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(54) Title: MULTIMODAL POLYETHYLENE COMPOSITION WITH IMPROVED HOMOGENEITY

(57) Abstract: The present invention in a first embodiment concerns a multimodal, preferably bimodal, polyethylene composition comprising a base resin which comprises (A) a first ethylene homo- or copolymer fraction, and (B) a second ethylene homo- or copolymer fraction, wherein fraction (A) has a lower molecular weight than fraction (B), the ratio of the MFR₂ of fraction (A) and the MFR₅ of the base resin being from 200 to 1500, and the composition has a white spot area of 1 % or below. In a second embodiment, the present invention concerns a polyethylene composition comprising a base resin comprising (A) a first ethylene homo- or copolymer fraction, and (B) a second ethylene homo- or copolymer fraction, wherein fraction (A) has a lower molecular weight than fraction (B), the ratio of the MFR₂ of fraction (A) and the MFR₅ of the base resin being from 200 to 1500, and the composition has a rating in the ISO 18553 white spot rating test of below 4.5. Furthermore, the present invention relates to a process for the production of said compositions as well as to the use said compositions for the production of an article, in particular a pipe.



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Multimodal Polyethylene Composition with Improved Homogeneity

The present invention concerns a multimodal, preferably bimodal, polyethylene composition comprising two ethylene homo- or copolymer
5 fractions with different molecular weight having improved homogeneity. Furthermore, the present invention relates to a process for the production of such a composition as well as to the use of such a composition for the production of a pipe.

Multimodal polyethylene compositions are frequently used e.g. for the
10 production of pipes due to their favourable physical and chemical properties as e.g. mechanical strength, corrosion resistance and long-term stability. When considering that the fluids, such as water or natural gas, transported in a pipe often are pressurized and have varying temperatures, usually within a range of 0°C to 50°C, it is obvious that the polyethylene
15 composition used for pipes must meet demanding requirements.

For multimodal polymers comprising more than one polymer fraction with different molecular weight, homogeneity is known to be a critical property, because low degrees of homogeneity adversely affect e.g. the surface properties and other properties of the polymer composition. For obtaining a
20 sufficient degree of homogeneity, mixing of the different fractions the composition is consisting of must be reached down to the microscopic scale.

When compounding multimodal polymer compositions e.g. for the production of pipes, so-called "white spots" occur in the compounded
25 material. These white spots usually have a size of below 10 to about 50 micrometer and consist of high molecular weight polymer particles that

have not been adequately compounded in the composition. Further, when compounding polymer compositions e.g. for the production of films, gel particles with a size of about 0.01 to 1 mm often occur. These gel particles also consist of high molecular weight polymer particles not adequately compounded and appear as disfiguring inhomogeneities in the finished film. Still further, inhomogeneities in multimodal polymer compositions may also cause waviness of the surface of articles produced thereof.

As a measure for the homogeneity in multimodal resins the ISO 18553 test can be applied. ISO 18553 originally is a method for rating pigmented spots, i.e. serves to determine how well pigments are dispersed in a polymer. As the dispersion of the pigment is dependent on the overall homogeneity of the polymer because inhomogeneities of the polymer are not coloured by the pigment, ISO 18553 can also be used as a measure for the homogeneity of a polymer by counting the non-coloured white spots and rating them according to the ISO 18553 scheme.

As a further measure for the homogeneity of a polymer, the white spot area test has been developed which to a far extent is based on the modified ISO 18553 white spot rating test as described in the above paragraph. This test is described in detail below.

It is known that homogeneity of a multimodal polymer composition can be improved by applying multiple compounding steps and/or particular compounding conditions to the resin coming from the reactor. These measures, however, have the disadvantage that they are associated with a significant increase in production costs for the composition.

It is, therefore, an object of the present invention to provide a multimodal polyethylene composition, in particular for the use as a pipe material, with

improved homogeneity and thus improved properties, including improved surface properties. In particular, it is an object of the present invention to provide such a multimodal polyethylene composition having improved homogeneity directly after its production. At the same time, the composition should have good processing and good mechanical properties.

The present invention thus provides in a first embodiment a polyethylene composition comprising a base resin which comprises

(A) a first ethylene homo- or copolymer fraction, and

(B) a second ethylene homo- or copolymer fraction,

wherein fraction (A) has a lower molecular weight than fraction (B), the ratio of the MFR_2 of fraction (A) and the MFR_5 of the base resin being from 200 to 1500 and the composition has a white spot area of 1 % or below.

