

CLAIMS:

1. A process for the preparation of a multimodal polyethylene comprising:

- (i) polymerising ethylene and optionally an α -olefin comonomer in a first slurry polymerisation stage to produce a first ethylene polymer; and
- (ii) polymerising ethylene and optionally an α -olefin comonomer, in the presence of said first ethylene polymer, in a second slurry polymerisation stage,

wherein said first and second polymerisation stages are carried out in the presence of an unsupported metallocene catalyst, a solution of said unsupported metallocene catalyst in a solvent is employed, and each polymerisation stage produces at least 5 %wt of said multimodal polyethylene, and said multimodal polyethylene has a multimodal molecular weight distribution, a weight average molecular weight of at least 50,000 g/mol and a bulk density of at least 250 g/dm³.

2. A process as claimed in claim 1, wherein said solvent is a C₃₋₁₀ saturated alkane, preferably a C₄₋₁₀ saturated alkane which is preferably selected from hexane and cyclohexane, or an aromatic hydrocarbon, preferably toluene.

~~3. A process as claimed in claim 2, wherein said solvent is a C₄₋₁₀ saturated alkane.~~

~~4. A process as claimed in claim 3, wherein said solvent is hexane or cyclohexane.~~

~~5. A process as claimed in claim 2, wherein said solvent is toluene.~~

~~36.~~ A process as claimed in any ~~one of claims 1 to 5~~preceding claim, wherein the metallocene catalyst is a complex of a group 3 to 10 metal, preferably a complex of a metal ion formed by a metal which is Zr, Hf or Ti, having at least two ligands, wherein each ligand is a substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted indenyl, substituted or unsubstituted fluorenyl or substituted or unsubstituted tetrahydroindenyl.

~~7. A process as claimed in any one of claims 1 to 6, wherein the metallocene catalyst is a complex of a metal ion formed by a metal which is Zr, Hf or Ti.~~

~~48.~~ A process as claimed in any preceding claim~~any one of claims 1 to 7~~, wherein said metallocene is a compound of formula (I):



wherein

each Cp is independently a substituted or unsubstituted, preferably unsubstituted, cyclic group having a delocalised system of pi electrons, more preferably a substituted or unsubstituted, preferably unsubstituted, cyclopentadienyl, indenyl, fluorenyl or tetrahydroindenyl;

L is a bridge of 1-7 atoms, preferably a methylene, ethylene or silyl bridge;

n is 0 or 1;

M is a transition metal of Group 3 to 10, preferably Ti, Zr or Hf; and

each X is independently a sigma-ligand.

~~9. A process as claimed in claim 8, wherein Cp is a substituted or unsubstituted cyclopentadienyl, substituted or unsubstituted indenyl, substituted or unsubstituted fluorenyl or substituted or unsubstituted tetrahydroindenyl.~~

~~10. A process as claimed in claim 8 or 9, wherein each Cp is unsubstituted.~~

~~11. A process as claimed in any one of claims 8 to 10, wherein n is 0.~~

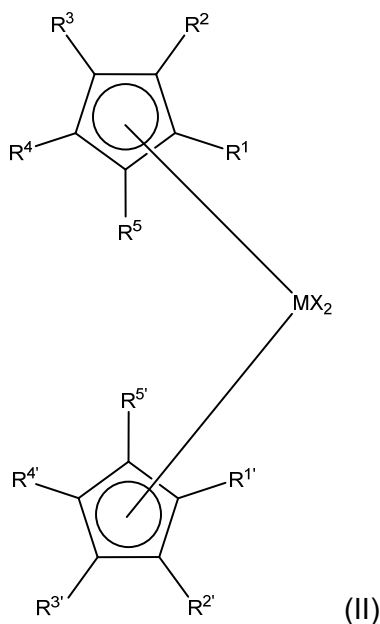
~~12. A process as claimed in any one of claims 8 to 10, wherein n is 1.~~

~~13. A process as claimed in claim 12, wherein L is a methylene, ethylene or silyl bridge.~~

~~14. A process as claimed in any one of claims 8 to 13, wherein M is Ti, Zr or Hf.~~

~~15.~~ A process as claimed in ~~any one of claims 8 to 14~~, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂ cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR'', -PR'', SiR'', -OSiR'', -NR''₂ or -CH₂Y wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, -NR''₂, -SR'', -PR'', -SiR'', or -OSi''₃ and wherein each R'' is independently a hydrogen or hydrocarbyl; or in the case of -NR''₂, the two substituents R'' can form a ring, together with the nitrogen atom to which they are attached.

