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(54) **COATING COMPOSITION, METHOD OF PREPARATION THEREOF AND SUBSTRATE COATED THEREWITH**

BESCHICHTUNGSZUSAMMENSETZUNG, HERSTELLUNGSVERFAHREN DAFÜR UND DAMIT BESCHICHTETES SUBSTRAT

COMPOSITION DE REVETEMENT, PROCEDE DE PREPARATION D'UNE TELLE COMPOSITION ET SUBSTRAT REVETU DE CETTE COMPOSITION

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(56) References cited:
WO-A-01/62847 WO-A-97/03139
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Description

Field of the invention

[0001] The present invention relates to a coating composition, to a method of preparing the coating composition, and to a substrate coated with said composition.

Technical background

[0002] Solid substrates are often provided with coatings e.g. for protection. As examples of such substrates may be mentioned pipes, tubes, profiles, wires, cables, etc. The coating preferably comprises a polymer composition that is melt coated on the substrate, e.g. by extrusion. Among the desired properties of the polymer coating composition it is particularly preferred that it has good melt coating processability, good environmental stress cracking resistance (ESCR), low shrinking, and high service temperature.

[0003] A coating composition comprising a multimodal ethylene polymer is known through WO 97/03139. This multimodal ethylene polymer contains from 80 to 100 % by weight of ethylene repeating units and from 0 to 20 % by weight of C_3 - C_{10} α -olefin repeating units, has a density of between 0.915 g/cm³ and 0.955 g/cm³, and is a blend of at least a first ethylene polymer having a first average molecular weight and a first molecular weight distribution and a second ethylene polymer having a second molecular weight, which is higher than said first molecular weight, and a second molecular weight distribution, said blend having a third molecular weight and a third molecular weight distribution. The multimodal ethylene polymer is said to have good processability and low shrinkage as well as superior environmental stress cracking resistance. Preferentially, the coating composition has an environmental stress cracking resistance (ESCR, F20) (ASTM D 1693/A, 10% Igepal) of at least 100 h, more preferentially at least 500 h, yet more preferentially at least 1000 h and most preferentially 2000 h. For the preparation of the multimodal ethylene polymer any kind of ethylene polymerisation catalyst, such as a chromium catalyst, a Ziegler-Natta catalyst or a group 4 transition metallocene catalyst may be used. No examples of metallocene catalysts are given, however, and all the multimodal ethylene polymers in the examples of WO 97/03139 have been prepared with the use of Ziegler-Natta catalysts.

[0004] In this connection WO 01/62847 should also be mentioned. This document relates to a process for coating a substrate by extrusion coating on the substrate 90-100 % by weight of a bimodal polyethylene composition that has been polymerised in the presence of a single site catalyst (SSC), and up to 10 % by weight of high pressure PE-LD. The coating composition has a melt flow rate (MFR₂) of 5 g/10 min or more. The specification indicates that the coating has a thickness of about 10-200 μ m and that it is applied on thin substrates like paper,

cardboard, polymer films, or aluminium foil.

[0005] WO 00/34341 discloses a heterogeneous olefin polymerization catalyst comprising a porous particulate support material having impregnated therein a metallocene catalyst the metal atom whereof is bound to an amide group which is not bound to an η -ligand of the metallocene, or the reaction product of said metallocene catalyst and a cocatalyst. No mention is made of coating compositions or the preparation thereof, particularly not steel pipe coating compositions.

[0006] Although the coating compositions according to the prior art such as WO 97/03139 are sufficient for many purposes there is always a need for still more improved coating compositions, especially with regard to the critical property of environmental stress cracking resistance (ESCR).

Summary of the invention

[0007] The present invention aims at fulfilling the above need and is based on the surprising discovery that the ESCR of the multimodal coating polymer is dramatically increased if the multimodal ethylene polymer is prepared in the presence of a single-site catalyst (SSC).

[0008] Thus, the present invention provides a coating composition, characterised in that it comprises a multimodal ethylene polymer, which contains from 80 to 99.8 % by weight of ethylene repeating units and from 0.2 to 20 % by weight of C_3 - C_{20} α -olefin repeating units, and is a blend of at least a first and a second ethylene polymer that are obtainable by a process comprising at least two steps in which:

said first ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; and said second ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; said steps being performed in any order and the ethylene polymer of each step being present in the following step(s), and producing a blend of from 20 to 80 % by weight of said first and from 80 to 20 % by weight of said second ethylene polymer, said blend having a density of 0.915-0.955 g/cm³, a melt flow rate, MFR₂, of 0.028-1.5 g/10 min., a molecular weight distribution, M_w/M_n , of 3-10, and a CTL 5.0 MPa-value according to ISO 6259 of at least 500 hrs.

[0009] The present invention further provides a process for producing a coating composition, characterised in that a multimodal ethylene polymer, which contains from 80 to 99.8 % by weight of ethylene repeating units and from 0.2 to 20 % by weight of C_3 - C_{20} α -olefin repeating units, and is a blend of at least a first and a second ethylene polymer is prepared by a process comprising at least two steps in which:

said first ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; and said second ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; said steps being performed in any order and the ethylene polymer of each step being present in the following step(s), and producing a blend of from 20 to 80 % by weight of said first and from 80 to 20 % by weight of said second ethylene polymer, said blend having a density of 0.915-0.955 g/cm³, a melt flow rate, MFR₂, of 0.028-1.5 g/10 min.; a molecular weight distribution, M_w/M_n , of 3-10; and a CTL 5.0 MPa-value according to ISO 6259 of at least 500 hrs.

[0010] Still further, the present invention provides a substrate coated with the above defined coating composition.

[0011] Further characterising features and advantages of the present invention will appear from the description below and the appended claims.

Detailed description of the invention

[0012] As indicated above the present invention relates to the coating of solid substrates, like those mentioned in WO 97/03139 such as pipes, tubes, profiles, wires, cables, etc. The substrate may be made of various materials, like those mentioned in WO 97/03139 such as metal like iron and steel, aluminium, concrete, ceramics, glass, etc. Preferably the invention relates to the coating of pipes, and most preferably to the coating of metal pipes.

[0013] When coating metal pipes it is preferred to first provide the pipe with a primer like an epoxy resin, and a layer of a coupling or compatibilizing agent like a carboxy modified polyethylene, preferably maleic anhydride grafted polyethylene polymer (0.20 % by weight maleic anhydride), before applying the coating.