The homogeneity of the composition in terms of its white spot area is measured after a single compounding step as defined in detail below. Usually, the composition, measured after said single compounding step, has a white spot area of 0.01 to 1 %.

Preferably, the composition measured after said single compounding step, has a white spot area of 0.7 % or below, usually then 0.01 to 0.7 %

Preferably, the polyethylene composition, measured after a single compounding step, has a rating in the ISO 18553 white spot rating test of below 4.5, more preferably below 3.

In a second embodiment, the present invention provides a polyethylene composition comprising a base resin comprising

(A) a first ethylene homo- or copolymer fraction, and

(B) a second ethylene homo- or copolymer fraction,

wherein fraction (A) has a lower molecular weight than fraction (B), the ratio of the MFR_2 of fraction (A) and the MFR_5 of the base resin being
5 from 200 to 1500 and the composition has a rating in the ISO 18553 white spot rating test of below 4.5.

As for the first embodiment, the measurement of the homogeneity in terms of the ISO 18553 white spot rating test is carried out after said single compounding step. Usually, the composition, after said single
10 compounding step, has a rating in the ISO 18553 white spot rating test of 0.01 to below 4.5.

Preferably, the composition has a rating in the ISO 18553 white spot rating test of below 3, usually then between 0.01 and below 3.

The polyethylene compositions according to the invention have an
15 improved microscopic mixing directly after their production, which is demonstrated by the fact that already after a single, usual compounding step a resin with an excellent homogeneity is obtained. Thus, the composition combines good mechanical with good surface properties and hence e.g. an improved impact strength with an improved appearance of the
20 final product.

The term "molecular weight" as used herein denotes the weight average molecular weight M_w .

The term "base resin" means the entirety of polymeric components in the polyethylene composition according to the invention, usually making up at
25 least 90 wt% of the total composition. Preferably, the base resin is

consisting of fractions (A) and (B), optionally further comprising a prepolymer fraction in an amount of up to 20 wt%, more preferably up to 10 wt% and most preferably up to 5 wt% of the total base resin.

In addition to the base resin, usual additives for utilization with polyolefins, such as pigments (for example carbon black), stabilizers (antioxidant agents), antacids and/or anti-UVs, antistatic agents and utilization agents (such as processing aid agents) may be present in the polyethylene composition. Preferably, the amount of these additives is 10 wt% or below, further preferred 8 wt% or below, of the total composition.

10 Preferably, the composition comprises carbon black in an amount of 8 wt% or below, further preferred of 1 to 4 wt%, of the total composition.

Further preferred, the amount of additives different from carbon black is 1 wt% or less, more preferably 0.5 wt% or less.

Usually, a polyethylene composition comprising at least two polyethylene fractions, which have been produced under different polymerisation conditions resulting in different (weight average) molecular weights for the fractions, is referred to as "multimodal". The prefix "multi" relates to the number of different polymer fractions the composition is consisting of. Thus, for example, a composition consisting of two fractions only is called "bimodal".

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The form of the molecular weight distribution curve, i.e. the appearance of the graph of the polymer weight fraction as function of its molecular weight, of such a multimodal polyethylene will show two or more maxima or at least be distinctly broadened in comparison with the curves for the individual fractions.

25

For example, if a polymer is produced in a sequential multistage process, utilising reactors coupled in series and using different conditions in each reactor, the polymer fractions produced in the different reactors will each have their own molecular weight distribution and weight average molecular weight. When the molecular weight distribution curve of such a polymer is recorded, the individual curves from these fractions are superimposed into the molecular weight distribution curve for the total resulting polymer product, usually yielding a curve with two or more distinct maxima.

10 In the following, preferred features for both embodiments of the polyethylene composition according to the invention are described.

In the polyethylene composition according to the invention, fraction (A) preferably has an MFR₂ of at least 100 g/10min, more preferably at least 200 g/10min, and most preferably at least 300 g/10min.

15 Furthermore, in the polyethylene composition, fraction (A) preferably has an MFR₂ of 2000 g/10min or less, more preferably of 1500 g/10min or less, and most preferably of 1000 g/10min or less.

The base resin preferably has an MFR₅ of 1 g/10min or below, more preferably of 0.8 g/10min or below, more preferably of 0.6 g/10min or below, and most preferably 0.4 g/10min or below.

