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Process for the preparation of ultrahigh molecular
weight polyethylene having a high bulk density

5 The invention relates to a process for the preparation of ultrahigh molecular weight polyethylene (UHMW-PE) having a bulk density of from 350 to 460 g/l, in particular 430 to 460 g/l.

10 Ultrahigh molecular weight polyethylene is understood as meaning linear polyethylenes obtained by the low pressure process and having viscometrically measured average molecular weights of at least 10^6 g/mol, in particular $2.5 \cdot 10^6$ g/mol to more than 10^7 g/mol. The above-mentioned molecular weights are determined from the solution viscosity according to the Margolies equation. The method used for this determination is described, for
15 example, in CZ Chemie Technik 4 (1974), 129 et seq.

UHMW-PE occupies a special position among the polyethylenes. It is distinguished by a number of physical characteristics which make it suitable for a wide range of potential applications. Its high resistance to wear,
20 its low coefficient of friction compared with other materials, its excellent toughness characteristics and its high thermal stability under load should be singled out. In addition, it is remarkably resistant to a large number of chemicals.

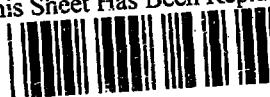
25 Owing to these particular mechanical, thermal and chemical properties, UHMW-PE is now used as a high quality speciality material in a very wide range of applications. Examples are the textile industry, mechanical engineering, the chemical industry and mining.

30 There are various known processes for the preparation of this special polyethylene grade. Low pressure polymerization of ethylene using Ziegler catalysts, i.e. mixtures of compounds of subgroups IV to VI of the Periodic Table of Elements with organometallic compounds of groups

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I to III of the Periodic Table, have proven suitable. Among the compounds of the elements of subgroups IV to VI, titanium compounds are the most important. The most frequently used organometallic compounds of groups I to III are alkylaluminums and alkylaluminum halides.

In general the Ziegler catalysts are prepared by reduction of Ti(IV) compounds, such as titanium tetrachloride or titanates, with organoaluminum compounds. This gives Ti(III) compounds, which are frequently isolated, suspended in a suitable medium and mixed with the activator required for the polymerization.

For the preparation of UHMW-PE by a process which has been tested, ethylene whose oxygen content is less than 5 ppm is polymerized at 30 to 130°C and pressures of 0.1 to 10 MPa using catalysts which contain titanium(III) halides and organoaluminum compounds in a molar ratio of 1 : 0.2 to 1 : 5, and monohydric or polyhydric aliphatic alcohols are added, in amounts of 2 to 10 mol, based on 1 kg of catalyst, to the reaction mixture during the polymerization. Diethylaluminum monochloride is used as the organoaluminum component of the catalyst (DE-C-2 361 508).

In a further process, unsaturated polymeric organoaluminum compounds, for example isoprenylaluminum or myrcenylaluminum, are used as the aluminum compound in the catalyst system (DE-C-2 361 052).

As a raw material, UHMW-PE is used predominantly in the form of powder. The powder morphology and consequently the bulk density are therefore important properties, on which its processibility depends. Thus, for example, the properties of the porous mouldings which are obtained by sintering pulverulent UHMW-PE, as well as the production of fibers having a high modulus or battery separators containing silica as a filler, are determined substantially by the size and shape of the polymer particles and



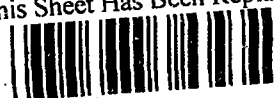
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furthermore by the width of the molecular weight distribution. However, the morphology of the powder is also important for the production process itself and for storage. Coarse particles having a narrow particle size distribution and high bulk density require less energy for drying, and storage requires less space.

The processes known to date for the preparation of UHMW-PE make it possible to influence the external shape of the polymer particles only within very narrow limits. It was therefore the object to develop a procedure which permits the preparation of pulverulent, ultrahigh molecular weight polyethylenes having a narrow granulometry and a selected bulk density. At the same time, high availability of the process is to be ensured through a low level of agglomeration and deposition in the reactor.