[0014] Preferably, the steel pipe coating is carried out on a coating line consisting of a preheating unit, a sidearm extruder or crosshead extruder, a vacuum calibration sleeve, a cooling unit, and a cutting unit. If a crosshead extruder is used it is fed with the multimodal ethylene polymer coating composition by a single screw extruder. Suitably, the screw extruder has a screw diameter of 60 mm, an L/D of 35 and a temperature profile of 200-240°C.

[0015] The steel pipe to be coated is preferably first provided with a primer layer of an epoxy resin. A suitable thickness of the primer layer is about 80 µm.

[0016] Further, on top of the primer layer a layer of a coupling or compatibilizing agent is preferably provided. This layer may preferably consist of the above mentioned maleic acid anhydride grafted polyethylene polymer and the thickness of the layer is suitably about 200 µm.

[0017] Thereafter the steel pipe is coated with the multimodal ethylene polymer by preheating the steel pipe

and feeding it through the crosshead with a suitable speed such as 1.2 m/min. In the crosshead the melted multimodal ethylene polymer is applied onto the steel pipe to a suitable thickness such as 3.0 mm.

[0018] Then the thus coated steel pipe enters the vacuum calibration sleeve, which is cooled by water of 20°C, and thereby calibrates and solidifies the coating on the steel pipe.

[0019] As an alternative to coating the steel pipe by feeding it through a side arm extruder, the preheated steel pipe which is optionally coated with a primer, may be rotated and fed past extruders having flat film dies for the optional layer of coupling/compatibilizing agent, and for the multimodal ethylene polymer cover layer.

[0020] By a multimodal ethylene polymer is meant an ethylene polymer having a broad molecular weight distribution produced by blending two or more ethylene polymer components with different molecular weights and different comonomer contents, by polymerising ethylene to different molecular weights and different comonomer contents in a process with two or more reactors in series or by dual-site catalysts in a single reactor or a tandem reactor. By contrast, a unimodal ethylene polymer is obtained from only one ethylene polymer component produced in only one step.

[0021] By molecular weight distribution (MWD) is meant the ratio of the weight average molecular weight (M_w) and the number average molecular weight (M_n), i.e. M_w/M_n .

[0022] By molecular weight is meant the weight average molecular weight (M_w), unless otherwise indicated.

[0023] The "melt flow rate" (MFR) of the polymer is determined in accordance with ISO 1133 and is indicated in g/10 min. The MFR is an indication of the flowability, and hence the processability, of the polymer. The higher the MFR, the lower the viscosity of the polymer. The MFR is determined at 190°C and at different loadings such as 2.1 kg (MFR₂), 5.0 kg (MFR₅), or 21 kg (MFR₂₁).

[0024] The environmental stress crack resistance (ESCR), i.e. the resistance of the polymer to crack formation under the action of mechanical stress and a reagent in the form of a surfactant, may be determined according to different methods. One method is ASTM D 1693 that employs the reagent 10% Igepal CO-630. The results are indicated as the percentage of cracked sample rods after a given time in hours. F20 means e.g. that 20% of the sample rods were cracked after the time indicated. This is the test method used in the above mentioned WO 97/03139.

[0025] Another method to determine the ESCR is ISO 6259. According to this test method the resistance of polymer sample rods to crack formation under the action of a constant tensile load (CTL) of 5.0 MPa and a reagent in the form of 10% Igepal CO-730 is determined. The result which is also referred to as the CTL 5.0 MPa-value, is indicated as the time in hours before the sample rods crack. This test method is used for determining ESCR at the present invention.

[0026] It should be stressed that ISO 6259 is a much more severe test method than ASTM D 1693 for determining ESCR.

[0027] As has been mentioned above the coating composition of the present invention comprises a multimodal ethylene polymer obtained by a multistep polymerisation process. Such multistep processes for the preparation of multimodal and especially bimodal olefin polymers in two or more polymerisation reactors in series are previously known and are exemplified by EP 040 992, EP 041 796, EP 022 376 and WO 92/12182.

[0028] According to these references each of said polymerisation steps may be performed in liquid phase, slurry phase or gas phase.

[0029] At the present invention it is preferred to perform the polymerisation steps as a combination of slurry polymerisation and gas phase polymerisation. Preferably, the first step is a slurry polymerisation and the second step is a gas phase polymerisation.

[0030] The slurry polymerisation is preferably performed in a so-called loop reactor. The gas phase polymerisation is performed in a gas phase reactor. The polymerisation steps may optionally be preceded by a prepolymerisation in which up to 20 % by weight, preferably 1-10 % by weight of the total amount of ethylene polymer is formed.

[0031] The molecular weight of the polymer formed during the multistep polymerisation may be controlled by the use of a chain transfer agent, preferably hydrogen. To control the molecular weight a suitable amount of hydrogen may be added to any step of the polymerisation.

[0032] In the production of a bimodal ethylene polymer, a first ethylene polymer is produced in a first reactor under certain conditions with respect to monomer composition, hydrogen-gas pressure, temperature, pressure, and so forth. After the polymerisation in the first reactor, the reaction mixture including the polymer produced is fed to a second reactor, where further polymerisation takes place under different conditions. Usually, a first polymer of high melt flow rate (low molecular weight) and with a moderate or small addition of comonomer, or no such addition at all, is produced in the first reactor, whereas a second polymer of low melt flow rate (high molecular weight) and with a greater addition of comonomer is produced in the second reactor. The resulting end product consists of an intimate mixture of the polymers 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. Since multimodal, and especially bimodal, polymers, preferably ethylene polymers, and the production thereof is well-known, no detailed description is called for here, but reference is made to the above documents.

[0033] The comonomer(s) for preparing the multimodal ethylene polymer of the present invention may be selected from α -olefins, and more particularly from C_3 - C_{20} α -olefins, such as 1-butene, 4-methyl-1-pentene,

1-hexene, 1-octene, 1-decene, and 1-eicosene. Preferably the comonomer is 1-butene or 1-hexene. As mentioned above the multimodal ethylene polymer contains 0.2-20 % by weight of comonomer repeating units. Preferably, the comonomer repeating units are divided among the polymer fractions of the polymerisation steps so that the first (low molecular weight) ethylene polymer contains 0-10 % by weight of comonomer repeating units, and the second (high molecular weight) ethylene polymer contains 1-25 % by weight, preferably 2-15 % by weight of comonomer repeating units.

[0034] Preferably, the polymerisation conditions in the preferred two-stage method are so chosen that a comparatively low-molecular polymer having a moderate, low or, which is preferred, no content of comonomer is produced in one stage, e.g. the first stage, owing to a high content of chain-transfer agent (hydrogen gas), whereas a high-molecular polymer having a higher content of comonomer is produced in another stage, e.g. the second stage. The order of these stages may, however, equally well be reversed.

