2,000,000 g/mol.

13. A polyethylene as claimed in any preceding claim, wherein said second higher molecular weight copolymer is present in an amount of 1.5-6 % wt.

14. A process for the preparation of a polyethylene as claimed in any one of claims 1 to 13 comprising polymerising ethylene and, as required, at least one other α-olefin to yield said polyethylene, wherein said polymerisation is carried out in at least three steps.

15. A process as claimed in claim 14, comprising the sequential steps (a)-(c):
   (i) polymerising ethylene and optionally an α-olefin comonomer in a first reactor to produce a lower molecular weight ethylene polymer;
   (ii) polymerising ethylene and an α-olefin comonomer in a second reactor to produce a first higher molecular weight ethylene copolymer; and
   (iii) polymerising ethylene and an α-olefin comonomer in a third reactor to produce a second higher molecular weight ethylene copolymer.

16. A process as claimed in claim 15 wherein, during said polymerisation to produce a first higher molecular weight ethylene copolymer, at least some of said lower molecular weight ethylene polymer is present in said second reactor.

17. A process as claimed in claim 15 or 16 wherein, during said polymerisation to produce a second higher molecular weight ethylene copolymer, said lower molecular weight ethylene polymer and said first higher molecular weight ethylene copolymer, are present in said third reactor.

18. A process as claimed in claim 14, comprising the sequential steps (a)-(c):
   (i) polymerising ethylene and optionally an α-olefin comonomer in a first reactor to produce a lower molecular weight ethylene polymer;
   (ii) polymerising ethylene and an α-olefin comonomer in a second reactor to produce a second higher molecular weight ethylene copolymer; and
(iii) polymerising ethylene and an α-olefin comonomer in a third reactor to produce a first higher molecular weight ethylene copolymer.

19. A process as claimed in claim 18 wherein, during said polymerisation to produce a second higher molecular weight ethylene copolymer, at least some of said lower molecular weight ethylene polymer is present in said second reactor.

20. A process as claimed in claim 18 or 19 wherein, during said polymerisation to produce a first higher molecular weight ethylene copolymer, said lower molecular weight ethylene polymer and said second higher molecular weight ethylene copolymer, are present in said third reactor.

21. A polyethylene obtainable by a process as claimed in any one of claims 14 to 20.


23. A composition as claimed in claim 22 having a FNCT time to failure of greater than 20 hours, e.g. as measured according to ISO16770 with 8.5MPa load at a temperature of 80°C

24. A composition as claimed in claim 22 or 23 having a Charpy Impact of greater than 12 kJ/m², e.g. as measured according to ISO179-1/1eA on compression moulded specimens at +23°C

25. A composition as claimed in any one of claims 22 to 24 having a Shore hardness of at least 50, e.g. as measured according to a digital shoremeter.

26. A composition as claimed in any one of claims 22 to 25 having an Abrasion resistance of at least 10%, e.g. as measured according to ISO 4649, type B test with force 10 N.

27. An article comprising a polyethylene as claimed in any one of claims 1-13 or a composition as claimed in any one of claims 22-26.
28. An article as claimed in claim 27 which is a pipe.

29. A process for the preparation of an article as claimed in claim 27 or 28, comprising moulding, e.g. blow moulding, a polyethylene as claimed in any one of claims 1-13 or a composition as claimed in any one of claims 22-26.

30. Use of a polyethylene as claimed in any one of claims 1-13 or a composition as claimed in any one of claims 22-26 in the manufacture of a pipe.

31. A process for the preparation of a polyethylene having a multimodal molecular weight distribution comprising the sequential steps (a)-(c):
   (i) 20-70% wt of a lower molecular weight ethylene polymer;
   (ii) 20-70% wt of a first higher molecular weight ethylene polymer; and
   (iii) 0.5-30% wt of a second higher molecular weight ethylene polymer,
wherein said process comprises the sequential steps (a)-(c):
   (a) polymerising ethylene and optionally an α-olefin comonomer in a first reactor to produce a lower molecular weight ethylene polymer;
   (b) polymerising ethylene and optionally an α-olefin comonomer in a second reactor to produce a second higher molecular weight ethylene polymer; and
   (c) polymerising ethylene and optionally an α-olefin comonomer in a third reactor to produce a first higher molecular weight ethylene polymer.

