Abstract:

Title: PROCESS FOR THE MANUFACTURE OF A MLXED CATALYST SYSTEM FOR THE COPOLYMERIZATION OF ETHYLENE WITH C1-C12 ALPHA-OLEFINs

A novel process for the manufacture of a mixed catalyst system by combining a Ziegler catalyst and a tridentate iron complex is described, which is characterized in that the reaction of a tridentate ligand with an iron compound is performed in an organic solvent containing less than 10 percent by weight, based on the total amount of the organic solvent, of electron donor compounds selected from the group consisting of ethers, aliphatic esters, aromatic esters, tertiary amines, amides, silanes, silazanes or orthoesters.
PROCESS FOR THE MANUFACTURE OF A MIXED CATALYST SYSTEM FOR THE
COPOLYMERIZATION OF ETHYLENE WITH C₁₋C₁₂ ALPHA-OLEFINS

The present invention relates to a process for the manufacture of mixed catalyst system comprising
a Ziegler catalyst and a tridentate iron catalysts. In addition, the invention relates to a mixed catalyst
system obtained by that process, to the use of that mixed catalyst system for the manufacture of
copolymers of ethylene and C₁₋C₁₂ alpha-olefins and to the copolymers so obtained.

In WO2008/125208 A2 catalyst systems are disclosed comprising Ziegler catalysts and tridentate
iron or cobalt catalysts. The tridentate iron or cobalt catalysts used in accordance with that
document are manufactured either according to the method described in WO98/27124 or according
to the method of Qian et al., Organometallics 2003, 22, 431-4321. Both methods are based on a
reaction of the particular preformed ligands with e.g. FeCl₂. The reaction between the ligand and the
Fe compound is always performed in THF as organic solvent. Also other methods described in the
prior art for the manufacture of the particular tridentate iron catalysts are performed in polar organic
solvents. In WO99/46302 e.g. the respective reaction (example 9.2) is performed in n-butanol.

The mixed catalyst systems obtained by the methods disclosed in the prior art have the
disadvantage that the ethylene co-polymers produced by these catalyst systems have a low
incorporation of comonomer in the high molecular weight polymer fraction. On the other hand it is
one of the purposes of applying mixed catalyst systems to provide a considerable incorporation of
comonomers into the high molecular weight polymer fraction because such copolymers have in
particular good physical properties.

It is thus the object of the present invention to provide process for the manufacture of a catalyst
system which, when used for the polymerization of ethylene together with C₁₋C₁₂ copolymers, results
in copolymers having a broad molecular weight distribution and a good comonomer incorporation
even at the very high molecular weight fraction of the copolymer.

We have found that this object can be achieved by using a process for the manufacture of a mixed
catalyst system by combining a Ziegler catalyst and a tridentate iron complex corresponding to the
general formula (A)
on a granular support and in which the tridentate iron complex (A) is obtained by the reaction of a ligand (L) with an iron compound FeX₃, wherein the variables have the following meaning:

E₁ - E₃ independently of one another are carbon, nitrogen or phosphorus,

R¹ - R³ are each, independently of one another, hydrogen, C₅-C₂₀-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl which may in turn bear C₁-C₁₀-alkyl groups as substituents, Cₕ-C₂₀-alkenyl, Cₗ-C₄₀-aryl, arylalkyl having from 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part,

-NR₁², -OR₁¹, or -SiR₂³ or a five-, six- or seven-membered heterocycle, which comprises at least one atom from the group consisting of nitrogen, phosphorus, oxygen and sulfur, where the radicals R¹ to R³ may also be substituted by halogen, -NR₁², -OR₁¹, or -SiR₂³ and/or two radicals R¹ to R³, in particular adjacent radicals, together with the atoms connecting them may be joined to form a preferably 5-, 6- or 7-membered ring or a preferably 5-, 6- or 7-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorus, oxygen and sulfur, where
are each, independently of one another, C<sub>1</sub>-C<sub>10</sub>-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C<sub>5</sub>-C<sub>12</sub>-alkenyl, C<sub>6</sub>-C<sub>22</sub>-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, where the organic radicals R<sup>11</sup> may also be substituted by halogens and/or two radicals R<sup>11</sup> may also be joined to form a five-, six- or seven-membered ring, or SiR<sup>12</sup> and

R<sup>12</sup> can be identical or different and can each be C<sub>1</sub>-C<sub>10</sub>-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C<sub>5</sub>-C<sub>12</sub>-alkenyl, C<sub>6</sub>-C<sub>22</sub>-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, C<sub>1</sub>-C<sub>10</sub>-alkoxy or C<sub>6</sub>-Cl<sub>10</sub>-aryloxy, where the organic radicals R<sup>12</sup> may also be substituted by halogens and/or two radicals R<sup>11</sup> may also be joined to form a five-, six- or seven-membered ring;

u independently of one another is 0 if the respective atom E is nitrogen or phosphorous and 1 if the respective atom E is carbon,

R<sup>4</sup>, R<sup>5</sup> are each, independently of one another, hydrogen, Cl-C<sub>22</sub>-alkyl, C<sub>2</sub>-C<sub>12</sub>-alkenyl, C<sub>6</sub>-C<sub>40</sub>-aryl, aryalkyl having from 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, -NR<sup>11</sup> or -SiR<sup>12</sup> where the radicals R<sup>4</sup> and R<sup>5</sup> may also be substituted by halogen and/or two radicals R<sup>4</sup> and R<sup>5</sup>, may be joined to form a preferably 5-, 6- or 7-membered ring or a preferably 5-, 6- or 7-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorous, oxygen and sulfur,

v independently of one another, are 0 or 1, and when v is 0 the bond between the nitrogen and the carbon atom bearing radical R<sup>4</sup> is a double bond and in formula (L) no hydrogen is covalently bonded to that nitrogen atom,

R<sup>6</sup> to R<sup>10</sup> are each, independently of one another, hydrogen, Cl-C<sub>20</sub>-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C<sub>2</sub>-C<sub>12</sub>-alkenyl, C<sub>6</sub>-C<sub>40</sub>-aryl, aryalkyl having from 1 to 10 carbon atoms in the alkyl radical and 6-20 carbon atoms in the aryl radical, halogen, -NR<sup>11</sup>, -OR<sup>11</sup> or -SiR<sup>12</sup>, where the organic radicals R<sup>6</sup> to R<sup>10</sup> may also be substituted by halogens and/or two vicinal radicals R<sup>6</sup> to R<sup>10</sup> may also be joined to form a five-, six- or seven-membered ring, and/or two vicinal radicals R<sup>6</sup> to R<sup>10</sup> are joined to form a five-, six- or seven-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorous, oxygen and sulfur,
M is iron,

X independently of one another are fluorine, chlorine, bromine, iodine, hydrogen, C-alkyl, C₂-C₆i₀-alkenyl, C₆-C₄0-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part,

-β-diketonate, -CO, BF₄⁻, PF₆⁻ or bulky non-coordinating anions, wherein the organic radicals X can also be substituted by halogens and/or at least one radical R thirteen, and the radicals X are optionally bonded with one another,

R thirteen independently of one another are hydrogen, C₁-C₆₂-alkyl, C₂-C₂₂-alkenyl, C₆-C₄₀-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, or SiR thirteen, wherein the organic radicals R thirteen can also be substituted by halogens, and/or in each case two radicals R thirteen can also be bonded with one another to form a five- or six-membered ring,

R fourteen independently of one another are hydrogen, C₁-C₆₀-alkyl, C₂-C₂₀-alkenyl, C₆-C₄₀-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, wherein the organic radicals R fourteen can also be substituted by halogens, and/or in each case two radicals R fourteen can also be bound to one another to form a five- or six-membered ring,

s is 1, 2, 3 or 4,

characterized in that the reaction of the tridentate ligand (L) with the iron compound MX₄ is performed in an organic solvent containing less than 10 percent by weight, based on the total amount of the organic solvent, of electron donor compounds selected from the group consisting of ethers, aliphatic esters, aromatic esters, tertiary amines, amides, silanes, silazanes or orthoesters.