20 Furthermore, the base resin preferably has an MFR₅ of 0.01 g/10min or higher, more preferably of 0.05 g/10min or higher, and most preferably of 0.1 g/10min or higher.

Preferably, in the polyethylene composition according to the invention the weight ratio of fractions (A):(B) in the base resin is 30:70 to 70:30.

25 Furthermore, fraction (A) preferably is an ethylene homopolymer.

Fraction (A) preferably has a density of 950 kg/m^3 or higher, more preferably 960 kg/m^3 or higher.

Further preferred, the weight average molecular weight of fraction (A) is from $5,000 \text{ g/mol}$ to $100,000 \text{ g/mol}$, more preferably is from $7,000$ to
5 $90,000 \text{ g/mol}$, and most preferably is from $10,000$ to $80,000 \text{ g/mol}$.

In the polyethylene composition according to the invention fraction (B) preferably is a copolymer of ethylene with at least one further alpha-olefin comonomer.

Preferably, the alpha-olefin comonomer of fraction (B) is having from 4 to
10 8 carbon atoms, and more preferably is selected from 1-butene, 1-hexene, 4-methyl-1-pentene and 1-octene.

Fraction (B) preferably has a density of 954 kg/m^3 or lower, more preferably of 952 kg/m^3 or lower, still more preferably of 950 kg/m^3 or lower, and most preferably of 940 kg/m^3 or lower.

15 Base resin preferably has a density of lower than 960 kg/m^3 .

The weight average molecular weight of the base resin preferably is from $100,000 \text{ g/mol}$ to $1,000,000 \text{ g/mol}$.

Preferably, the composition has a white spot area of 0.7 % or below, usually between 0.01 to 0.7 %

20 The polyethylene composition according to any the invention preferably has a shear thinning index $\text{SHI}_{(2.7/210)}$ of at least 5, more preferably at least 10, still more preferably at least 20 and most preferably at least 40.

Furthermore, the polyethylene composition preferably has a shear thinning index $SHI_{(2.7/210)}$ of 300 or less, more preferably 290 or less, still more preferably 220 or less and most preferably 200 or less.

5 The SHI is the ratio of the viscosity of the polyethylene composition at different shear stresses. In the present invention, the shear stresses at 2.7 kPa and 210 kPa are used for calculating the $SHI_{2.7/210}$ which may serve as a measure of the broadness of the molecular weight distribution.

Furthermore, the polyethylene composition preferably has a viscosity at a shear stress of 2.7 kPa $\eta_{(2.7)}$ of 10,000 to 500,000 Pas, more preferably of
10 50,000 to 400,000 Pas, and most preferably of 75,000 to 350,000 Pas.

Where herein preferred features of fractions (A) and/or (B) of the composition of the present invention are given, these values are generally valid for the cases in which they can be directly measured on the respective fraction, e.g. when the fraction is separately produced or produced in the
15 first stage of a multistage process.

However, the base resin may also be and preferably is produced in a multistage process wherein e.g. fractions (A) and (B) are produced in subsequent stages. In such a case, the properties of the fractions produced in the second and third step (or further steps) of the multistage process can
20 either be inferred from polymers, which are separately produced in a single stage by applying identical polymerisation conditions (e.g. identical temperature, partial pressures of the reactants/diluents, suspension medium, reaction time) with regard to the stage of the multistage process in which the fraction is produced, and by using a catalyst on which no previously
25 produced polymer is present. Alternatively, the properties of the fractions produced in a higher stage of the multistage process may also be calculated,

e.g. in accordance with B. Hagström, Conference on Polymer Processing (The Polymer Processing Society), Extended Abstracts and Final Programme, Gothenburg, August 19 to 21, 1997, 4:13.

Thus, although not directly measurable on the multistage process products,
5 the properties of the fractions produced in higher stages of such a multistage process can be determined by applying either or both of the above methods. The skilled person will be able to select the appropriate method.

The polyethylene composition according the invention preferably is
10 produced so that at least one of fractions (A) and (B), preferably (B), is produced in a gas-phase reaction.

Further preferred, one of the fractions (A) and (B) of the polyethylene composition, preferably fraction (A), is produced in a slurry reaction, preferably in a loop reactor, and one of the fractions (A) and (B),
15 preferably fraction (B), is produced in a gas-phase reaction.

Further, the polyethylene base resin preferably is produced in a multistage process. Polymer compositions produced in such a process are also designated as "in-situ"-blends.