32. A process as claimed in claim 31 wherein, during said polymerisation to produce a second higher molecular weight ethylene copolymer, at least some of said lower molecular weight ethylene polymer is present in said second reactor.

33. A process as claimed in claim 31 or 32 wherein, during said polymerisation to produce a first higher molecular weight ethylene copolymer, said lower molecular weight ethylene polymer and said second higher molecular weight ethylene copolymer, are present in said third reactor.

34. A process as claimed in any one of claims 31 to 33, wherein said lower molecular weight ethylene polymer is an ethylene homopolymer.
35. A process as claimed in any one of claims 31 to 34, wherein said first higher molecular weight ethylene polymer is an ethylene copolymer.

36. A process as claimed in any one of claims 31 to 35, wherein said second higher molecular weight ethylene polymer is an ethylene copolymer.

37. A process as claimed in any one of claims 31 to 36, wherein the amount of said second higher molecular weight ethylene polymer is 1 to 15 % wt, more preferably 1.5 to 9.5 % wt.

38. A process as claimed in any one of claims 31 to 37 wherein said second higher molecular weight ethylene polymer has a higher comonomer content than said first higher molecular weight ethylene polymer.
Application No: GB1201578.0
Claims searched: 1-30
Examiner: Mr Jason Scott
Date of search: 31 May 2012

**Patents Act 1977: Search Report under Section 17**

**Documents considered to be relevant:**

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| X        | 1, 14, 21, 22 and 27-30 at least | US 2011/318559 A
BASELL POLYOLEFINE See whole document and especially claim 13 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22 and 27-30 at least | US 2011/171450 A
BASELL POLYOLEFINE See whole document and especially claim 11 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22 and 27-30 at least | US 2008/090968 A
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22 and 27-30 at least | US 2010/301054 A
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22, 27, 29 and 30 at least | US 2008/139750 A
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22, 27, 29, and 30 at least | WO 2006/053740 A
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22, and 27-30 at least | US 6713561 B
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |
| X        | 1, 14, 21, 22, and 27-30 at least | WO 2011/000497 A
BASELL POLYOLEFINE See whole document and especially claim 1 teaching a trimodal polyethylene composition. |

Categories:
- X Document indicating lack of novelty or inventive
- A Document indicating technological background and/or state
## Field of Search:
Search of GB, EP, WO & US patent documents classified in the following areas of the UKC:

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- WPI
- EPODOC

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**Patents Act 1977**
**Further Search Report under Section 17**

**Documents considered to be relevant:**

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Basell Polyolefine - see e.g. claims 11-13 and example 1 |
| X        | 31-38              | US 2011/171450 A  
Basell Polyolefine - see e.g. claims 11-13 and example 1 |
| X        | 31-38              | US 2008/090968 A  
Basell Polyolefine - see e.g. claims 1-12 and example 1 |
| X        | 31-38              | US 2010/301054 A  
Basell Polyolefine - see e.g. claims 1-11 and example 1 |
| X        | 31-38              | US 2008/139750 A  
Basell Polyolefine - see e.g. claims 1-13 and example 1 |
| X        | 31-38              | WO 2006/053740 A  
Basell Polyolefine - see e.g. claims 1-11 and example 1 |
| X        | 31-38              | US 6713561 B  
Basell Polyolefine - see e.g. examples 1-12 and examples 1-4 |
| X        | 31-38              | WO 2011/000497 A  
Basell Polyolefine - see e.g. claims 1-16 and example 1 |
| X        | 31-38              | US 2009/0105422 A1  
Basell Polyolefine - see e.g. claims 9-22 and example 1 |

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