The present invention further provides a mixed catalyst system which is produced by the above-mentioned process, the use of such mixed catalyst system for the manufacture of copolymers of ethylene and C₂-Cl₂ alpha-olefins, and copolymers of ethylene and C₃-Cl₂ alpha-olefins obtained with such mixed catalyst system.

A general preparation process of a iron complex having a tridentate iron complex is disclosed in WO 98/27124 A1 and in Qian et al., Organometallics 2003, 22, 4312-4321.
Ziegler component

Catalyst components of the Ziegler type are well known and described in the prior art, for example in ZIEGLER CATALYSTS 363-386 (G. Fink, R. Mulhaupt and H. H. Brintzinger, eds., Springer-Verlag 1995).

The catalyst of the Ziegler type preferably comprises a solid component comprising a compound of titanium or vanadium, a compound of magnesium and optionally but preferably a particulate inorganic oxide as support.

The particulate inorganic support used in the present invention is preferably based on a refractory oxide. It may contain hydroxyl functional groups. The support can have a specific surface area (BET) of 50 to 1 000 m²/g, e.g. 100 to 600 m²/g and a pore volume of 0.5 to 5 ml/g, e.g. 1 to 3 ml/g. The quantity of hydroxyl groups in the support depends on the support employed, on its specific surface area, on the physico-chemical treatment and on the drying to which it may have been subjected beforehand. A granular support which is ready for use generally contains from 0.1 to 5, preferably from 0.5 to 3 millimols of hydroxyl groups per gram. The granular support is preferably anhydrous at the time of its use in the catalyst preparation. For this purpose, it is preferably dehydrated by means which are known per se, such as a heat treatment ranging from 100°C to 950°C, e.g. 150°C to 800°C. The support can be chosen, in particular, from a silica, an alumina, a silica-alumina, or a mixture of these oxides. It can consist of particles which have a weight-average diameter ranging from 20 to 250 µm, preferably 30 to 200 µm, especially 50 to 150 mm. Preferably, particles of the support used, are spherical or spheroidal.

The support is preferably contacted with an organosilicon compound. The organosilicon compound can have the general formula SiR₁⁵₋₁₅ Y₄₋₄m in which R₁⁵ is an alkyl group having for example from 1 to 6 carbon atoms, Y a halogen atom such as chlorine or bromine, or an alkoxy group having for example from 1 to 6 carbon atoms and m is from 1 to 4, preferably from 1 to 3. Silanes such as diethoxymethylsilane (DEODMS), methyltrimethoxysilane, methyltrithoxysilane and tetraethoxysilane can be used. The organosilicon compound can also be a compound comprising trialkylsilyl radicals and amine groups, preferably a silazane or a disilazane such as hexamethyldisilazane (CH₃)₃Si-NH-Si(CH₃)₃ (HMDS).

The contact between the support and the organosilicon compound is preferably the first step in the preparation of the catalyst. Thus, the organosilicon compound can advantageously be used in order to decrease the content of hydroxyl functional groups in the support by reacting with the said groups. The contact can be, for example, carried out in a liquid hydrocarbon using from 0.1 to 10 mols, preferably from 0.5 to 5 mols, of organosilicon compound per g of granular support, at a temperature ranging from 20 to 120°C, preferably 50 to 100°C. This can take from 10 minutes to 10 hours. At the
end of this contact step the granular support obtained is washed once or several times with a liquid hydrocarbon.

Usually the support is treated with a dialkylmagnesiunn compound. The dialkylmagnesiunn compound is preferably of general formula MgR\textsubscript{16}R\textsubscript{17} optionally mixed or complexed with a trialkylaluminium of general formula AlR\textsubscript{19}R\textsubscript{20} in which R\textsubscript{16}, R\textsubscript{17}, R\textsubscript{19} and R\textsubscript{20} are identical or different alkyl radicals containing from 1 to 12 carbon atoms, preferably from 2 to 8 carbon atoms. The quantity of trialkylaluminium used preferably does not exceed a molar ratio of 1:1 relative to the dialkylmagnesiunn. In particular the molar ratio is from 0.01/1 to 1/1, e.g. 0.1/1 to 0.5/1.

Dibutylmagnesium, dihexylmagnesium, butylethylmagnesium, ethylhexylmagnesium or butyloctylmagnesium is preferably employed. The preferred trialkylaluminium compound is triethylaluminium. The contact step between the support and the dialkylmagnesiunn is preferably performed following the contact between the support and the organosilicon compound. It can be, for example, carried out as described in EP-A 453 088. Typically, from 0.1 to 8, preferably from 0.5 to 4 millimols of dialkylmagnesiunn per g of granular support are used. The support obtained can contain from 0.1 to 4, preferably from 0.5 to 2.5 millimols of magnesium per g of support. It can be washed with a liquid hydrocarbon.

The process for preparing the Ziegler catalyst further comprises contacting the support with a monochloro-organic compound. This compound can be a secondary or preferably tertiary alkyl monochloride containing 3 to 19, preferably 3 to 13 carbon atoms and having the following general formula R\textsubscript{3}R\textsubscript{22}R\textsubscript{3}CCI in which R\textsubscript{1} and R\textsubscript{22} are identical or different alkyl radicals containing from 1 to 6, e.g. 1 to 4 carbon atoms such as methyl, ethyl or n-propyl and R\textsubscript{23} is a hydrogen atom or, preferably, an alkyl radical containing from 1 to 6, e.g. 1 to 4 carbon atoms, identical to or different from R\textsubscript{1} and R\textsubscript{22}, such as methyl, ethyl or n-propyl. Secondary propyl chloride, secondary butyl chloride, but especially tertbutyl chloride are preferred.

The monochloro-organic compound can also be a secondary or preferably tertiary cycloalkyl monochloride of general formula: (CH\textsubscript{2})\textsubscript{n}CR\textsubscript{24}CCI in which R\textsubscript{24} is a hydrogen atom or, preferably, an alkyl radical containing from 1 to 6, e.g. 1 to 4 carbon atoms such as methyl or ethyl and n is a number from 4 to 8, e.g. 5 to 8, especially 5. Such a compound can be cyclohexyl chloride or 1-methyl-1 chlorocyclohexane.