A multistage process is defined to be a polymerisation process in which a
20 polymer comprising two or more fractions is produced by producing each or at least two polymer fraction(s) in a separate reaction stage, usually with different reaction conditions in each stage, in the presence of the reaction product of the previous stage which comprises a polymerisation catalyst.

Accordingly, it is preferred that fraction (A) and (B) of the polyethylene
25 composition are produced in different stages of a multistage process.

Preferably, the multistage process comprises at least one gas phase stage in which, preferably, fraction (B) is produced.

Further preferred, fraction (B) is produced in a subsequent stage in the presence of fraction (A) which has been produced in a previous stage.

5 It is previously known to produce multimodal, in particular bimodal, olefin polymers, such as multimodal polyethylene, in a multistage process comprising two or more reactors connected in series. As an example of this prior art, mention may be made of EP 517 868, which is hereby incorporated by way of reference in its entirety, including all its preferred
10 embodiments as described therein, as a preferred multistage process for the production of the polyethylene composition according to the invention.

Preferably, the main polymerisation stages of the multistage process are such as described in EP 517 868, i.e. the production of fractions (A) and (B) is carried out as a combination of slurry polymerisation for fraction
15 (A)/gas-phase polymerisation for fraction (B). The slurry polymerisation is preferably performed in a so-called loop reactor. Further preferred, the slurry polymerisation stage precedes the gas phase stage.

Optionally and advantageously, the main polymerisation stages may be preceded by a prepolymerisation, in which case up to 20 % by weight, preferably 1 to 10 % by weight, more preferably 1 to 5 % by weight, of the
20 total base resin is produced. The prepolymer is preferably an ethylene homopolymer (HDPE). At the prepolymerisation, preferably all of the catalyst is charged into a loop reactor and the prepolymerisation is performed as a slurry polymerisation. Such a prepolymerisation leads to
25 less fine particles being produced in the following reactors and to a more homogeneous product being obtained in the end.

In the production of the base resin Ziegler-Natta (ZN) or metallocene catalysts are preferably used, more preferably Ziegler-Natta catalysts.

The catalyst may be supported, e.g. with conventional supports including silica, Al-containing supports and magnesium dichloride based supports.
5 Preferably the catalyst is a ZN catalyst, more preferably the catalyst is non-silica supported ZN catalyst, and most preferably MgCl_2 -based ZN catalyst.

The Ziegler-Natta catalyst further preferably comprises a group 4 (group numbering according to new IUPAC system) metal compound, preferably titanium, magnesium dichloride and aluminium.

10 The catalyst may be commercially available or be produced in accordance or analogously to the literature. For the preparation of the preferable catalyst usable in the invention reference is made to WO2004055068 and WO2004055069 of Borealis and EP 0 810 235. The content of these documents in its entirety is incorporated herein by reference, in particular
15 concerning the general and all preferred embodiments of the catalysts described therein as well as the methods for the production of the catalysts. Particularly preferred Ziegler-Natta catalysts are described in EP 0 810 235.

The resulting end product consists of an intimate mixture of the polymers
20 from the two reactors, the different molecular weight distribution curves of these polymers together forming a molecular weight distribution curve having a broad maximum or two maxima, i.e. the end product is a bimodal polymer mixture.

It is preferred that the multimodal base resin of the polyethylene
25 composition according to the invention is a bimodal polyethylene mixture consisting of fractions (A) and (B), optionally further comprising a small

prepolymerisation fraction in the amount as described above. It is also preferred that this bimodal polymer mixture has been produced by polymerisation as described above under different polymerisation conditions in two or more polymerisation reactors connected in series.

5 Owing to the flexibility with respect to reaction conditions thus obtained, it is most preferred that the polymerisation is carried out in a loop reactor/a gas-phase reactor combination.

Preferably, the polymerisation conditions in the preferred two-stage method are so chosen that the comparatively low-molecular polymer having no content of comonomer is produced in one stage, preferably the first stage,

10 owing to a high content of chain-transfer agent (hydrogen gas), whereas the high-molecular polymer having a content of comonomer is produced in another stage, preferably the second stage. The order of these stages may, however, be reversed.

15 In the preferred embodiment of the polymerisation in a loop reactor followed by a gas-phase reactor, the polymerisation temperature in the loop reactor preferably is 85 to 115 °C, more preferably is 90 to 105°C, and most preferably is 92 to 100°C, and the temperature in the gas-phase reactor preferably is 70 to 105 °C, more preferably is 75 to 100°C, and

20 most preferably is 82 to 97°C.