~~516.~~ A process as claimed in any preceding claim~~any one of claims 1 to 9~~, wherein said metallocene is of formula (II):



wherein

M is a transition metal of Group 4 to 6;

each X is independently a sigma-ligand, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂-cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR'', -PR'', -SiR'', -OSiR'', -NR''₂ or -CH₂-Y, wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, NR''₂, -SR'', -PR'', -SiR'', or -OSiR''₃ and wherein each R'' is independently a hydrogen or hydrocarbyl; or in the case of -NR''₂, the two substituents R'' can form a ring, together with the nitrogen atom to which

they are attached, preferably each X is independently halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryl, C₇₋₂₀ arylalkenyl or -NR["]₂.

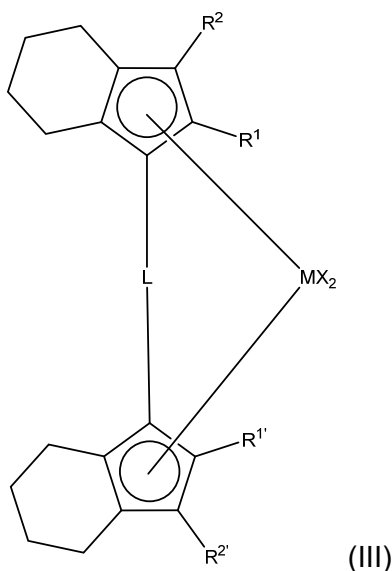
;

R¹ and R^{1'} are each independently C₁₋₂₀ hydrocarbyl; and

R², R^{2'}, R³, R^{3'}, R⁴, R^{4'}, R⁵ and R^{5'} are each independently H or a C₁₋₂₀ hydrocarbyl-

or

~~17. A process as claimed in any one of claims 1 to 9, wherein said metallocene is of~~
formula (III):



wherein

M is a transition metal of Group 4 to 6, preferably Ti, Zr or Hf;

each X is independently a sigma-ligand, preferably wherein each X is independently H, halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₂₋₂₀ alkenyl, C₂₋₂₀ alkynyl, C₃₋₁₂-cycloalkyl, C₆₋₂₀ aryl, C₆₋₂₀ aryloxy, C₇₋₂₀ arylalkyl, C₇₋₂₀ arylalkenyl, -SR["], -PR["]₃, -SiR["]₃, -OSiR["]₃, -NR["]₂ or -CH₂-Y, wherein Y is C₆₋₂₀ aryl, C₆₋₂₀ heteroaryl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryloxy, NR["]₂, -SR["], -PR["]₃, -SiR["]₃, or -OSiR["]₃ and wherein each R["] is independently a hydrogen or hydrocarbyl; or in the case of -NR["]₂, the two substituents R["] can form a ring, together with the nitrogen atom to which they are attached, preferably each X is independently halogen, C₁₋₂₀ alkyl, C₁₋₂₀ alkoxy, C₆₋₂₀ aryl, C₇₋₂₀ arylalkenyl or -NR["]₂.

;

R^1 , $R^{1'}$, R^2 , $R^{2'}$, are each independently H or a C_{1-20} hydrocarbyl; and
 L is a bridge of 1-4 C-atoms and 0-4 heteroatoms, wherein each of the bridge atoms may bear independently substituents; or a bridge of 1-3 hetero atoms, preferably a methylene, ethylene or silyl bridge.

~~18. A process as claimed in claim 17, wherein M is Ti, Zr or Hf.~~

~~19. A process as claimed in claim 17 or 18, wherein each X is independently H, halogen, C_{1-20} alkyl, C_{1-20} alkoxy, C_{2-20} alkenyl, C_{2-20} alkynyl, C_{3-12} cycloalkyl, C_{6-20} aryl, C_{6-20} aryloxy, C_{7-20} arylalkyl, C_{7-20} arylalkenyl, SR'' , PR''_3 , SiR''_3 , $OSiR''_3$, NR''_2 or CH_2Y , wherein Y is C_{6-20} aryl, C_{6-20} heteroaryl, C_{1-20} alkoxy, C_{6-20} aryloxy, NR''_2 , SR'' , PR''_3 , SiR''_3 , or $OSiR''_3$ and wherein each R'' is independently a hydrogen or hydrocarbyl; or in the case of NR''_2 , the two substituents R'' can form a ring, together with the nitrogen atom to which they are attached.~~

~~20. A process as claimed in claim 19 wherein each X is independently halogen, C_{1-20} alkyl, C_{1-20} alkoxy, C_{6-20} aryl, C_{7-20} arylalkenyl or NR''_2 as defined above.~~

~~21. A process as claimed in any one of claims 17 to 20, wherein R^1 , $R^{1'}$, R^2 , $R^{2'}$ are each independently H.~~

~~22. A process as claimed in any one of claims 17 to 21, wherein L is a methylene, ethylene or silyl bridge.~~