[0035] As mentioned above, the multimodal ethylene polymer of the present invention has an MFR_2 of 0.028-1.5 g/10 min. This is a necessary condition for the multimodal ethylene polymer to be adequately coatable on the substrate. Preferably, the multimodal ethylene polymer has an MFR_2 of 0.05-1.0 g/10 min, most preferably 0.1-0.8 g/10 min. In order to obtain a multimodal ethylene polymer with the required MFR it is preferred that the low molecular weight ethylene polymer fraction (preferably the first ethylene polymer) has an MFR_2 of 30-1000 g/10 min, more preferably 50-500 g/10 min, most preferably 100-300 g/10 min.

[0036] To be suitably processable and coatable the multimodal ethylene polymer of the invention further has an MWD of 3-10.

[0037] As indicated above, the density of the multimodal ethylene polymer of the present invention is 0.915-0.955 g/cm³, preferably 0.935-0.955 g/cm³, most preferably 0.940-0.950 g/cm³.

[0038] The weight ratio between the first ethylene polymer and the second ethylene polymer is between 20:80 and 80:20, preferably between 30:70 and 70:30, more preferably between 40:60 and 60:40 and most preferably between 40:60 and 51:49.

[0039] As mentioned above, a characteristic feature of the present invention is that the multimodal ethylene polymer is prepared by polymerisation using a single-site catalyst (SSC).

[0040] More particularly, according to one aspect the SSC used at the present invention is a SSC disclosed in WO 95/12622 and WO 01/62847 and having the general formula:



wherein

X_1 and X_2 are either the same or different and are se-

lected from a group containing halogen, methyl, benzyl or hydrogen;

Hf is hafnium;

Cp is a cyclopentadienyl group; and

R₁ and R₂ are the same or different and selected from the group of linear and branched hydrocarbyl groups containing 1-10 carbon atoms.

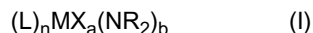
[0041] Particularly suitable complexes of the kind described above are bis-(n-butyl cyclopentadienyl)hafnium dihalides. Another group of suitable complexes are the siloxy-substituted bridged bis-indenyl zirconium dihalides, which are disclosed in WO 97/28170.

[0042] These catalysts are typically supported on a solid carrier, but they may also be used unsupported. The carrier is typically inorganic, and suitable materials comprise, e.g., silica (preferred), silica-alumina, magnesium oxide, titanium oxide, zirconium oxide and magnesium silicate (cf. also WO 95/12622). The catalysts are normally used together with an aluminumoxane cocatalyst. Suitable cocatalysts are, e.g., methylaluminumoxane (MAO), tetraisobutylaluminumoxane (TIBAO) and hexaisobutylaluminumoxane (HIBAO). The cocatalyst is preferably supported on the carrier, typically together with the catalyst complex, although the cocatalyst may optionally be fed into the reactor separately.

[0043] A catalyst based on bis-(n-butyl cyclopentadienyl)-hafnium dihalide complex supported on a silica or a silica-alumina carrier together with a methylaluminumoxane cocatalyst is suitable to be run in a process including a loop reactor and a gas phase reactor. Especially suitable is a catalyst based on bis-(n-butyl cyclopentadienyl)hafnium dichloride. Both the complex and the cocatalyst are supported on the carrier.

[0044] According to another aspect the SSC is a catalyst as disclosed in WO 00/34341 and comprising a porous particulate support material having impregnated therein a metallocene catalyst the metal atom whereof is bound to an amide group which is not bound to an η -ligand of the metallocene, or the reaction product of said metallocene catalyst and a cocatalyst.

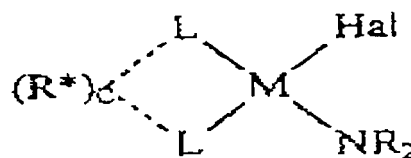
[0045] Suitably, the metallocene-amide is of the formula I



where n is 1, 2 or 3; a is 0, 1, 2, 3 or 4; b is 1, 2, 3, 4 or 5; n+a+b is the total coordination number for M; M is a catalytically active transition metal or lanthanide; each L, which may be the same or different, is an η -ligand, optionally linked via a bridging group R* to a second group L or to a metal-coordinating group X; each X is a metal coordinating group; and each R, which may be the same or different is a hydrocarbyl group or two groups R, together with the intervening nitrogen, are an optionally substituted, nitrogen bound heterocyclic group, where R (or a heterocyclic group NR₂) may contain heteroatoms such as Si, N, P, B, O, S, etc.

[0046] In a preferred embodiment, the metallocene-

amide is of formula II



(where each L is a η -ligand, M is a group 3 to 8 transition metal or a lanthanide, Hal is a halide, c is 0 or 1, R*, where present, is a bridging group linking two η -ligands L, and each R, which may be the same or different, is a hydrocarbyl group containing up to 8 carbons or the two R groups together with the intervening nitrogen form a heterocyclic group having up to 9 ring atoms, and R or NR₂ may contain other heteroatoms as mentioned above) or the reaction product of a metallocene of formula I and a cocatalyst.

[0047] In the metallocene-amide the catalytically active metal is preferably zirconium, hafnium or titanium (i.e. M is Zr, Hf or Ti).

[0048] In the SSC the porous support may be any porous, substantially inert support, such as an inorganic oxide or salt or an organic material, e.g. a metal or pseudometal oxide or halide or an organic polymer, for example silica, alumina, zirconia, silica-alumina, magnesium chloride, titanium dioxide, magnesium oxide, aluminium phosphate or an acrylate, methacrylate, polyethylene, polypropylene, polystyrene, or styrene-divinylbenzene polymer. Particularly preferably the support is a fine-grained inorganic oxide such as an inorganic oxide of an element of Group 2, 4, 13 or 14 of the Periodic Table of Elements, most preferably silica, alumina or a mixture or derivative of these.

[0049] Where a cocatalyst is used, it may be used separately but more preferably it is also loaded onto the porous support material. In this event it is preferred to allow the catalyst and the cocatalyst to react in a liquid phase and to load the reaction product onto the support. If used separately, the cocatalyst may for example be added into the polymerization reactor together with the supported metallocene-amide. Preferred as cocatalysts are the aluminoxanes, in particular the C₁₋₁₀ alkylaluminoxanes, most particularly methylaluminumoxane (MAO).