A chain-transfer agent, preferably hydrogen, is added as required to the reactors, and preferably 200 to 800 moles of H₂/kmoles of ethylene are added to the reactor, when the LMW fraction is produced in this reactor, and 0 to 50 moles of H₂/kmoles of ethylene are added to the gas phase

25 reactor when this reactor is producing the HMW fraction.

Preferably, the base resin of the polyethylene composition is produced with a rate of at least 5 tons/h, more preferably at least 10 ton/h, and most preferably at least 15 tons/h.

5 The composition of the invention preferably is produced in a process comprising compounding step, wherein the composition of the base resin, i.e. the blend, which is typically obtained as a base resin powder from the reactor, is extruded in an extruder and then pelletised to polymer pellets in a manner known in the art.

10 Optionally, additives or other polymer components can be added to the composition during the compounding step in the amount as described above. Preferably, the composition of the invention obtained from the reactor is compounded in the extruder together with additives in a manner known in the art.

15 The extruder may be e.g. any conventionally used extruder. As an example of an extruder for the present compounding step may be those as supplied by Japan steel works, Kobe steel or Farrel-Pomini, e.g. JSW 460P.

In one embodiment, the extrusion step is carried out using production rates of at least 400, at least 500, at least 1000 kg/h may be used in said compounding step.

20 In another embodiment the compounding step can be effected with production rate of at least 5 tons/h, preferably at least 15 tons/h, more preferably at least 20 or 25 tons/h or even at least 30 or more tons/h, such as at least 50, such 1-50, preferably 5-40, 10-50, in some embodiments 10-25 tons/h.

Alternatively, production rates at least 20 tons/h, preferably at least 25 tons/h, even at least 30 tons/h, e.g. 25-40 tons/h may be desired during the compounding step.

5 The present multimodal polyethylene composition of the invention enables such production rates within the property window of the invention, i.e. with various property combinations of MFR's of the fractions and of final base resin variations together with excellent homogeneity, just to mention few.

Preferably, in said extrusion step, a total SEI (specific energy input) of the extruder may be at least 150, 150-400, 200-350, 200-300 kWh/ton.

10 It is known that the temperature of the polymer melt may vary in the extruder, the highest (max) melt temperature of the composition in the extruder during the extrusion step is typically more than 150°C, suitably between 200 to 350°C, preferably 250 to 310°C, more pref. 250 to 300°C.

15 The benefit of the invention is that an excellent homogeneity can be obtained without extensive mixing, already by effecting once the compounding step, e.g. the preferable extrusion with production rates as defined above, and additionally, together with the high level homogeneity desirable polymer properties can be achieved/maintained.

20 Furthermore, the present invention relates to a process for the production of a polyethylene composition as described hereinbefore comprising the steps of

- i) polymerising ethylene monomers, and optionally one or more alpha-olefin comonomers, in the presence of a Ziegler-Natta catalyst to obtain a first ethylene homo- or copolymer fraction (A)

- 5 ii) polymerising ethylene monomers, and optionally one or more
 alpha-olefin comonomers, in the presence of a Ziegler-Natta
 catalyst to obtain a second ethylene homo- or copolymer
 fraction (B) having a higher average molecular weight than
 fraction (A)

wherein the second polymerisation step is carried out in the presence of the
polymerization product of the first step.

Preferably, the polymerization to obtain fraction (A) is carried out in a loop
reactor.

- 10 Furthermore, the polymerization to obtain fraction (B) is preferably carried
out in a gas phase reactor.

The first polymerisation step preferably is preceded by a prepolymerisation
step in which preferably at most 20 wt%, more preferably at most 10 wt%
and still more preferably at most 5 wt% of the total base resin is produced.

- 15 Still further, the present invention relates to an article, preferably a pipe,
comprising a polyethylene composition as described above or obtainable by
a process as described above, and to the use of such a polyethylene
composition for the production of an article, preferably a pipe.

Experimental and Examples

- 20 1. Definitions and measurement methods

a) Molecular weight

The weight average molecular weight M_w and the molecular weight
distribution ($MWD = M_w/M_n$ wherein M_n is the number average molecular

weight and M_w is the weight average molecular weight) is measured by a method based on ISO 16014-4:2003. A waters 150CV plus instrument was used with column 3 x HT&E styragel from Waters (divinylbenzene) and trichlorobenzene (TCB) as solvent at 140 °C. The column set was
5 calibrated using universal calibration with narrow MWD PS standards (the Mark Howings constant K : $9.54 \cdot 10^{-5}$ and a : 0.725 for PS, and K : $3.92 \cdot 10^{-4}$ and a : 0.725 for PE). The ratio of M_w and M_n is a measure of the broadness of the distribution, since each is influenced by the opposite end of the "population".