~~23. A process as claimed in any preceding claim any one of claims 1 to 22, wherein said metallocene is $(nBuCp)_2HfCl_2$, $(Ind)_2ZrCl_2$, Et-(tetrahydroindenyl) $_2ZrCl_2$ or $(nBuCp)_2ZrCl_2$.~~

~~24. A process as claimed in any preceding claim any one of claims 1 to 23, wherein an aluminoxane cocatalyst is employed.~~

~~25. A process as claimed in claim 24, preferably wherein:~~

-a solution of said aluminoxane cocatalyst in a solvent, preferably a C₃₋₁₀ saturated alkane, more preferably a C₄₋₁₀ saturated alkane which is preferably selected from hexane and cyclohexane, or an -aromatic hydrocarbon, preferably toluene, is employed; or
a mixture of an aluminoxane cocatalyst and metallocene, diluted in a C₄₋₁₀ saturated alkane or toluene, is employed.-

26. — ~~A process as claimed in claim 25, wherein said solvent is a C₃₋₁₀ saturated alkane or an aromatic hydrocarbon.~~

27. — ~~A process as claimed in claim 26, wherein said solvent is a C₄₋₁₀ saturated alkane.~~

28. — ~~A process as claimed in claim 27, wherein said solvent is hexane or cyclohexane.~~

29. — ~~A process as claimed in claim 26, wherein said solvent is toluene.~~

30. — ~~A process as claimed in claim 24, wherein a mixture of an aluminoxane cocatalyst and metallocene, diluted in a C₄₋₁₀ saturated alkane or toluene, is employed.~~

834. A process as claimed in any preceding claim~~any one of claims 1 to 30~~, wherein:
said process is semi-continuous or continuous, preferably continuous;
_____said first and/or second slurry polymerisation is carried out in an aliphatic hydrocarbon diluent;_-

32. — ~~A process as claimed in any one of claims 1 to 31, wherein said first and/or said second polymerisation stage is carried out in the presence of hydrogen;_-~~

33. — ~~A process as claimed in any one of claims 1 to 32, wherein there is no reactor fouling in said first and/or said second polymerisation stage; and/or_-~~

34. — ~~A process as claimed in any one of claims 1 to 33, wherein said second polymerisation is carried out in the presence of hydrogen.~~

~~35. — A process as claimed in any one of claims 1 to 33, wherein said second polymerisation is carried out in the absence of hydrogen.~~

~~36. — A process as claimed in any one of claims 1 to 35, wherein there is no reactor fouling in said second polymerisation stage.~~

~~937. A process as claimed in any preceding claim ~~any one of claims 1 to 36,~~ wherein said process consists of a first polymerisation stage, which preferably produces 1 to 65 %wt of said multimodal polyethylene, and a second polymerisation stage, which preferably produces 35 to 99 %wt of said multimodal polyethylene.~~

~~38. — A process as claimed in any one of claims 1 to 37, wherein said first polymerisation stage produces 5 to 65 %wt of said multimodal polyethylene.~~

~~39. — A process as claimed in any one of claims 1 to 38, wherein said second polymerisation stage produces 35 to 95 %wt of said multimodal polyethylene.~~

~~1040. A process as claimed in any one of claims 1 to 36 or any one of claims 38 to 39 when not dependent on claim 37~~to 8, wherein said process consists of a first polymerisation stage, which preferably produces 1 to 65 %wt of said multimodal polyethylene, a second polymerisation stage, which preferably produces 35 to 99 %wt of said multimodal polyethylene, and a third polymerisation stage, preferably wherein said third polymerisation stage is carried out in slurry conditions and/or produces 0.5-30 wt% of said multimodal polyethylene.

~~41. — A process as claimed in claim 40, wherein said third polymerisation is carried out in slurry conditions.~~

~~42. — A process as claimed in claim 40 or 41, wherein said third polymerisation stage produces 0.5-30 wt% of said multimodal polyethylene.~~

1143. A process as claimed in ~~any one of claims 40 to 42~~claim 10, comprising the sequential steps (a)-(c):

- (a) polymerising ethylene and optionally an α -olefin comonomer in the first polymerisation stage to produce a lower molecular weight ethylene (LMW) polymer;
- (b) polymerising ethylene and optionally an α -olefin comonomer in the second polymerisation stage to produce a first higher molecular weight ethylene polymer (HMW1); and
- (c) polymerising ethylene and optionally an α -olefin comonomer in the third polymerisation stage to produce a second higher molecular weight ethylene polymer (HMW2), wherein the molecular weight of the components increases in the order $LMW < HMW1 < HMW2$.

or

~~44.~~ A process as claimed in ~~any one of claims 40 to 42~~, comprising the sequential steps (a)-(c):

- (a) polymerising ethylene and optionally an α -olefin comonomer in the first polymerisation stage to produce a lower molecular weight ethylene polymer (LMW);
- (b) polymerising ethylene and optionally an α -olefin comonomer in the second polymerisation stage to produce a second higher molecular weight ethylene polymer (HMW2); and
- (c) polymerising ethylene and optionally an α -olefin comonomer in the third polymerisation stage to produce a first higher molecular weight ethylene polymer (HMW1), wherein the molecular weight of the components increases in the order $LMW < HMW1 < HMW2$.