The monochloro-organic compound can also be a compound containing at least one aryl radical, of general formula: R\textsubscript{25}R\textsubscript{26}R\textsubscript{27}CCI in which R\textsubscript{25} is an aryl radical containing from 6 to 16, e.g. 6 to 10 carbon atoms and R\textsubscript{26} and R\textsubscript{27} are identical or different radicals chosen from hydrogen, alkyl radicals containing from 1 to 6, e.g. 1 to 4 carbon atoms such as methyl, ethyl or n-propyl, and aryl radicals containing from 6 to 16, e.g. 6 to 10 carbon atoms, identical to or different from R\textsubscript{25}. The aryl radicals for R\textsubscript{25}, R\textsubscript{26} and/or R\textsubscript{27} are usually aromatic hydrocarbyl groups such as phenyl, toluyl or naphthyl.
Benzyl chloride and 1-phenyl-1-chloroethane are preferred.

The contact step between the granular support and the monochloro-organic compound is in most cases preferably carried out following the contact step between the support and the dialkylmagnesium compound and can, for example, be carried out as described in EP-A-0 453 088. Typically, from 0.2 to 10 millimols of monochloro-organic compound are used per g of granular support.

The process comprises also contacting the support with a tetravalent titanium compound. The tetravalent titanium compound is preferably soluble in the hydrocarbon liquid medium in which the catalyst is prepared. Preferably, the tetravalent titanium compound is of general formula: \( \text{Ti(OR}^{2n})_{n}Z_{4-n} \) in which \( R \) is an alkyl radical containing from 1 to 6, e.g. 2 to 4 carbon atoms, e.g. methyl, ethyl, propyl, isopropyl or butyl, \( Z \) is a chlorine or bromine atom, \( n \) is whole or fractional from 0 to 4, e.g. 0 to 3. The use of titanium tetrachloride and isopropoxy titanium (IV) is preferred. However, when the catalyst is used for the manufacture of a linear low density polyethylene, it is preferred to use a low halogenated titanium compound, for example, a compound having the above formula in which \( n \) is greater than 0.5. Preferably, from 0.05 to 1 mol of titanium is used per mol of magnesium in the support.

According to the invention, the granular support is preferably not contacted with an electron-donor compound, preferably the resultant catalyst composition comprises a content of electron-donor compounds as low as possible. The resultant catalyst should comprise not more than 0.05 mol preferably not more than 0.01 mol of electron donor compound per mol of magnesium in the granular support. Typical electron donor compounds are ethers, such as propyl ether or butyl ether; a cyclic ether, such as tetrahydrofuran, or dioxane; a polyether, preferably a diether such as dimethyl ethylene glycol ether or 2,2-dimethoxypropane. Further electron donor compounds are aliphatic esters, such as ethyl acetate; aromatic esters, such as ethylbenzoate; an aromatic polyester such as dibutyl phthalate; a tertiary amine, such as triethylamine; an amide such as dimethylformamide; a silane, such as tetraethoxysilane, methyltriethoxysilane, methyltrimethoxysilane or dichlorodimethoxysilane; a silazane, such as hexamethyldisilazane; or orthoester such as triethylorthooacetate. Typical electron donor compounds are tetrahydrofuran, triethylorthooacetate, dimethylformamide or tetraethoxysilane.

The process can also comprise one or more contacts between the granular support and an organometallic compound, in addition to the dialkylmagnesium compound, which can be used to reduce the titanium compound. The reduction of the titanium compound can be partial. The organometallic compound is typically a compound of a metal belonging to group II or III of the periodic classification of the elements. For example, it is possible to use organoaluminium, organomagnesium or organozinc compounds. It is preferred to use triethylaluminium.
triisobutylaluminium, tri-n-hexylaluminium or tri-n-octylaluminium.

The contact step between the support and the organometallic compound is preferably performed prior to contacting the support with the titanium compound. It is advantageously also performed after contacting the support with the monochloro-organic compound. The step can be carried out in a liquid hydrocarbon, such as n-heptane, using from 0.1 to 5 mol organometallic compound per mol of magnesium in the support. Typically, from 0.2 to 1 mol of organometallic compound per mol of magnesium in the support is used. It is preferably carried out at a temperature from 20 to 120°C, preferably 20 to 100°C and usually takes from 10 minutes to 10 hours. The obtained support can be washed once or several times with a liquid hydrocarbon.

According to the present invention, the support or the final catalyst can be dried for example at a temperature from 20 to 200°C, preferably from 50 to 150°C. The drying operation can be carried out by passing a stream of dry nitrogen through the stirred support or final catalyst. Preferably, the support is dried after being contacted with an electron donor compound. It also can be dried after being contacted with an organometallic compound.

Tridentate iron complex

According to this invention the second active catalyst component is an iron complex of the general formula (A),

wherein the variables have the meaning defined above.

The substituents $R^1$-$R^3$ can be varied within a wide range. Possible carboorganic substituents $R^1$-$R^3$ are, for example, the following: C$_1$-C$_{12}$-alkyl which may be linear or branched, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear C$_1$-C$_{10}$-alkyl groups as substituents,
e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, \(C_2-C_{22}\)-alkenyl which may be linear, cyclic or branched and in which the double bond may be internal or terminal, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, \(C_6-C_{40}\)-aryl which may be substituted by further alkyl groups, e.g. phenyl, naphthyl, biphenyl, anthranyl, \(o\)-, \(m\)-, \(p\)-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, \(o\)-, \(m\)-, \(p\)-methylbenzyl, 1- or 2-ethylphenyl, where two vicinal radicals \(R^1\) to \(R^3\) are optionally joined to form a 5-, 6- or 7-membered carbon ring or a five-, six- or seven-membered heterocycle containing at least one atom from the group consisting of N, P, O and S and/or the organic radicals \(R^1\)-\(R^3\) are unsubstituted or substituted by halogens such as fluorine, chlorine or bromine. Furthermore, \(R^1\)-\(R^3\) can also be amino \(NR_{12}\) or \(N(SiR_{12})_{2}\), alkoxy or arloxy \(OR_{11}\), for example dimethylamino, N-pyrrolidinyl, picolinyl, methoxy, ethoxy or isopropoxy or halogen such as fluorine, chlorine or bromine.

Preferred radicals \(R^1\)-\(R^3\) are hydrogen, methyl, trifluoromethyl, ethyl, \(n\)-propyl, isopropyl, \(n\)-butyl, isobutyl, tert-butyl, \(n\)-pentyl, \(n\)-hexyl, \(n\)-heptyl, \(n\)-octyl, \(n\)-decyl or \(n\)-dodecyl, 5- to 7-membered cycloalkyl which is unsubstituted or bears a \(C_1-C_{10}\)-alkyl group and/or \(C_6-C_{10}\)-aryl group as substituent, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, \(C_2-C_{22}\)-alkenyl which is linear, cyclic or branched and in which the double bond is internal or terminal, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, \(C_6-C_{22}\)-aryl which is may be substituted by further alkyl groups, e.g. phenyl, naphthyl, biphenyl, anthranyl, \(o\)-, \(m\)-, \(p\)-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, \(o\)-, \(m\)-, \(p\)-methylbenzyl, 1- or 2-ethylphenyl, where the organic radicals \(R^4\) and \(R^5\) are unsubstituted or substituted by halogens such as fluorine, chlorine or bromine. Furthermore, \(R^4\) and \(R^5\) can be amino \(NR_{11}\) or \(N(SiR_{12})_{2}\), for example dimethylamino, N-pyrrolidinyl or picolinyl. Possible radicals \(R^{10}_{12}\) in organosilicon substituents \(SiR^{10}_{13}\) are the same carboorganic radicals as described above for \(R^1\)-\(R^3\) in formula (A), where two radicals \(R^{12}\) may also be joined to form a 5- or 6-membered ring, e.g. trimethylsilyl, triethylsilyl, butyldimethylsilyl, tributylsilyl, tert-butylsilyl, triallylsilyl, triphenylsilyl or dimethylphenylsilyl. These \(SiR_{12}\) radicals can also be bound via nitrogen to the carbon bearing them.
Preferred radicals $R^4$ are hydrogen, methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl or benzyl, in particular hydrogen or methyl.