[0050] Such aluminoxanes may be used as the sole cocatalyst or alternatively may be used together with other cocatalysts. Thus besides or in addition to aluminoxanes, other complex forming catalyst activators may be used. In this regard mention may be made of the silver and boron compounds known in the art. What is required of such activators is that they should react with the metallocene-amide to yield an organometallic cation and a non-coordinating anion.

[0051] For more information regarding the preferred single-site catalysts used in the present invention reference is made to the above-mentioned WO 01/62847 and

WO 00/34341 which are both included herein by reference.

[0052] As mentioned earlier, a very important characteristic feature of the present invention is that the multimodal ethylene polymer has an ESCR or CTL 5.0 MPa-value, determined according to ISO 6259 of at least 500 hrs, preferably at least 2000 hrs, more preferably at least 6000 hrs. In view of WO 97/03139 it was very surprising and unexpected that such extremely high ESCR-values could be obtained by using a SSC when polymerising the multimodal ethylene polymer. Thus, WO 97/03139 discloses an ESCR according to ASTM D 1693 A, 10% Igepal of most preferably 2000 hrs. This, value is, however, not directly comparable with the above CTL 5.0 MPa-value of preferably at least 6000 hrs at the present invention, because the CTL 5.0 MPa-value, according to ISO 6259, is determined under much more severe conditions than ASTM D 1693 A. Thus, a bimodal ethylene polymer according to WO 97/03139 prepared by using a Ziegler-Natta catalyst and having an ESCR, determined according to ASTM D 1693 A, of > 5000 hrs, i.e. very much higher than what is disclosed in WO 97/03139, only achieved an ESCR of 241 hrs, determined according to ISO 6259, although at CTL 4.6 MPa, i.e. at more lenient conditions than CTL 5.0. Thus, a multimodal ethylene polymer according WO 97/03139 which has an ESCR of > 5000 hrs, determined according to ASTM D 1693 A, has an ESCR, according to ISO 6259 and determined at a CTL of 5.0 MPa, of less than 241 hrs. This means that by using a SSC for preparing the multimodal ethylene polymer in accordance with the present invention a polymer is obtained that has an ESCR value that is more than 6 times higher than a multimodal ethylene polymer prepared using a Ziegler-Natta catalyst. This is extremely surprising and not to be expected in view of WO 97/03139 in spite of the general statement therein that any kind of polymerisation catalyst inter alia a group 4 transition metallocene catalyst may be used.

[0053] To further facilitate the understanding of the present invention an example is given below. This example is only given for illustrative purposes and is not meant to limit the invention in any way.

Example 1

[0054] Polymerisations were done in a 5.2 l bench-scale reactor that contained a pre-mixing chamber (PMC reactor). Ethylene, hydrogen and comonomer were mixed and heated in the PMC before introduction to the reactor and were added continuously during polymerisation. Polymerisations were done in isobutane at 80°C and about 20 bar. A supported single site catalyst based on di-n-butyl-cyclopentadienyl hafnium dichloride activated with MAO was used as a catalyst.

[0055] Bimodal polymerisations were done in slurry-slurry phases. It is possible to simulate the slurry-gas phase conditions and perform the polymerisations as slurry-gas phase. As gas-phase polymerisations take

several hours, it was decided to do the polymerisations in a time saving way. A unimodal polymerisation was done before the bimodal run in order to find out suitable polymerisation conditions to reach MFR, density and comonomer content of the first step. The same conditions were then used in the first step of the bimodal run.

[0056] In the first stage an ethylene homopolymer with a density of 0.970-0.975 g/cm³ was prepared using a supported single site catalyst of the above described metallocene type with an aluminoxane cocatalyst. The MFR₂ of the ethylene homopolymer of the first stage was < 150 g/10 min and its estimated molecular weight was < 29 000 g/mol.

[0057] The polymerisation was continued in a second polymerisation stage to prepare an ethylene/1-hexene copolymer. No fresh catalyst was added in the second polymerisation stage. The comonomer content of the copolymer produced in the second stage was 2.4 % by weight (0.9 mol%). The amount of polymer produced in the second stage was 50 % of the total amount of polymer produced, i.e. the weight ratio between material produced in the different stages was 50:50.

[0058] The final bimodal ethylene polymer product, which is a blend of the ethylene homopolymer of the first stage and the ethylene-1-hexene copolymer of the second stage had a density of 0.944 g/cm³, an MFR₂ of 0.6 g/10 min, and an MFR₂₁ of 22 g/10 min. The molecular weight distribution (M_w/M_n) was 6.2.

[0059] The bimodal polymer obtained was used in a coating composition for the coating of a steel pipe as described earlier.

[0060] The environmental stress cracking resistance (ESCR) of the bimodal polymer was determined according to the method ISO 6259 under the action of a constant tensile load (CTL) of 5.0 MPa and a reagent in the form of Igepal CO-730 as described above. Very surprisingly, the ESCR according to this severe method was determined to be > 12 000 hrs. As a comparison and as mentioned above, a similar coating composition according to WO 97/03139 prepared by using a Ziegler-Natta catalyst achieved a value according to ISO 6259 at a CTL of 4.6 MPa, i.e. at more lenient conditions, of only 241 hrs. This shows the very substantial technical progress achieved by the present invention.

[0061] The polyethylene according to WO 97/03139 used for comparison had been prepared by producing a homopolymer in a prepolymerisation reactor at 70°C. The H₂/C₂ molar ratio was 0.15 and C₄/C₂ 0.04. The material was transported to a loop-reactor and polyethylene with an MFR₂ of 400 g/10 min and a density of 965 kg/m³ was produced. The material produced in the loop-reactor was then transported into a gas-phase reactor. The material taken out from the gas-phase reactor had an MFR₂ = 0.4 g/10 min and a density of 942 kg/m³. The ratio between the amounts produced in the prepolymerisation reactor/loop-reactor/gas-phase reactor was 2:43:55.

Example 2

[0062] Polyethylene was prepared in a bench-reactor at 90°C. The polymerisation media was iso-butane. The total pressure was 24.2 bar. No comonomer was added to the reactor. Hydrogen was fed together with ethylene. The concentration of hydrogen was 3700 ppm in the ethylene. The partial pressure of ethylene was 6.5 bar. 1940 g polymer with an MFR₂ of 134 g/10 min was produced. The density was 975 kg/m³. This polymer was later used as one component for blending.

[0063] One more component to be used for blending was prepared in a bench-reactor. The reactor temperature was 65°C. The polymerisation media was iso-butane. The total pressure was 20 bar. The comonomer content was 2.5 % by weight in the iso-butane. No hydrogen was fed to the reactor. The partial pressure was 10.3 bar. The polymerisation time was 60 min. 2510 g polymer with an MFR₂ of 0.07 g/10 min and an M_w = 285000 and a density of 916 kg/m³ was produced. The MWD was 2.6.