1245. A process as claimed in any preceding claim~~any one of claims 1 to 44~~, wherein there is no reactor fouling in said second polymerisation stage.

1346. A process as claimed in ~~any one of claims 40 to 44~~claim 10 or claim 11, wherein there is no reactor fouling in said third polymerisation stage.

~~47. — A process as claimed in any one of claims 1 to 46, wherein said process is semi-continuous or continuous.~~

~~48. — A process as claimed in claim 47, wherein said process is continuous.~~

1449. A process as claimed in any one of claims 1 to 39 or claim 12 ~~any one of claims 45 to 48 when not dependent on claims 40 to 44~~, wherein said multimodal polyethylene has a bimodal molecular weight distribution.

1550. A process as claimed in any one of claims 1 to ~~336, 40 to 44~~10, 11, 13, or 46 ~~or any one of claims 38, 39, 45, 47, or 48~~claim 12 when not dependent on claim ~~937~~, wherein said multimodal polyethylene has a trimodal molecular weight distribution.

1651. A process as claimed in any preceding claim ~~any one of claims 1 to 50~~, wherein said multimodal polyethylene has:
a Mw of 100,000 to 250,000 g/mol.

~~52. — A process as claimed in any one of claims 1 to 51, wherein said multimodal polyethylene has
a Mn of 18,000 to 40,000 g/mol.~~

~~53. — A process as claimed in any one of claims 1 to 52, wherein said multimodal polyethylene has a MWD of greater than 1 and no more than 25.~~

~~54. — A process as claimed in any one of claims 1 to 53, wherein said multimodal polyethylene has a MFR₂ of 0.005 to 0.2 g/10min.~~

~~55. — A process as claimed in any one of claims 1 to 54, wherein said multimodal polyethylene has a MFR₅ of 0.05 to 1 g/10min.
an ash content of 0 to 800 wt ppm
a density of 920 to 980 kg/dm³
a bulk density of 250 to 400 g/dm³; and/or~~

less than 100 wt ppm of material of hardness more than 3 on Moh's scale.

1756. A process as claimed in any preceding claim~~any one of claims 1 to 55~~, wherein said multimodal polyethylene comprises 0.5 to 10 %wt comonomer.

~~57. A process as claimed in any one of claims 1 to 56, wherein said multimodal polyethylene has a density of 920 to 980 kg/dm³.~~

~~58. A process as claimed in any one of claims 1 to 57, wherein said multimodal polyethylene has a bulk density of 250 to 400 g/dm³.~~

~~59. A process as claimed in any one of claims 1 to 58, wherein said multimodal polyethylene has an ash content of 0 to 800 wt ppm.~~

~~60. A process as claimed in any one of claims 1 to 59, wherein said multimodal polyethylene contains less than 100 wt ppm of material of hardness more than 3 on Moh's scale.~~

1864. A process as claimed in any preceding claim~~any one of claims 1 to 60~~, wherein said multimodal polyethylene is in the form of particles.

1962. A process as claimed in any preceding claim~~any one of claims 1 to 61~~, wherein said first ethylene polymer has a MFR₂ of at least 10 g/10min.

~~63. A process as claimed in any one of claims 1 to 62, wherein said first ethylene polymer has, preferably, a MFR₂ of 10 to 1000 g/10min.~~

2064. A multimodal polyethylene obtained by a process as claimed in any preceding claim~~any one of claims 1 to 63~~.

2165. A metallocene multimodal polyethylene comprising:

- i) a multimodal molecular weight distribution;

- ii) a weight average molecular weight of at least 50,000 g/mol;
- iii) a MFR₂ of less than 0.2 g/10min;
- iv) a MFR₅ of less than 1 g/10min;
- v) a bulk density of at least 250 g/dm³; and
- vi) an ash content of less than 800 ppm wt.

~~66.~~—A metallocene multimodal polyethylene as claimed in claim 65, wherein and preferably wherein said metallocene multimodal polyethylene contains less than 100 wt ppm of material of hardness more than 3 on Moh's scale.

2267. A process for preparing a pipe comprising:

- i) preparing a multimodal polyethylene by the process claimed in any one of claims 1 to 1963; and
- ii) extruding said multimodal polyethylene to produce pipe.

2368. A pipe obtained by a process as claimed in claim 2267.

~~69.~~—A pipe or comprising a metallocene multimodal polyethylene as claimed in any one of claims ~~64 to 66~~20 to 21.