The present object is achieved by a process for the preparation of pulverulent polyethylene having a viscometrically measured molecular weight of at least 10^6 g/mol and a bulk density of 350 to 460 g/l, in particular 430 to 460 g/l, by polymerization of ethylene at temperatures of 30 to 130°C and pressures of 0.05 to 4 MPa in the presence of a mixed catalyst, comprising a titanium component and an organic aluminum compound, and a molecular weight regulator. In the process, the titanium component is obtained by reaction in two stages, in a first stage a titanium(IV) compound being reacted with an organic aluminum compound at -40 to 140°C in a molar ratio of titanium to aluminum of 1 : 0.1 to 1 : 0.6 to give a titanium(III) compound and, in a second stage, the reaction product of the first stage being after-treated with an organic aluminum compound at -10 to 150°C in a molar ratio of titanium to aluminum of 1 : 0.01 to 1 : 5 and the titanium component being formed into the mixed catalyst with an organic aluminum compound in a molar ratio of titanium to aluminum of 1 : 1 to 1 : 15.

The novel process makes it possible to tailor the bulk

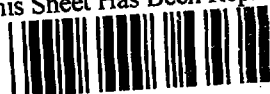


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density of ultrahigh molecular weight polyethylene by variation of the aftertreatment of the titanium(III) compound of the first reaction stage with an organic aluminum compound in the range of 350 to 460 g/l, in particular 430 to 460 g/l. The bulk density is understood as meaning the value determined according to DIN 53 468.

For the preparation of the titanium(III) compounds, titanium(IV) compounds are used as starting materials in the first stage. Compounds of the general formula $Ti(OR^1)_nX$, where n is an integer from 1 to 4, R^1 are identical or different hydrocarbon radicals, in particular alkyl radicals having 1 to 18, preferably 2 to 8, carbon atoms, and X is halogen, in particular chlorine or bromine, are suitable. $TiCl_4$, $TiBr_4$, $Ti(OC_2H_5)_4$, $Ti(OC_2H_5)_3Cl$, and $Ti(Oi-C_4H_9)_3Cl$, may be mentioned as examples. Organic aluminum compounds which may be used, according to the invention, for the reduction of the Ti(IV) compounds are of the general formula AlR^2_mX , where m is 0, 1 or 2, R^2 are identical or different alkyl radicals having 1 to 12, in particular 2 to 6, carbon atoms and X is halogen, in particular chlorine or bromine. Examples of such compounds are triethylaluminum, triisobutylaluminum, diethylaluminum chloride and ethylaluminum dichloride. Polymeric organic aluminum compounds which are obtained by reaction of lithium aluminum hydride or trialkylaluminums or dialkylaluminum hydrides whose alkyl radicals each have 1 to 16 carbon atoms with C_4 - C_{20} -diolefins, in particular C_4 - C_{12} -diolefins, are also suitable. In contrast to the mononuclear trialkylaluminum compounds and the alkylaluminum halides, they are polynuclear. The reaction products of $Al(i-C_4H_9)_3$ or $Al(i-C_4H_9)_2H$ with isoprene ("isoprenylaluminum") are preferably used. The aluminum compounds may be used in pure form or as a mixture of two or more compounds.

The reaction of the Ti(IV) compound with the organic



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aluminum compound is carried out in an inert solvent at temperatures of -40 to 140°C , preferably -20 to 120°C . The concentrations of the reactants in the starting solutions are 0.1 to 9.1 mol of Ti(IV) compound/l of solvent and 0.05 to 1.0 mol of Al compound/l of solvent, in particular 5.0 - 9.1 mol of Ti(IV) compound and 0.2 - 0.9 mol of Al compound, in each case per 1 of solvent. 0.1 to 0.6 , preferably 0.3 to 0.5 , mol of aluminum in the form of an organic aluminum compound is used per mol of titanium(IV). Aliphatic hydrocarbons have proven suitable as inert solvents. Depending on the temperature, the reaction is complete after 1 to 600 min. The degree of reduction determined by cerimetry is at least 95% .

According to the invention, the reduction is followed by an aftertreatment of the reduction product with an organic aluminum compound, as a second stage. For this purpose, said reduction product is filtered off from the suspension, washed with the solvent or suspending medium and suspended again in an inert organic solvent. However, the suspension obtained in the reduction can also be directly used. Such a procedure is advisable whenever the reduction of the titanium(IV) compound is carried out by means of the aluminum compound using a molar ratio of titanium to aluminum of about $1:0.5$.