[0064] The two separately produced polyethylenes were compounded in the compounding equipment FLEXTRAL at 210°C. The MFR₂ of the blend was 0.36 g/10 min. The density was 940.3 kg/m³. The CTL 5.0 MPa was > 6165 hrs (still running).

Claims

1. A coating composition, **characterised in that** it comprises a multimodal ethylene polymer, which contains from 80 to 99.8 % by weight of ethylene repeating units and from 0.2 to 20 % by weight of C₃-C₂₀ α-olefin repeating units, and is a blend of at least a first and a second ethylene polymer that are obtainable by a process comprising at least two steps in which:

said first ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; and

said second ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system;

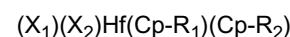
said steps being performed in any order and the ethylene polymer of each step being present in the following step(s), and producing a blend of from 20 to 80 % by weight of said first and from 80 to 20 % by weight of said second ethylene polymer, said blend having a density of 0.915-0.955 g/cm³, a melt flow rate, MFR₂, of 0.028-1.5 g/10 min., a molecular weight distribution, M_w/M_n, of 3-10, and a CTL 5.0 MPa-value according to ISO 6259 of at least 500 hrs.

2. A coating composition according to claim 1, wherein the composition has a CTL 5.0 MPa-value according to ISO 6259 of at least 12 000 hrs.

3. A coating composition according to claim 1 or 2, wherein the multimodal ethylene polymer contains C₃-C₂₀ α-olefin repeating units selected from 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and 1-eicosene.

4. A coating composition according to claim 3, wherein said second ethylene polymer has a content of 1.0-25 % by weight of C₃-C₂₀ α-olefin repeating units.

5. A coating composition according to any one of the preceding claims, wherein the single site catalyst system comprises a complex having the general formula:



wherein

X₁ and X₂ are either the same or different and are selected from a group containing halogen, methyl, benzyl or hydrogen;

Hf is hafnium;

Cp is a cyclopentadienyl group; and

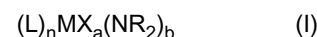
R₁ and R₂ are the same or different and selected from the group of linear and branched hydrocarbyl groups containing 1-10 carbon atoms.

6. A coating composition according to claim 5, wherein the single site catalyst also comprises an aluminum-moxane cocatalyst.

7. A coating composition according to claim 5 or 6, wherein the single site catalyst is supported on a solid carrier.

8. A coating composition according to any one of claims 1-4, wherein the single site catalyst system comprises a porous particulate support material having impregnated therein a metallocene catalyst the metal atom whereof is bound to an amide group which is not bound to an η-ligand of the metallocene, or the reaction product of said metallocene catalyst and a cocatalyst.

9. A coating composition according to claim 8, wherein the metallocene catalyst is of the formula I



where n is 1, 2 or 3; a is 0, 1, 2, 3 or 4; b is 1, 2, 3, 4 or 5; n+a+b is the total coordination number for M; M is a catalytically active transition metal or lanthanide; each L, which may be the same or different, is

an η -ligand, optionally linked via a bridging group R^* to a second group L or to a metal-coordinating group X; each X is a metal coordinating group; and each R, which may be the same or different is a hydrocarbyl group or two groups R, together with the intervening nitrogen, are an optionally substituted, nitrogen bound heterocyclic group.

10. A coating composition according to claim 8 or 9, wherein the support material has impregnated therein the reaction product of said metallocene catalyst and an aluminoxane cocatalyst.

11. A process for producing a coating composition, **characterised in that** the coating composition comprises a multimodal ethylene polymer, which contains from 80 to 99.8 % by weight of ethylene repeating units and from 0.2 to 20 % by weight of C_3 - C_{20} α -olefin repeating units, and is a blend of at least a first and a second ethylene polymer is prepared by a process comprising at least two steps in which:

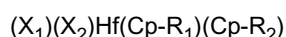
said first ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system; and

said second ethylene polymer is prepared by polymerising ethylene and optional comonomer(s) in the presence of a single site catalyst system;

said steps being performed in any order and the ethylene polymer of each step being present in the following step(s), and producing a blend of from 20 to 80 % by weight of said first and from 80 to 20 % by weight of said second ethylene polymer, said blend having a density of 0.915-0.955 g/cm³, a melt flow rate, MFR₂, of 0.028-1.5 g/10 min, a molecular weight distribution, M_w/M_n , of 3-10, and a CTL 5.0 MPa-value according to ISO 6259 of at least 500 hrs.

12. A method according to claim 11, wherein at least the second ethylene polymer is prepared in the presence of a comonomer selected from 1-butene, 1-hexene, 4-methyl-1-pentene, 1-octene, 1-decene, and 1-eicosene.

13. A method according to claim 11 or 12, wherein the polymerisation is carried out in the presence of a single site catalyst system comprising a complex having the general formula:



wherein

X_1 and X_2 are either the same or different and are selected from a group containing halogen, methyl, benzyl or hydrogen;

Hf is hafnium;

Cp is a cyclopentadienyl group; and

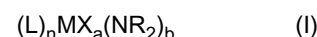
R_1 and R_2 are the same or different and selected from the group of linear and branched hydrocarbyl groups containing 1-10 carbon atoms.

14. A process according to claim 13, wherein the single site catalyst also comprises an aluminoxane cocatalyst.

15. A process according to claim 13 or 14, wherein the single site catalyst is supported on a solid carrier.

16. A process according to claim 11 or 12, wherein the polymerisation is carried out in the presence of a single site catalyst system comprising a porous particulate support material having impregnated therein a metallocene catalyst the metal atom whereof is bound to an amide group which is not bound to an η -ligand of the metallocene, or the reaction product of said metallocene catalyst and a cocatalyst.

17. A process according to claim 16, wherein the metallocene catalyst is of the formula I



where n is 1, 2 or 3; a is 0, 1, 2, 3 or 4; b is 1, 2, 3, 4 or 5; n+a+b is the total coordination number for M; M is a catalytically active transition metal or lanthanide; each L, which may be the same or different, is an η -ligand, optionally linked via a bridging group R^* to a second group L or to a metal-coordinating group X; each X is a metal coordinating group; and each R, which may be the same or different is a hydrocarbyl group or two groups R, together with the intervening nitrogen, are an optionally substituted, nitrogen bound heterocyclic group.