10 b) Density

Density is measured according to ISO 1872, Annex A.

c) Melt Flow Rate/Flow Rate Ratio

The melt flow rate (MFR) is determined according to ISO 1133 and is indicated in g/10 min. The MFR is an indication of the flowability, and
15 hence the processability, of the polymer. The higher the melt flow rate, the lower the viscosity of the polymer. The MFR is determined at 190°C and may be determined at different loadings such as 2.16 kg (MFR₂), 5 kg (MFR₅) or 21.6 kg (MFR₂₁).

The quantity FRR (flow rate ratio) is an indication of molecular weight
20 distribution and denotes the ratio of flow rates at different loadings. Thus, FRR_{21/5} denotes the value of MFR₂₁/MFR₅.

d) Rheological parameters

Rheological parameters such as Shear Thinning Index SHI and Viscosity are determined by using a rheometer, preferably a Rheometrics Phisica

MCR 300 Rheometer. The definition and measurement conditions are described in detail on page 8 line 29 to page 11, line 25 of WO 00/22040.

e) Measurement of Homogeneity

The polymer composition according to the present invention has an improved homogeneity directly after its production in the polymerisation reactor. However, as, first, homogeneity is usually measured only on a compounded composition, and, second, the way in which compounding is carried out has a decisive influence on the homogeneity of the compounded composition, it is important that the compounding conditions to which the composition is subjected and the compounding equipment used are/is clearly defined before homogeneity of the composition is determined, e.g. in terms of the white spot area test or the modified ISO 18553 white spot rating test as described below.

Accordingly, homogeneity of the compositions described herein is determined after a single compounding step only, which is to be carried out as follows:

The base resin powder coming from the reactor is transferred, e.g. via intermediate holding tanks (50-250 tons), to the compounding unit without extra handling like grinding or cooling or similar processes.

The powder is then poured into the inlet of the compounder together with the appropriate amounts of additives. The additives can be, typically, stearates, antioxidants, UV-stabilisers, or pigments/carbon blacks. The additives can be added as a pure component or as a master batch with a PE carrier.

The base resin plus additives are then passed through the compounding unit only once.

No material that has passed the compounder once is allowed to be transferred back to the inlet of the compounder for further work nor is it
5 allowed to pass the compounded material further to a second processing unit.

The idea of the single compounding step is that a reactor powder is allowed *only one single pass* through the compounding unit.

The equipment to be used for the single compounding step is a twin-screw
10 extruder like counter rotating equipment as supplied by Japan steel works, e.g. CIM JSW 460P or equivalent equipment.

Typical compounding conditions in the single compounding step used in CIM JSW 460P having a screw diameter of 460 mm are:

production: 25 to 30 tons/h

15 mixer specific energy input (SEI): 260 kWh/ton

gear pump SEI: 19 kWh/ton

Temp. before gear pump: 290 °C

Temp. after gear pump: 300 °C

suction pressure gear pump: 1.6 bar

20 mixer speed: 400 rpm

The white spot area of the once compounded composition is determined at least partly following ISO 18553, as follows:

A sample of a composition (including a pigment to make the inhomogeneities visible, e.g. carbon black in an amount of around 2.5 wt%) which is obtained after a single compounding step as described above, is analysed by first obtaining 6 microtome cuts of 6 different parts of the sample (thickness < 60 micrometer, diameter 3 to 5 mm).

The cuts are evaluated at a magnification of 100, and the size, i.e. the part of the surface, of the non-coloured inclusions ("white spots", agglomerates, particles) on a total surface of each cut of 0.7 mm² is determined. All white spots with a diameter > 5 microns are counted. The "white spot area" is then expressed as the averaged fraction of the white spots on the total surface of the sample cut.

f) Measurement of homogeneity - Rating in modified ISO 18553 white spot rating test

In addition to the white spot area test, homogeneity complementary is determined according to the modified ISO 18553 white spot rating test. In this test, inhomogeneities of the composition present after a single compounding step as described above, which appear as white spots, are determined and rated according to the rating scheme given in ISO 18553. The lower the composition is rated in this test, the better is the homogeneity of the composition.