The variable $v$ denotes the number of $R^5$ radicals. It is especially preferred that $v$ is 0 and $R^5$ forms a double bond to the nitrogen atom bearing the aryl substituent.

The substituents $R^6$-$R^{10}$ can be varied within a wide range. Possible carboorganic substituents $R^6$-$R^{10}$ are, for example, the following: $C_1$-$C_{22}$-alkyl which may be linear or branched, e.g. methyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-hexyl, n-heptyl, n-octyl, n-nonyl, n-decyl or n-dodecyl, 5- to 7-membered cycloalkyl which may in turn bear a $C_1$-$C_{10}$-alkyl group and/or $C_0$-$C_{10}$-aryl group as substituents, e.g. cyclopropyl, cyclobutyl, cyclopentyl, cyclohexyl, cycloheptyl, cyclooctyl, cyclononyl or cyclododecyl, $C_2$-$C_{22}$-alkenyl which may be linear, cyclic or branched and in which the double bond may be internal or terminal, e.g. vinyl, 1-allyl, 2-allyl, 3-allyl, butenyl, pentenyl, hexenyl, cyclopentenyl, cyclohexenyl, cyclooctenyl or cyclooctadienyl, $C_0$-$C_{22}$-aryl which may be substituted by further alkyl groups, e.g. phenyl, naphthyl, biphenyl, anthranyl, o-, m-, p-methylphenyl, 2,3-, 2,4-, 2,5- or 2,6-dimethylphenyl, 2,3,4-, 2,3,5-, 2,3,6-, 2,4,5-, 2,4,6- or 3,4,5-trimethylphenyl, or arylalkyl which may be substituted by further alkyl groups, e.g. benzyl, o-, m-, p-methylbenzyl, 1- or 2-ethylphenyl, where two vicinal radicals $R^6$-$R^{10}$ are optionally joined to form a 5-, 6- or 7-membered ring and/or a five-, six- or seven-membered heterocycle containing at least one atom from the group consisting of N, P, O and S and/or the organic radicals $R^6$-$R^{10}$ are unsubstituted or substituted by halogens such as fluorine, chlorine or bromine. Furthermore, $R^6$-$R^{10}$ can also be amino NR$_2$ or N(SiR$_3$)$_2$, alkoxy or aryloxy OR$^1$, for example dimethy lamino, N-pyrrolidinyl, picolinyl, methoxy, ethoxy or isopropoxy or halogen such as fluorine, chlorine or bromine. Possible radicals $R^{12}$ in organosilicon substituents SiR$_2$ are the same carboorganic radicals as have been described above for in formula (A).

Preferred radicals $R^5$, $R^7$ are methyl, trifluoromethyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl, allyl, benzyl, phenyl, fluorine, chlorine and bromine.

In particular, $R^5$ are each a $C_1$-$C_{22}$-alkyl which may also be substituted by halogens, in particular a $C_1$-$C_{22}$-aryl which may also be substituted by halogens, e.g. methyl, trifluoromethyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl, or a halogen such as fluorine, chlorine or bromine and $R^7$ are each a halogen such as fluorine, chlorine or bromine. Particular preference is given to $R^5$ each being a $C_1$-$C_{22}$-alkyl which may also be substituted by halogens, in particular a $C_1$-$C_{22}$-aryl which may also be substituted by halogens, e.g. methyl, trifluoromethyl, ethyl, n-propyl, n-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl and $R^7$ each being a halogen such as fluorine, chlorine or bromine.
In a preferred embodiment of the invention the process for the manufacture of a mixed catalyst system is applied to a tridentate iron complex in which \( R^6 \) or \( R^7 \) is halogen, most preferably chlorine. In that case the other substituent \( R^6 \) or \( R^7 \) is preferably a hydrogen or a \( \text{Cl-C}_8 \) alkyl group, preferably a methyl group.

Preferred radicals \( R^5-R^{10} \) are hydrogen, methyl, trifluoromethyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl, allyl, benzyl, phenyl, fluorene, chlorine and bromine, in particular hydrogen. It is in particular preferred, that \( R^5 \) are each methyl, trifluoromethyl, ethyl, n-propyl, isopropyl, n-butyl, isobutyl, tert-butyl, n-pentyl, n-hexyl, n-heptyl, n-octyl, vinyl, allyl, benzyl, phenyl, fluorene, chlorine or bromine and \( R^6 \) and \( R^{10} \) are each hydrogen.

In the most preferred embodiment the radicals \( R^5 \) and \( R^{10} \) are identical, \( R^6 \) are identical, \( R^9 \) are identical, and \( R^{10} \) are identical.

In a preferred embodiment of the invention the process for the manufacture of a mixed catalyst system is applied to a tridentate iron complex in which \( E^1-E^3 \) are all carbon.

The ligands \( X \) result, for example, from the choice of the appropriate starting iron compounds used for the synthesis of the iron complexes, but can also be varied afterwards. Possible ligands \( X \) are, in particular, the halogens such as fluorine, chlorine, bromine or iodine, in particular chlorine. Alkyl radicals such as methyl, ethyl, propyl, butyl, vinyl, allyl, phenyl or benzyl are also usable ligands \( X \). As further ligands \( X \), mention may be made, purely by way of example and in no way exhaustively, of trifluoroacetate, \( \text{BF}_4^- \), \( \text{PF}_6^- \) and weakly coordinating or noncoordinating anions (cf., for example, S. Strauss in Chem. Rev. 1993, 93, 927-942), e.g. \( \text{B}([\text{C}_2\text{F}_5])_4^- \). Amides, alkoxides, sulfonates, carboxylates and \( \beta \)-diketonates are also particularly useful ligands \( X \). Some of these substituted ligands \( X \) are particularly preferably used since they are obtainable from cheap and readily available starting materials. Thus, a particularly preferred embodiment is that in which \( X \) is dimethylamide, methoxide, ethoxide, isopropoxide, phenoxide, naphthoxide, triflate, p-toluenesulfonate, acetate or acetylacetonate.

The number \( s \) of the ligands \( X \) depends on the oxidation state of \( M \). The number \( s \) can thus not be given in general terms. The oxidation state of \( M \) in catalytically active complexes is usually known to those skilled in the art. However, it is also possible to use complexes whose oxidation state does not correspond to that of the active catalyst. Such complexes can then be appropriately reduced or oxidized by means of suitable activators. Preference is given to using iron complexes in the oxidation state +3 or +2.

In contrast to the complexes known in prior art the iron complexes useful for the mixed catalyst system do not comprise any electron donor compounds as a further ligand such as, for example,
ethers, ketones, aldehydes, esters, tertiary amines, amides, silanes, silazanes, orthoesters, sulfides or phosphines which are bound to the iron. According to the state of the art these electron donor ligands often are still present as residual solvent from the preparation of the iron complexes.