18. A process according to claim 16 or 17, wherein the support material has impregnated therein the reaction product of said metallocene catalyst and an aluminoxane cocatalyst.

19. A coated substrate, **characterised in that** it is coated with a coating composition according to any one of claims 1-10.

20. A coated substrate according to claim 19, wherein the substrate is a metal pipe.

Patentansprüche

1. Beschichtungszusammensetzung, **dadurch gekennzeichnet, daß** sie ein multimodales Ethylenpolymer umfaßt, das 80 bis 99,8 Gew.-% Ethylen-Struktureinheiten und 0,2 bis 20 Gew.-% C_3 - C_{20} - α -

Olefin-Struktureinheiten umfaßt und ein Gemisch von zumindest einem ersten und einem zweiten Ethylenpolymer ist, die nach einem Verfahren erhalten werden können, das mindestens zwei Schritte umfaßt, wobei:

das erste Ethylenpolymer durch Polymerisieren von Ethylen und gegebenenfalls Comonomer(en) in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren hergestellt ist; und das zweite Ethylenpolymer durch Polymerisieren von Ethylen und gegebenenfalls Comonomer(en) in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren hergestellt ist;

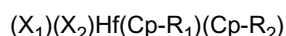
wobei die Schritte in irgendeiner Reihenfolge durchgeführt werden und das Ethylenpolymer jedes Schritts in dem (den) folgenden Schritt(en) vorliegt und ein Gemisch aus 20 bis 80 Gew.-% des ersten und 80 bis 20 Gew.-% des zweiten Ethylenpolymers erzeugen, wobei das Gemisch eine Dichte von 0,915 bis 0,955 g/cm³, eine Schmelzflußrate MFR₂ von 0,028 bis 1,5 g/10 min, eine Molekulargewichtsverteilung M_w/M_n von 3 bis 10 und einen Wert für CTL 5,0 MPa gemäß ISO 6259 von mindestens 500 h hat.

2. Beschichtungszusammensetzung nach Anspruch 1, wobei die Zusammensetzung einen Wert für CTL 5,0 MPa gemäß ISO 6259 von mindestens 12000 h hat.

3. Beschichtungszusammensetzung nach Anspruch 1 oder 2, wobei das multimodale Ethylenpolymer C₃-C₂₀- α -Olefin-Struktureinheiten enthält, die aus 1-Buten, 1-Hexen, 4-Methyl-1-penten, 1-Octen, 1-Decen und 1-Eicosen ausgewählt sind.

4. Beschichtungszusammensetzung nach Anspruch 3, wobei das zweite Ethylenpolymer einen Gehalt an C₃-C₂₀- α -Olefin-Struktureinheiten von 1,0 bis 25 Gew.-% aufweist.

5. Beschichtungszusammensetzung nach einem der vorstehenden Ansprüche, wobei das Katalysatorsystem mit einheitlichen aktiven Zentren einen Komplex mit der allgemeinen Formel umfaßt:



worin

X₁ und X₂ jeweils gleich oder verschieden sind und aus der Gruppe ausgewählt sind, die Halogen, Methyl, Benzyl oder Wasserstoff einschließt;

Hf Hafnium ist;

Cp eine Cyclopentadienylgruppe ist; und

R₁ und R₂ gleich oder verschieden sind und aus der Gruppe von linearen und verzweigten Kohlenwas-

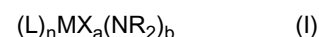
serstoffresten mit 1 bis 10 Kohlenstoffatomen ausgewählt sind.

6. Beschichtungszusammensetzung nach Anspruch 5, wobei der Katalysator mit einheitlichen aktiven Zentren auch einen Aluminoxan-Cokatalysator umfaßt.

7. Beschichtungszusammensetzung nach Anspruch 5 oder 6, wobei der Katalysator mit einheitlichen aktiven Zentren auf einem festen Träger getragen wird.

8. Beschichtungszusammensetzung nach einem der Ansprüche 1 bis 4, wobei das Katalysatorsystem mit einheitlichen aktiven Zentren ein poröses partikelförmiges Trägermaterial umfaßt, in das ein Metallocenkatalysator, dessen Metallatom mit einer Amidgruppe verbunden ist, die nicht an einen η -Liganden des Metallocens gebunden ist, oder das Reaktionsprodukt des Metallocenkatalysators und eines Cokatalysators imprägniert ist.

9. Beschichtungszusammensetzung nach Anspruch 8, wobei der Media Formel I hat



worin n gleich 1, 2 oder 3 ist; a gleich 0, 1, 2, 3 oder 4 ist; b gleich 1, 2, 3, 4 oder 5 ist; n+a+b die gesamte Koordinationszahl für M ist; M ein katalytisch wirksames Übergangsmetall oder Lanthanoid ist; L, das gleich oder verschieden sein kann, jeweils ein η -Ligand ist, der gegebenenfalls über einen Brückenrest R* an eine zweite Gruppe L oder an eine sich an ein Metall koordinativ anlagernde Gruppe X gebunden ist; X jeweils eine sich an ein Metall koordinativ anlagernde Gruppe ist; und R, das gleich oder verschieden sein kann, jeweils ein Kohlenwasserstoffrest ist oder zwei Reste R zusammen mit dem dazwischenliegenden Stickstoff eine gegebenenfalls substituierte, mit Stickstoff verbundene heterocyclische Gruppe sind.

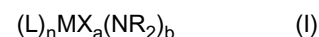
10. Beschichtungszusammensetzung nach Anspruch 8 oder 9, wobei das Reaktionsprodukt des Metallocenkatalysators und eines Aluminoxan-Cokatalysators in das Trägermaterial imprägniert ist.