2. Polyethylene compositions

Production of polyethylene compositions base resins was performed in a multistage reaction comprising a first polymerisation stage in slurry in a

50 dm³ loop reactor, followed by transferring the slurry to a 500 dm³ loop reactor wherein polymerisation was continued in slurry to produce the low molecular weight component (fraction (A)), and a second polymerisation in a gas phase reactor in the presence of the product from the second loop reactor to produce the comonomer containing high molecular weight component (fraction (B)). As comonomer, butene-1 has been used.

As a catalyst, *Lynx 200* available from Engelhard Corporation Pasadena, U.S.A. has been used for all examples according to the invention.

In comparative example 1, a catalyst prepared according to example 1 of EP 0 688 794 has been used.

The polymerisation conditions applied and the properties of the polymers obtained are listed in Table 1.

After production of fraction (B) (and hence the complete base resin), the obtained polymer powder was transferred to an extruder where it was compounded together with 2.5 wt% carbon black according to the procedure described under item e) above.

Table 1:

	Example 1	Example 2	Comp. Ex. 1
Prepolymeriser Conditions/Product Properties			
Temp. °C	40	40	
MFR ₂ [g/10min]		10	40
MFR ₅ [g/10min]	1.46		
Amount [wt%]	2	2	1.5
Loop Reactor Conditions/Product Properties (fraction (A))			
Temp. [°C]	95	95	95
Pressure [bar]	56	56	58
C ₂ concentr. [mol%]	1.8	1.8	
H ₂ /C ₂ [mol/kmol]	840	760	381
Amount [wt%]	48	48	47
MFR ₂ [g/10min]	304	342	364
Density [kg/m ³]	>970	>970	> 970
Gas Phase Reactor Conditions/Product Properties (base resin)			
Temp. [°C]	85	85	85
Pressure [bar]	20	20	20
C ₂ concentr. [mol%]	4	4	
H ₂ /C ₂ [mol/kmol]	33	34	5
comonomer/C ₂ ratio [mol/kmol]	108 (butene-1)	99 (butene-1)	72 (butene-1)
MFR ₅ [g/10min]	0.23	0.26	0.21
MFR ₂₁ [g/10min]	7.6	6.9	7.1
FRR _{21/5}	33	31	34
Density [kg/m ³]	948	948	950
Amount [wt%]	50	50	51
Compounded Composition			
MFR ₅ [g/10min]	0.26	0.23	0.25
MFR ₂₁ [g/10min]	9.2	7.6	9.05
FRR _{21/5}	35.1	33.5	35.9
Density [kg/m ³]	958	959	960
White spot ISO 18553 rating test	2.7	4.2	6.1
White Spot Area [%]	0.5	0.1	2.4
SHI _(2,7/210)	52.5	47.4	56.9
Eta _{2,7} [kPas]	251	260	247
Eta ₇₄₇ [kPas]	487	451	464
M _w [kD]		263	283
M _n [kD]		6.03	6.38
MWD		43,6	44.4

Claims

1. A polyethylene composition comprising a base resin which comprises

- 5 (A) a first ethylene homo- or copolymer fraction, and
(B) a second ethylene homo- or copolymer fraction,

wherein fraction (A) has a lower molecular weight than fraction (B), the ratio of the MFR₂ of fraction (A) and the MFR₅ of the base resin being from 200 to 1500, and the composition has a white spot area of 1 % or
10 below.

2. A polyethylene composition comprising a base resin comprising

- (A) a first ethylene homo- or copolymer fraction, and
(B) a second ethylene homo- or copolymer fraction,

wherein fraction (A) has a lower molecular weight than fraction (B), the
15 ratio of the MFR₂ of fraction (A) and the MFR₅ of the base resin being from 200 to 1500, and the composition has a rating in the ISO 18553 white spot rating test of below 4.5.

3. A polyethylene composition according to claim 1 wherein the composition has a rating in the ISO 18553 white spot rating test of below
20 4.5.