Thus, according to this invention, it is essential that the tridentate iron complex (A) is obtained by the reaction of a ligand (L) with a iron compound FeXs and that reaction is performed in an organic solvent containing less than 10 percent by weight, based on the total amount of the organic solvent, of electron donor compounds selected from the group consisting of ethers, aliphatic esters, aromatic esters, tertiary amines, amides, silanes, silazanes or orthoesters. Preferably the organic solvent contains less than 5 percent by weight of the electron donor compounds and most preferably less than 1 percent by weight, based on the total amount of the organic solvent, of the electron donor compound. The reaction of ligand (L) with the iron compound is preferably performed in an aromatic organic solvent such as toluene with less than 10 percent by weight of electron donor compounds.

In a preferred embodiment of this invention the electron donor compounds which should be present only in a limited amount, are selected from the group consisting of tetrahydrofuran, triethylorthoacetate, dimethylformamide and tetraethoxysilane. Most preferably the organic solvent shall contain less than 10 percent by weight, ideally less than 1 percent by weight, based on the total amount of organic solvent, of tetrahydrofuran.

In a preferred embodiment the tridentate iron complex is prepared according to a method wherein to a solution of ligand in a non-polar solvent an iron halogenide is added in a molar excess to the ligand. During the preparation process it is preferred that no compounds shall be used forming electron donor ligands during preparation of the complex.

The catalyst composition of the invention or the catalyst system is suitable for preparing polyethylene which has advantageous use and processing properties.

The combination of the Ziegler catalyst and the tridentate iron complex (A) on a granular support can be performed in different ways. It is possible to contact the tridentate iron complex with the supported Ziegler catalyst and then activate the tridentate iron complex (A) with suitable activators. Such activators are well known in the art. Suitable activators are e.g. non-coordinating anions such as boronic acid derivatives and in particular tetraalkylammonium salts of tetrakis-pentafluorophenyl borate can be used for activating the tridentate iron complex (A). Also very convenient is the use of methylalumoxane (MAO).

According to a preferred embodiment of the instant invention the process for the manufacture of the mixed catalyst system comprises a step in which the tridentate iron complex is activated with methyl
alumoxane in a solvent, preferably in toluene, and the resulting solution is combined with a supported Ziegler catalyst.

The mixed catalyst system obtained by the process according to the instant invention reveals surprising properties. When used for the polymerization of ethylene with alpha-olefins the resulting copolymers have a broad molecular weight distribution and have in particular a considerable comonomer content in the very high molecular weight fraction. Such comonomer content is very desirable is not obtained using similar catalyst systems manufactured by other processes.

Because of the significant comonomer incorporation in the high molecular weight fraction the mixed catalyst system according to this invention is in particular suitable for the manufacture of copolymers of ethylene and C₃⁻Cl₂ alpha-olefins and in particular C₃⁻C₈ alpha-olefins.

In the copolymerization process of the invention, ethylene is polymerized with α-olefins having from 3 to 12 carbon atoms. Preferred α-olefins are linear or branched C₃⁻Cl₂ 1-alkenes, preferably linear C₃⁻Cl₂ 1-alkenes such as propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene, 1-decene or branched C₃⁻Cl₂ 1-alkenes such as 4-methyl-1-pentene. Particularly preferred α-olefins are C₄⁻ C₁₂ 1-alkenes, preferably linear C₄⁻Cl₂ 1-alkenes and in particular 1-butene and 1-hexene. It is also possible to polymerize mixtures of various α-olefins. Preference is given to polymerizing ethylene with at least one α-olefin selected from the group consisting of propene, 1-butene, 1-pentene, 1-hexene, 1-heptene, 1-octene and 1-decene. Monomer mixtures comprising at least 50 mol% of ethylene are preferably used.

The copolymers of this invention show improved comonomer incorporation at very high molecular weights. With the mixed catalyst systems achieved by the process of this invention copolymers can be obtained which show in addition to the comonomer incorporated in polymer chains having a molecular weight between 10 000 and 100 000 g/mol a further peak of comonomer incorporation at very higher molecular weights, usually at a molecular weight between 100 000 and 1 000 000 g/mol. In copolymer products prepared by mixed catalyst systems known in the prior art the comonomer distribution has only one maximum at the mean molecular weight of the higher molecular weight component while at highest molecular weights the comonomer incorporation decreases to almost zero. With the new catalyst system of the present invention it is possible to provide copolymer products showing comonomer incorporation even at highest molecular weights. These copolymer products have advantages in view of abrasion and stress cracking resistance.

The mixed catalyst systems of this invention can be used for the manufacture of copolymers of ethylene with C₂⁻Cl₂ alpha-olefins. The respective processes for the polymerization of ethylene with α-olefins can be carried out using all industrially known polymerization processes at temperatures in the range from 60 to 350°C, preferably from 0 to 200°C and particularly preferably from 70 to 150°C, and under pressures of from 0.5 to 4000 bar, preferably from 1 to 100 bar and particularly preferably
from 3 to 40 bar. The polymerization can be carried out in a known manner in bulk, in suspension, in the gas phase or in a supercritical medium in the customary reactors used for the polymerization of olefins. It can be carried out batchwise or preferably continuously in one or more stages. High-pressure polymerization processes in tube reactors or autoclaves, solution processes, suspension processes, stirred gas-phase processes and gas-phase fluidized-bed processes are all possible.

The mean residence times of catalyst particles in the reactors are usually from 0.5 to 5 hours, preferably from 0.5 to 3 hours. The advantageous pressure and temperature ranges for carrying out the polymerizations usually depend on the polymerization method. In the case of high-pressure polymerization processes, which are usually carried out at pressures of from 1000 to 4000 bar, preferably from 2000 to 3500 bar, high polymerization temperatures are generally also set. Advantageous temperature ranges for these high-pressure polymerization processes are from 200 to 320°C, preferably from 220 to 290°C. In the case of low-pressure polymerization processes, a temperature which is at least a few degrees below the softening temperature of the polymer is generally set. In particular, temperatures of from 50 to 180°C, preferably from 70 to 120°C, are set in these polymerization processes. In the case of suspension polymerizations, the polymerization is usually carried out in a suspension medium, preferably in an inert hydrocarbon such as isobutane or mixtures of hydrocarbons or else in the monomers themselves. The polymerization temperatures are generally in the range -20 to 115°C and the pressure is generally in the range from 1 to 100 bar. The solids content of the suspension is generally in the range from 10 to 80%. The polymerization can be carried out either batchwise, e.g. in stirring autoclaves, or continuously, e.g. in tube reactors, preferably in loop reactors.

Among the polymerization processes mentioned, gas-phase polymerization, in particular in gas-phase fluidized-bed reactors, solution polymerization and suspension polymerization, in particular in loop reactors and stirred tank reactors, are particularly preferred. The gas-phase polymerization can also be carried out in the condensed or supercondensed mode, in which part of the recycle gas is cooled to below the dew point and recirculated as a two-phase mixture to the reactor. Furthermore, it is possible to use a multizone reactor in which two polymerization zones are linked to one another and the polymer is passed alternately through these two zones a number of times, with the two zones also being able to have different polymerization conditions. Such a reactor is described, for example, in WO 97/04015. The different or identical polymerization processes can, if desired, be connected in series and thus form a polymerization cascade, as, for example, in the Hostalen® process. Operation of two or more identical or different processes in parallel reactors is also possible. Furthermore, molar mass regulators, for example hydrogen, or customary additives such as antistatics can also be concomitantly used in the polymerizations.