11. Verfahren zur Herstellung einer Beschichtungszusammensetzung, **dadurch gekennzeichnet, daß** die Beschichtungszusammensetzung ein multimodales Ethylenpolymer umfaßt, das 80 bis 99,8 Gew.-% Ethylen-Struktureinheiten und 0,2 bis 20 Gew.-% C₃-C₂₀- α -Olefin-Struktureinheiten umfaßt und ein Gemisch von zumindest einem ersten und einem zweiten Ethylenpolymer ist, hergestellt nach einem Verfahren, das mindestens zwei Schritte umfaßt, wobei:

- das erste Ethylenpolymer durch Polymerisieren von Ethylen und gegebenenfalls Comonomer(en) in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren hergestellt wird; und
- das zweite Ethylenpolymer durch Polymerisieren von Ethylen und gegebenenfalls Comonomer(en) in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren hergestellt wird;
- wobei die Schritte in irgendeiner Reihenfolge durchgeführt werden und das Ethylenpolymer jedes Schritts in dem (den) folgenden Schritt(en) vorliegt und ein Gemisch aus 20 bis 80 Gew.-% des ersten und 80 bis 20 Gew.-% des zweiten Ethylenpolymers erzeugen, wobei das Gemisch eine Dichte von 0,915 bis 0,955 g/cm³, eine Schmelzfließrate MFR₂ von 0,028 bis 1,5 g/10 min, eine Molekulargewichtsverteilung M_w/M_n von 3 bis 10 und einen Wert für CTL 5,0 MPa gemäß ISO 6259 von mindestens 500 h hat.
12. Verfahren nach Anspruch 11, wobei zumindest das zweite Ethylenpolymer in Gegenwart eines Comonomers hergestellt wird, das aus 1-Buten, 1-Hexen, 4-Methyl-1-penten, 1-Octen, 1-Decen und 1-Eicosen ausgewählt ist.
13. Verfahren nach Anspruch 11 oder 12, wobei die Polymerisation in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren durchgeführt wird, das einen Komplex mit der allgemeinen Formel umfaßt:
- $$(X_1)(X_2)Hf(Cp-R_1)(Cp-R_2)$$
- worin X₁ und X₂ jeweils gleich oder verschieden sind und aus der Gruppe ausgewählt sind, die Halogen, Methyl, Benzyl oder Wasserstoff einschließt; Hf Hafnium ist; Cp eine Cyclopentadienylgruppe ist; und R₁ und R₂ gleich oder verschieden sind und aus der Gruppe von linearen und verzweigten Kohlenwasserstoffresten mit 1 bis 10 Kohlenstoffatomen ausgewählt sind
14. Verfahren nach Anspruch 13, wobei der Katalysator mit einheitlichen aktiven Zentren auch einen Aluminoxan-Cokatalysator umfaßt.
15. Verfahren nach Anspruch 13 oder 14, wobei der Katalysator mit einheitlichen aktiven Zentren auf einem festen Träger getragen wird.
16. Verfahren nach Anspruch 11 oder 12, wobei die Polymerisation in Gegenwart eines Katalysatorsystems mit einheitlichen aktiven Zentren durchgeführt

wird, das ein poröses partikelförmiges Trägermaterial umfaßt, in das ein Metallocenkatalysator, dessen Metallatom mit einer Amidgruppe verbunden ist, die nicht an einen η-Liganden des Metallocens gebunden ist, oder das Reaktionsprodukt des Metallocenkatalysators und eines Cokatalysators imprägniert ist.

17. Verfahren nach Anspruch 16, wobei der Metallocenkatalysator die Formel I hat:



worin n gleich 1, 2 oder 3 ist; a gleich 0, 1, 2, 3 oder 4 ist; b gleich 1, 2, 3, 4 oder 5 ist; n+a+b die gesamte Koordinationszahl für M ist; M ein katalytisch wirksames Übergangsmetall oder Lanthanoid ist; L, das gleich oder verschieden sein kann, jeweils ein η-Ligand ist, der gegebenenfalls über einen Brückenrest R* an eine zweite Gruppe L oder an eine sich an ein Metall koordinativ anlagernde Gruppe X gebunden ist; X jeweils eine sich an ein Metall koordinativ anlagernde Gruppe ist; und R, das gleich oder verschieden sein kann, jeweils ein Kohlenwasserstoffrest ist oder zwei Reste R zusammen mit dem dazwischenliegenden Stickstoff eine gegebenenfalls substituierte, mit Stickstoff verbundene heterocyclische Gruppe sind.

18. Verfahren nach Anspruch 16 oder 17, wobei das Reaktionsprodukt des Metallocenkatalysators und eines Aluminoxan-Cokatalysators in das Trägermaterial imprägniert ist.

19. Beschichtetes Substrat, **dadurch gekennzeichnet, daß** es mit einer Beschichtungszusammensetzung nach einem der Ansprüche 1 bis 10 beschichtet ist,

20. Beschichtetes Substrat nach Anspruch 19, wobei das Substrat ein Metallrohr ist.

Revendications

1. Composition de revêtement **caractérisée en ce qu'elle** comprend un polymère d'éthylène multimodal qui contient de 80 à 99,8 % en poids d'unités répétitives d'éthylène et de 0,2 à 20 % en poids d'unités répétitives d'oléfine-α en C₃-C₂₀, et laquelle est un mélange d'au moins un premier et d'un second polymère d'éthylène qui peuvent être obtenus par un procédé comprenant au moins deux étapes dans lequel :

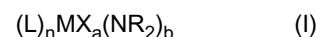
ledit premier polymère d'éthylène est préparé par polymérisation d'éthylène et d'un (de) comonomère(s) facultatif(s) en présence d'un système de catalyseur à un seul site ; et

- ledit second polymère d'éthylène est préparé par polymérisation et d'un (de) comonomère(s) facultatif(s) en présence d'un système de catalyseur à un seul site ;
 lesdites étapes étant dans un ordre quelconque et le polymère d'éthylène dans chaque étape étant présent dans l'(les) étape(s) suivante(s), et produisant un mélange de 20 à 80 % en poids dudit premier et de 80 à 20 % en poids dudit second polymère d'éthylène, ledit mélange ayant une densité de 0,915-0,955 g/cm³, un indice de fusion, MFR₂, de 0,028-1,5 g/10 min, une distribution de poids moléculaire M_w/M_n, de 3-10 et une valeur CTL 5,0 MPa selon ISO 6259 d'au moins 500 h.
2. Composition de revêtement selon la revendication 1, dans laquelle la composition présente une valeur CTL 5,0 MPa selon ISO 6259 d'au moins 12 000 h.
 3. Composition de revêtement selon la revendication 1 ou 2, dans laquelle le polymère d'éthylène multimodal contient des unités répétitives d'oléfine-α en C₃-C₂₀ choisies parmi le 1-butène, le 1-hexène, le 4-méthyl-1-pentène, le 1-octène, le 1-décène et le 1-éicosène.
 4. Composition de revêtement selon la revendication 3, dans laquelle ledit second polymère d'éthylène présente une teneur de 1,0-25 % en poids d'unités répétitives d'oléfine-α en C₃-C₂₀.
 5. Composition de revêtement selon l'une quelconque des revendications précédentes, dans laquelle le système de catalyseur à un seul site comprend un complexe ayant la formule générale