4. A polyethylene composition according to claims 1, 2 or 3 wherein fraction (A) has an MFR₂ of 100 g/10min or more.

5. A polyethylene composition according to any of the preceding claims wherein the base resin has an MFR₅ of 1 g/10min or below.
6. A polyethylene composition according to any of the preceding claims wherein the weight ratio of fractions (A):(B) in the base resin is 30:70 to
5 70:30.
7. A polyethylene composition according to any of the preceding claims wherein the MFR₅ of the composition is 0.6 g/10min or below.
8. A polyethylene composition according to any of the preceding claims wherein fraction (A) is an ethylene homopolymer.
- 10 9. A polyethylene composition according to any of the preceding claims wherein fraction (A) has a density of 950 kg/m³ or higher.
10. A polyethylene composition according to any of the preceding claims wherein fraction (B) is a copolymer of ethylene with at least one further alpha-olefin comonomer.
- 15 11. A polyethylene composition according to any of the preceding claims wherein fraction (B) has a density of lower than 954 kg/m³.
12. A polyethylene composition according to any of the preceding claims wherein the composition has a SHI_(2.7/210) of 5 to 300.
13. A polyethylene composition according to any of the preceding claims
20 wherein the base resin has been produced in a multistage process.
14. A process for the production of a polyethylene composition according to any of the preceding claims comprising the steps of

- i) polymerising ethylene monomers, and optionally one or more alpha-olefin comonomers, in the presence of a Ziegler-Natta catalyst to obtain a first ethylene homo- or copolymer fraction (A)
 - 5 ii) polymerising ethylene monomers, and optionally one or more alpha-olefin comonomers, in the presence of a Ziegler-Natta catalyst to obtain a second ethylene homo- or copolymer fraction (B) having a higher average molecular weight than fraction (A)
- 10 wherein the second polymerisation step is carried out in the presence of the polymerization product of the first step.
15. A process according to claim 14 wherein the polymerization to obtain fraction (A) is carried out in a slurry reactor.
16. A process according to claims 14 or 15 wherein the polymerization
15 to obtain fraction (B) is carried out in a gas phase reactor.
17. An article comprising a polyethylene composition according to any of claims 1 to 13.
18. An article according to claim 17 wherein the article is a pipe.
19. Use of a polyethylene composition according to any of claims 1 to 13
20 for the production of an article.
20. Use according to claim 19 wherein the article is a pipe.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/EP2005/011719

A. CLASSIFICATION OF SUBJECT MATTER

C08L23/06 C08L23/04 C08F10/02 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)

C08L 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, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 455 642 B1 (MYHRE OLE JAN ET AL) 24 September 2002 (2002-09-24) the whole document	1-20
X	EP 1 146 078 A (BOREALIS TECHNOLOGY OY) 17 October 2001 (2001-10-17) the whole document	1-20
X	US 6 545 093 B1 (DE LANGE PAULUS ET AL) 8 April 2003 (2003-04-08) the whole document	1-20
A	EP 1 460 105 A (BOREALIS TECHNOLOGY OY) 22 September 2004 (2004-09-22) the whole document	1-20

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

☒ Patent family members are listed in annex.

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INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/EP2005/011719

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6455642	B1	24-09-2002	AT 255606 T 15-12-2003
		AU 4042799 A 29-11-1999	
		AU 741875 B2 13-12-2001	
		AU 4042899 A 29-11-1999	
		BR 9910294 A 16-01-2001	
		CA 2331628 A1 18-11-1999	
		CN 1130387 C 10-12-2003	
		CN 1125091 C 22-10-2003	
		DE 69913346 D1 15-01-2004	
		DE 69913346 T2 14-10-2004	
		EP 1086155 A1 28-03-2001	
		EP 1090048 A1 11-04-2001	
		ES 2211091 T3 01-07-2004	
		FI 981034 A 09-11-1999	
		WO 9958583 A1 18-11-1999	
		WO 9958584 A1 18-11-1999	
		JP 2002514665 T 21-05-2002	
		US 6642323 B1 04-11-2003	
		ZA 200006010 A 24-04-2001	
EP 1146078	A	17-10-2001	AU 5472101 A 30-10-2001
			BR 0110067 A 31-12-2002
			CN 1422302 A 04-06-2003
			WO 0179347 A2 25-10-2001
			PL 358104 A1 09-08-2004
			US 2003149162 A1 07-08-2003
US 6545093	B1	08-04-2003	AT 285442 T 15-01-2005
			CN 1324383 A 28-11-2001
			DE 19849426 A1 04-05-2000
			WO 0024821 A1 04-05-2000
			EP 1141118 A1 10-10-2001
			ES 2235519 T3 01-07-2005
			JP 2002528586 T 03-09-2002
EP 1460105	A	22-09-2004	NONE