The following examples illustrate the invention without restricting its scope.

Analytical methods:
Density was determined according to DIN EN ISO 1183-1:2004, Method A (Immersion) with compression moulded plaques of 2 mm thickness. The compression moulded plaques were prepared with a defined thermal history: Pressed at 180°C, 20MPa for 8 min with subsequent crystallization in boiling water for 30 min.

The melt flow rate MFR21.6 was determined according to DIN EN ISO 1133:2005, condition G at a temperature of 190°C under a load of 21.6 kg.

The recording of the GPC (Gel Permeation Chromatography) curves was carried out by high-temperature gel permeation chromatography using a method described in ISO 16014-1:2003(E) and ISO 16014-4:2003(E): solvent 1,2,4-trichlorobenzene (TCB), temperature of apparatus and solutions 135 °C and as concentration detector a PolymerChar (Valencia, Paterna 46980, Spain) IR-4 infrared detector, capable for use with TCB. A WATERS Alliance 2000 equipped with the following precolumn SHODEX UT-G and separation columns SHODEX UT 806 M (3x) and SHODEX UT 807 connected in series was used. The solvent was vacuum distilled under nitrogen and was stabilized with 0.025 wt.-% of 2,6-di-tert-butyl-4-methylphenol. The flow rate used was 1 mL/min, the injection was 400 μl and polymer concentration was in the range of 0.01 wt.-% < cone. < 0.05 wt.-%. The molecular weight calibration was established by using monodisperse polystyrene (PS) standards from Polymer Laboratories (now Varian Inc., Essex Road, Church Stretton, Shropshire, SY6 6AX, UK) in the range from 580 g/mol up to 11600000 g/mol and additionally Hexadecane. The calibration curve was then adapted to Polyethylene (PE) by means of the Universal Calibration method according to ISO 16014-2:2003(E). The Mark-Houwing parameters used were for PS: kPS= 0.000121 dL/g, aPS=0.706 and for PE kPE= 0.000406 dL/g, aPE =0.725, valid in TCB at 135 °C. Data recording, calibration and calculation was carried out using NTGPC_Control_V6.3.00 and NTGPC_V6.4.05 (hs GmbH, Hühnstraße 36, D-55437 Ober-Hilbersheim), respectively.

The determination of the short chain branching (SCB/1000C) distribution across the molecular weight distribution was carried out by high-temperature gel permeation chromatography using a method described in ISO 16014-1:2003(E) and ISO 16014-4:2003(E): solvent 1,2,4-trichlorobenzene (TCB), temperature of apparatus and solutions 135 °C. As concentration and composition detector a PolymerChar (Valencia, Paterna 46980, Spain) IR-5 infrared detector was used. For concentration detection the CH signal and for composition determination the CH₃ and the CH₂ signal were recorded. A Polymer Laboratories (now Agilent Technologies Netherlands B.V, Groenelaan 5, 1186 AA Amstelveen, Nederland) PL-XT 220 equipped with the following precolumn SHODEX UT-G and separation column SHODEX UT 806M 20C was used. The solvent was vacuum distilled under nitrogen and used without stabilizer. The flow rate used was 2.5 mL/min, the injection was 400 μl and polymer concentration was in the range of 1.5 mg/mL < cone. < 2.5 mg/mL. The molecular
weight calibration was established by using monodisperse polystyrene (PS) standards from Polymer Laboratories (now Agilent Technologies Netherlands B.V., Groenelaan 5, 1186 AA Amstelveen, Nederland) in the range from 580 g/mol up to 11600000 g/mol and additionally Hexadecane. The calibration curve was then adapted to Polyethylene (PE) by means of the Universal Calibration method according to ISO 16014-2:2003(E). The Mark-Houwling parameters used were for PS: \( k_{ps} = 0.000121 \) dL/g, \( a_{ps} = 0.706 \) and for PE \( k_{pe} = 0.000406 \) dL/g, \( a_{pe} = 0.725 \), valid in TCB at 135 °C. The CH\(_2\)/COOCC calibration in the range of 0 to 30 CH\(_2\)/1000C was carried out using metalloocene-PEs with hexene content determined by means of \(^{13}\)C NMR. The CH\(_2\)/CH\(_2\) signal ratio at the peak maximum was correlated to the SCB/1000C content of the calibration polymers using a second order fit. The SCB/1000C distribution results of the analyzed samples were obtained by correcting the CH\(_2\)/1000C distribution with the CH\(_2\)/1000C contribution of the chain ends. Data recording, calibration and calculation was carried out using Chromatographica_M_V1.0.10 and Chromatographica V 1.0.10 (hs GmbH, Hauptstraße 36, D-55437 Ober-Hilbersheim), respectively.

Example 1

100 g (228 mmol) of 2,6-bis[1-(2-chloro-4,6-dimethylphenylimino)ethyl]pyridine were solved in 680 ml toluene at 38°C in argon atmosphere. To this solution 68 g (0.342 mmol/1.5 eq.) FeCl\(_2\)·4 H\(_2\)O in 90 ml methanol (sat. solution) were added within 10 min. The solution was stirred at room temperature for 3 h. Precipitation started immediately after addition of the iron salt. The suspension was filtered and the filter cake was washed twice with 150 ml methanol in each case, twice with 150 ml toluene in each case, twice with 150 ml heptane in each case and dried.

Example 2

A) Preparation of the Ziegler catalyst

A four liter four-necked round-bottomed flask was charged with 220 g silica gel (Sylpol® 2127) obtained from Grace GmbH & Co. KG, Worms, which had previously been calcinated for 6 hours at 600°C and 700 mL of heptane. The temperature was raised to 50°C. Thereafter hexamethyldisilazane (1.5 mmol per gram of silica gel) obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany was added dropwise within 3 min at 50°C and stirred for 30 min. The liquid phase was decanted and the solid was washed with heptane (500 mL) in three portions. 330 mL of a 1 M in heptane solution of dibutylmagnesium (obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were added at 22°C within 10 minutes and then the suspension was heated to 50°C and stirred for 60 minutes. The temperature was reduced to 22°C and 60 mmol of tert-butyl chloride (obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were added at 22°C. The temperature was increased to 50°C and the suspension was stirred for 60 minutes.
Titanium(IV) chloride (0.15 mmol per gram of silica gel) obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany and 30 ml of heptane were placed in a 250 mL four-necked round-bottomed glass flask and 33 mmol titanium(IV) isopropoxide (obtained from Sigma-Aldrich Chemie GmbH, Steinheim, Germany) were added dropwise within 10 minutes. The solution was stirred for 30 min, added to the suspension prepared above and stirred for 120 min at 50°C. The formed solid was isolated by filtration at 22°C and then washed with heptane (500 ml) in three portions. The catalyst was dried under vacuum at 22°C. Yield: 442 g of a brown powder

The resulting suspension was filtered and washed 3 times with a total of 500 ml of heptane.

The solid was dried at RT at 0 bar.