$$(X_1)(X_2)Hf(Cp-R_1)(Cp-R_2)$$
 dans laquelle
 X₁ et X₂ sont soit identiques soit différents et sont choisis parmi un atome d'halogène, un groupe méthyle, benzyle ou un atome d'hydrogène ;
 Hf est l'hafnium ;
 Cp est un groupe cyclopentadiényle ; et
 R₁ et R₂ sont identiques ou différents et choisis parmi des groupes hydrocarbyle linéaires et ramifiés contenant 1-10 atomes de carbone.
 6. Composition de revêtement selon la revendication 5, dans laquelle le catalyseur à un seul site comprend également un cocatalyseur d'aluminoxane.
 7. Composition de revêtement selon la revendication 5 ou 6, dans laquelle le catalyseur à seul site est supporté sur un support solide.
 8. Composition de revêtement selon l'une quelconque

des revendications 1-4, dans laquelle le système de catalyseur à un seul site comprend un matériau de support particulaire poreux ayant, imprégné dans celui-ci, un catalyseur de métallocène dont l'atome de métal est lié à un groupe amide qui n'est pas lié à un ligand η du métallocène, ou le produit de réaction audit catalyseur de métallocène et d'un cocatalyseur.

9. Composition de revêtement selon la revendication 8, dans laquelle le catalyseur de métallocène est de la formule I



dans laquelle n est égal à 1, 2 ou 3 ; a est égal à 0, 1, 2, 3 ou 4 ; b est égal à 1, 2, 3, 4 ou 5 ; n+a+b est le nombre de coordination totale pour M ; M est un métal de transition ou un lanthanide catalytiquement actif ; chaque L, qui peut être identique ou différent, est un ligand n facultativement lié via un groupe de pontage R* à un second groupe L ou un groupe X coordonnant un métal ; chaque X est un groupe coordonnant un métal ; et chaque R, qui peut être identique ou différent, est un groupe hydrocarbyle ou deux groupes R, en association avec l'azote intervenant, constituent un groupe hétérocyclique, lié à l'azote, facultativement substitué.

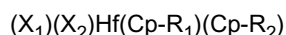
10. Composition de revêtement selon la revendication 8 ou 9, dans laquelle le matériau de support présente, imprégné dans celui-ci, le produit de réaction dudit catalyseur de métallocène et d'un cocatalyseur d'aluminoxane.
11. Procédé pour la production d'une composition de revêtement, **caractérisé en ce que** la composition de revêtement comprend un polymère d'éthylène multimodal qui contient de 80 à 99,8 % en poids d'unités répétitives d'éthylène et de 0,2 à 20 % en poids d'unités répétitives d'oléfine-α en C₃-C₂₀, et laquelle est un mélange d'au moins un premier et d'un second polymère d'éthylène qui est préparé par un procédé comprenant au moins deux étapes dans lequel :

ledit premier polymère d'éthylène est préparé par polymérisation d'éthylène et d'un (de) comonomère(s) facultatif(s) en présence d'un système de catalyseur à un seul site ; et
 ledit second polymère d'éthylène est préparé par polymérisation d'éthylène et d'un (de) comonomère(s) facultatif(s) en présence d'un système de catalyseur à un seul site ;
 lesdites étapes étant réalisées dans un ordre quelconque et le polymère d'éthylène de chaque étape étant présent dans l'(les) étape(s) suivante(s), et produisant un mélange de 20 à 80 %

en poids dudit premier et de 80 à 20 % en poids dudit second polymère d'éthylène, ledit mélange ayant une densité de 0,915-0,955 g/cm³, un indice de fusion, MFR₂, de 0,028-1,5 g/10 min, une distribution de poids moléculaire, M_w/M_n, de 3-10 et une valeur CTL 5,0 MPa selon ISO 6259 d'au moins 500 h.

12. Procédé selon la revendication 11, dans lequel au moins le second polymère d'éthylène est préparé en présence d'un comonomère choisi parmi le 1-butène, le 1-hexène, le 4-méthyl-1-pentène, le 1-octène, le 1-décène et le 1-éicosène.

13. Procédé selon la revendication 11 ou 12, dans lequel la polymérisation est réalisée en présence d'un système de catalyseur à un seul site comprenant un complexe ayant la formule générale :



dans laquelle

X₁ et X₂ sont soit identiques soit différents et sont choisis parmi un atome d'halogène, un groupe méthyle, benzyle ou un atome d'hydrogène;

Hf est l'hafnium ;

Cp est un groupe cyclopentadiényle ; et

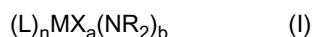
R₁ et R₂ sont identiques ou différents et choisis parmi des groupes hydrocarbyle et ramifiés contenant 1-10 atomes de carbone.

14. Procédé selon la revendication 13, dans lequel le catalyseur à un seul site comprend également un cocatalyseur d'aluminoxane.

15. Procédé selon la revendication 13 ou 14, dans lequel le catalyseur à seul site est supporté sur un support solide.

16. Procédé selon la revendication 11 ou 12, dans lequel la polymérisation est réalisée en présence d'un système de catalyseur à un seul site comprenant un matériau de support particulaire poreux ayant, imprégné dans celui-ci, un catalyseur de métallocène dont l'atome de métal est lié à un groupe amide qui n'est pas lié à un ligand η du métallocène, ou le produit de réaction dudit catalyseur de métallocène et d'un cocatalyseur.

17. Procédé selon la revendication 16, dans lequel le catalyseur de métallocène est de la formule I



dans laquelle n est égal à 1, 2 ou 3 ; a est égal à 0, 1, 2, 3 ou 4 ; b est égal à 1, 2, 3, 4 ou 5 ; n+a+b est le nombre total de coordination pour M ; M est un métal de transition ou un lanthanide catalytiquement

actif ; chaque L, qui peut être identique ou différent, est un ligand η, facultativement lié via un groupe de pontage R* à un second groupe L ou un groupe X coordonnant un métal ; chaque X est un groupe coordonnant un métal ; et chaque R, qui peut être identique ou différent, est un groupe hydrocarbyle ou deux groupes R, en association avec l'azote intervenant, constituent un groupe hétérocyclique, lié à l'azote, facultativement substitué.

18. Procédé selon la revendication 16 ou 17, dans lequel le matériau de support présente, imprégné dans celui-ci, le produit de réaction dudit catalyseur de métallocène et d'un cocatalyseur d'aluminoxane.

19. Substrat revêtu **caractérisé en ce qu'il** est revêtu avec une composition de revêtement selon l'une quelconque des revendications 1-10.

20. Substrat revêtu selon la revendication 19, dans lequel le substrat est un tuyau en métal.