B) Combining the Ziegler catalyst with the tridentate iron complex and MAO

99.2 g of the Ziegler catalyst component prepared in A) were suspended in 300 mL of toluene. 2.98 mmol of the 2,6-bis[1-(2-chloro-4,6-dimethylphenylimino)ethyl]pyridine iron(II) dichloride prepared in Example 1 were dissolved in 94 mL of a 30 wt.-% solution of methylaluminoxane in toluene (corresponding to 446.5 mmol aluminum; obtained from Albemarle Corporation, Baton Rouge, USA) and stirred for 90 min. The dark brown solution was added dropwise to the suspension of the Ziegler catalyst component in toluene at 22°C and the catalyst was thereafter stirred for 120 min at 22°C.

The solid product was isolated by filtration at 22°C, washed with 200 mL of heptane and dried under vacuum at 22°C for 2 hours. The mixed catalyst had an iron content of 30 µg/µmol Fe per gram of Ziegler catalyst component prepared in Example 2(A).

Examples 3 and 4

Polymerization in fluidized bed reactor

The polymerization was carried out in a stainless steel fluidized bed reactor having an internal diameter of 200 mm equipped with a gas circulation system, cyclone, heat exchanger, control systems for temperature and pressure and feeding lines for ethylene, 1-hexene, nitrogen, hexane and hydrogen. The reactor pressure was controlled to be 2.4 MPa. The catalyst prepared as described in Example 2B was injected in a discontinuous way by means of dosing valve with nitrogen at a rate of 1 g/h into the reactor. In addition, triisobutylaluminum ("TIBA", obtained from Chemtura Organometallics GmbH, Bergkamen, Germany) was added to the reactor in the amount indicated in Table 1. 12 ppm Costelan AS 100 obtained from H. Costenoble GmbH & Co. KG,

Eschborn, Germany and 12 ppm Atmer 163 obtained from of Croda GmbH, Nettetal, Germany were metered into the reactor, where the amount of added Costelan AS 100 or Atmer 163 is specified as weight ratio to the produced polyethylene. Subsequently the feed of ethylene and 1-hexene in the ratio indicated in Table 1 was started.
When reaching steady state in the reactor, the reactor was discharging about 5 kg/h of polyethylene. The hold-up in the reactor was controlled to be 15 kg, giving a mean residence time of 3 hours in the reactor. The discharged polymer powder was dried in a continuous way by flushing with nitrogen. 100 kg of each example were collected and pelletized in a Kobe LCM 50 extruder with a throughput of 57 kg/h and a specific energy of 0.260 kWh/kg. The reaction conditions in the polymerization reactor and the properties of the obtained pelletized polyethylenes are reported in Table 1.

Comparative example C5

Polymerization was carried out as described above with the mixed catalyst prepared as described in Example 2B, except that in the preparation of the catalyst the 2,6-bis[1-(2-chloro-4,6-dimethylphenylimino)ethyl]pyridine was solved in THF instead of in toluene before reacting it with FeCl₂·4 H₂O. All other conditions described in Example 1 were unchanged.

<table>
<thead>
<tr>
<th>Reactor conditions</th>
<th>Example 3</th>
<th>Example 4</th>
<th>Example C5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reactor temperature [°C]</td>
<td>83</td>
<td>83</td>
<td>83</td>
</tr>
<tr>
<td>Reactor pressure [MPa]</td>
<td>2.4</td>
<td>2.4</td>
<td>2.4</td>
</tr>
<tr>
<td>TIBA feed [g/h]</td>
<td>0.10</td>
<td>0.15</td>
<td>0.10</td>
</tr>
<tr>
<td>Ethylene [vol-%]</td>
<td>33</td>
<td>46</td>
<td>48</td>
</tr>
<tr>
<td>H₂ [vol-%]</td>
<td>0.6</td>
<td>0.85</td>
<td>0.5</td>
</tr>
<tr>
<td>Hexene [vol-%]</td>
<td>2.5</td>
<td>2.0</td>
<td>2.4</td>
</tr>
<tr>
<td>Hexene/Ethylene [g/g]</td>
<td>0.060</td>
<td>0.070</td>
<td>0.055</td>
</tr>
</tbody>
</table>

Table 1

Figure 1 shows the molecular weight distribution and the comonomer distribution of polyethylene polymers obtained with the mixed catalyst systems as described in examples 3, 4 and comparative example C5.
Claims

1. A process for the manufacture of a mixed catalyst system by combining a Ziegler catalyst and a tridentate iron complex corresponding to the general formula (A)

![Diagram](A)

on a granular support and in which the tridentate iron complex (A) is obtained by the reaction of a ligand (L)

![Diagram](L)

with an iron compound FeX₅, wherein the variables have the following meaning:

- E₁ - E₃ independently of one another are carbon, nitrogen or phosphorus,
- R¹ - R³ are each, independently of one another, hydrogen, Cl-C₅₂-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl which may in turn bear C₅-C₂₀-alkyl groups as substituents, C₂-C₅₂-alkenyl, C₃-C₄₀-aryl, arylalkyl having from 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part,
- -NR₉, -OR, or -SiR₉₃ or a five-, six- or seven-membered heterocycle, which comprises at least one atom from the group consisting of nitrogen, phosphorus, oxygen and sulfur, where the radicals R¹ to R³ may also be substituted by halogen,
-NR \[^{11}\]_2\,-\mathrm{OR} \[^{11}\], or -\mathrm{SiR} \[^{12}\]_2\, and/or two radicals R\[^{1}\] to R\[^{3}\], in particular adjacent radicals, together with the atoms connecting them may be joined to form a preferably 5-, 6- or 7-membered ring or a preferably 5-, 6- or 7-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorus, oxygen and sulfur, where

\[ \mathrm{R}^{11} \]

each, independently of one another, C\[^{1}\]_\mathrm{r}C\[^{10}\]-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C\[^{2}\]_2- C\[^{22}\]-alkenyl, C\[^{6}\]_6- C\[^{22}\]-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, where the organic radicals R\[^{11}\] may also be substituted by halogens and/or two radicals R\[^{11}\] may also be joined to form a five-, six- or seven-membered ring;

\[ \mathrm{R}^{12} \]

can be identical or different and can each be C\[^{1}\]_\mathrm{r}C\[^{10}\]-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C\[^{2}\]_2- C\[^{22}\]-alkenyl, C\[^{6}\]_6- C\[^{22}\]-aryl, alkylaryl having from 1 to 10 carbon atoms in the alkyl part and from 6 to 20 carbon atoms in the aryl part, C\[^{1}\]_\mathrm{r}C\[^{6}\]-alkoxy or C\[^{6}\]_6\mathrm{Cl}\_\mathrm{o}\,aryloxy, where the organic radicals R\[^{12}\] may also be substituted by halogens and/or two radicals R\[^{4}\]+R\[^{5}\] may also be joined to form a five-, six- or seven-membered ring;

\[ \mathrm{R}^{4}, \mathrm{R}^{5} \]

each, independently of one another, hydrogen, ClC\[^{2}\]_2-alkyl, C\[^{2}\]_2C\[^{22}\]-alkenyl, C\[^{6}\]_6- C\[^{40}\]-aryl, arylalkyl having from 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, -NR \[^{11}\]_2, or -\mathrm{SiR} \[^{12}\]_2, where the radicals R\[^{4}\] and R\[^{5}\] may also be substituted by halogen and/or two radicals R\[^{4}\] and R\[^{5}\], may be joined to form a preferably 5-, 6- or 7-membered ring or a preferably 5-, 6- or 7-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorus, oxygen and sulfur;

\[ \mathrm{v} \]

independently of one another, are 0 or 1, and when \( v \) is 0 the bond between the nitrogen and the carbon atom bearing radical R\[^{4}\] is a double bond and in formula (L) no hydrogen is covalently bonded to that nitrogen atom;

\[ \mathrm{R}^{6} \text{ to } \mathrm{R}^{10} \]

each, independently of one another, hydrogen, ClC\[^{2}\]_2-alkyl, 5- to 7-membered cycloalkyl or cycloalkenyl, C\[^{2}\]_2C\[^{22}\]-alkenyl, C\[^{6}\]_6C\[^{40}\]-aryl, arylalkyl having from 1 to 10 carbon atoms in the alkyl radical and 6-20 carbon atoms in the aryl radical, halogen, -NR \[^{12}\]_2, -\mathrm{OR} \[^{11}\] or -\mathrm{SiR} \[^{12}\]_2, where the organic radicals R\[^{6}\] to R\[^{10}\] may also be substituted by halogens and/or two vicinal radicals R\[^{6}\] to R\[^{10}\] may also be joined to
form a five-, six- or seven-membered ring, and/or two vicinal radicals \( R^6 \) to \( R^1_6 \) are joined to form a five-, six- or seven-membered heterocycle which comprises at least one atom selected from the group consisting of nitrogen, phosphorus, oxygen and sulfur,

\[
M \quad \text{is iron,}
\]

\[
X \quad \text{independently of one another are fluorine, chlorine, bromine, iodine, hydrogen, } C_1^1, C_2^1 \text{-alkyl, } C_2^1 \text{-Cl}_2^1 \text{-alkenyl, } C_6^1 \text{-C}_{40}^1 \text{-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part,}
\]

\[
-NR^1_{13}, -OR^1_{13}, -SR^1_{13}, -SO^1_{2}R^1_{13}, -OC(0)R^1_{13}, -CN, -SCN,
\]

\[
\beta \text{-diketonate, } -CO, BF_{4}^-, PF_{6}^- \text{ or bulky non-coordinating anions, wherein the organic radicals } X \text{ can also be substituted by halogens and/or at least one radical } R^1_{3}, \text{ and the radicals } X \text{ are optionally bonded with another,}
\]

\[
R^1_{3} \quad \text{independently of one another are hydrogen, } C_1^1 \text{-C}_{22}^1 \text{-alkyl, } C_2^1 \text{-C}_{22}^1 \text{-alkenyl, } C_6^1 \text{-C}_{40}^1 \text{-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, or } SiR^1_{3}, \text{ wherein the organic radicals } R^1_{3} \text{ can also be substituted by halogens, and/or in each case two radicals } R^1_{3} \text{ can also be bonded with one another to form a five- or six-membered ring,}
\]

\[
R^1_{4} \quad \text{independently of one another are hydrogen, } C_1^1 \text{-C}_{20}^1 \text{-alkyl, } C_2^1 \text{-C}_{20}^1 \text{-alkenyl, } C_6^1 \text{-C}_{40}^1 \text{-aryl, arylalkyl having 1 to 16 carbon atoms in the alkyl part and 6 to 20 carbon atoms in the aryl part, wherein the organic radicals } R^1_{4} \text{ can also be substituted by halogens, and/or in each case two radicals } R^1_{4} \text{ can also be bound to one another to form a five- or six-membered ring,}
\]

\[
s \quad \text{is } 1, 2, 3 \text{ or } 4,
\]

characterized in that the reaction of the tridentate ligand (L) with the iron compound \( MX_n \) is performed in an organic solvent containing less than 10 percent by weight, based on the total amount of the organic solvent, of electron donor compounds selected from the group consisting of ethers, aliphatic esters, aromatic esters, tertiary amines, amides, silanes, silazanes or orthoesters.

2. A process according to claim 1 in which the organic solvent contains less than 1 percent by weight, based on the total amount of the organic solvent, of the electron donor compounds.
3. A process according to any of the claims 1 or 2 in which the electron donor compounds are selected from the group consisting of tetrahydrofuran, triethylorthoacetate, dimethylformamide and tetraethoxysilane.

4. A process according to any of the preceding claims in which $E^1 - E^3$ are all carbon.

5. A process according to any of the preceding claims in which either $R^6$ or $R^7$ is halogen.

6. A process according to any of the preceding claims in which $v$ is 0 and the bond between the nitrogen and the carbon atom bearing radical $R^4$ is a double bond and in formula (L) no hydrogen is covalently bonded to that nitrogen atom.

7. A process according to any of the preceding claims in which the tridentate iron complex is activated with methylalumoxane in a solvent and the resulting solution is combined with a supported Ziegler catalyst.

8. A mixed catalyst system obtained by a process according to any of the preceding claims.

9. The use of a mixed catalyst system as claimed in claim 8 for the manufacture of copolymers of ethylene and $C_3$-$C_2$ alpha-olefins.

10. Copolymers of ethylene and $C_3$-$C_2$ alpha-olefins obtained by a mixed catalyst system as claimed in claim 8.
FIG. 1

molecular weight distribution (dc/dlogM) of polymer example 3

molecular weight distribution (dc/dlogM) of polymer example 4

molecular weight distribution (dc/dlogM) of polymer example C5

short chain branching (SCB/1000 carbon atoms) of polymer example 3

short chain branching (SCB/1000 carbon atoms) of polymer example 4

short chain branching (SCB/1000 carbon atoms) of polymer example C5
### A. CLASSIFICATION OF SUBJECT MATTER

**INV. C08F210/16**

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

- C08F
- B01J

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic database consulted during the international search (name of database and, where practicable, search terms used)

- EPO-Internal
- WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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<td>US 2010/093956 Al (MIHAN SHAHRAM [DE] ET AL) 15 April 2010 (2010-04-15) paragraphs [0007], [0017], [0050], [0061], [0064], [0095] paragraphs [0120] - [0125]; claims 1, 7, 8, 10, 11; examples 1-3, 5-7</td>
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Further documents are listed in the continuation of Box C.
See patent family annex.

**Date of the actual completion of the international search**

20 July 2012

**Date of mailing of the international search report**

31/07/2012

**Name and mailing address of the ISA**

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**Authorized officer**

Bork, Ana-Mari a
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<td>A</td>
<td>CHEN Y ET AL: &quot;HALOGEN-SUBSTITUTED 2,6-BIS(IMINO) PYRIDYL I RON AND COBALT COMPLEXES: HIGHLY ACTIVE CATALYSTS FOR POLYMERIZATION AND 0LIGOMERIZATION OF ETHYLENE&quot;, ORGANOMETALLICS, ACS, WASHINGTON, DC, US, vol. 22, no. 21, 13 October 2003 (2003-10-13), pages 4312-4321, XP001189819, ISSN: 0276-7333, DOI: 10.1021/0M0302894, page 4313, Scheme 1; page 4318, right-hand column, paragraph 3</td>
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<td>BIRT0VSEK ET AL: &quot;Novel olefin polymerization catalysts based on iron and cobalt &quot;, CHEMICAL COMMUNICATIONS - CHEMCOM; [6015D], ROYAL SOCIETY OF CHEMISTRY, GB, no. 7, 1 January 1998 (1998-01-01), page 849/850, XP002086893, ISSN: 1359-7345, DOI: 10.1039/A801933I, Scheme 1</td>
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