For the aftertreatment, the reduction product is reacted with an organic aluminum compound, which is added as a solution or suspension. The reactants are allowed to act on one another over a period of 1 to 1200 min and at temperatures of -10 to 150°C , preferably 0 to 70°C , while stirring. The organic aluminum compounds used are mono-nuclear or polynuclear mono- or dialkylaluminum halides, or trialkylaluminum compounds. In order to prevent over-reduction and hence inhibition of the catalyst, isoprenylaluminum is preferably used. The reaction is detectable externally from a deepening of the color of the titanium compound from reddish brown to brownish black. As investigations have shown, the reaction



involves not a progressive reduction of the titanium(IV) compound but the irreversible increase in the molecular ratio of aluminum to titanium in the solid. While this ratio is 0.2 to 0.33 : 1 in the reduction product, it increases to about 0.4 to 0.6 : 1 as a result of the treatment with the organic aluminum compound. The molar ratio of titanium to aluminum during the aftertreatment, the reaction time, the reduction potential of the alkyl-aluminum and the reaction temperature are critical for the magnitude of the increase. Usually, a molar ratio of titanium to aluminum of 1 : 0.01 to 1 : 5, preferably 1 : 0.4 to 1 : 1.2, is maintained. The molar ratio of aluminum to titanium in the product of the aftertreatment ("titanium component") determines the polymer morphology and hence the particle size distribution of the bulk density of the polymer. Molar titanium/aluminum ratios in the lower range during the aftertreatment give bulk densities below 400 g/l while those in the upper range give bulk densities below 430 to 460 g/l. The catalyst suspension thus obtained can be used directly or after being filtered off and, for example, washed with the suspending medium.

For formation of the catalyst, the titanium component is activated with an organoaluminum compound. As in the reduction, the aluminum compound may be used in pure form or as a mixture of two or more compounds, triisobutyl-aluminum or isoprenylaluminum preferably being used as the activator. The molar ratio of titanium (based on the amount of titanium originally used as Ti(IV) compound) to aluminum in the mixed catalyst is 1 : 1 to 1 : 15, preferably 1 : 2 to 1 : 10.

The polymerization is carried out in suspension in one or more stages, continuously or batchwise, at temperatures of 30 to 130°C, preferably 60 to 100°C and an ethylene partial pressure of less than 4.0 MPa, preferably 0.05 to 0.8 MPa.



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5 The inert diluents usually used for the Ziegler low-pressure process, such as aliphatic or cycloaliphatic hydrocarbons, e.g. butane, pentane, hexane, cyclohexane, nonane and decane, are suitable as a reaction medium for the polymerization. Furthermore, gasoline or hydrogenated diesel oil fractions which have been carefully freed from oxygen, sulfur compounds and moisture may also be used. Their boiling range is between -5 and 220°C, preferably between 65 and 180°C.

10 The molecular weights of the polymers can be adjusted in a known manner by means of molecular weight regulators, preferably hydrogen. The ratio of ethylene partial pressure to hydrogen partial pressure is at least 10, preferably 40 to 1600.

15 The polymer is separated off from the suspending medium under an inert gas and is dried. In the absence of air and moisture, the suspending agent is reused for the polymerization without any intermediate treatment.

20 In the Examples which follow, the invention is described in detail but is not restricted to the embodiments shown.

The following values are stated for describing the polymers:

25 Mean particle diameter: determined by laser diffraction using the particle size analyzer Helos-Rhodos measurement and evaluation system from Sympatec GmbH; optical concentration about 10%.

s value: this serves as a measure of the width of the particle size distribution and is expressed by the formula

30

$$s = \log \frac{d(90)}{d(10)}$$

d(90) and d(10) are the particle sizes at 90% and at 10%,



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obtained from the cumulative distribution; s increases with increasing width of the particle size distribution. ZST or flow value: this serves as a measure of the molecular weight and is determined according to DIN

5 53 493;

Bulk density: determined according to DIN 53 468

Example 1

1.1. Preparation of the base catalyst (catalyst according to the prior art)

10 44.1 l of titanium tetrachloride are metered into 230 l of a 20% strength by weight solution of isoprenylaluminum (IPRA) in 200 mol of hexane in an inert gas atmosphere and while stirring at a temperature of -10°C in the course of 7 hours (corresponding to a ratio of 1 mol of

15 Ti to 0.5 mol of Al).

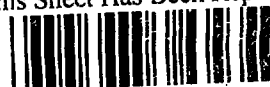
The reaction is complete after 3 hours. More than 96% of the Ti(IV) used are reduced to Ti(III).

1.2. Polymerization using the catalyst prepared according to 1.1.

20 The polymerization is carried out in one stage in a continuously operated plant with recycling of the reaction medium. Gasoline purified over molecular sieves and having a boiling range of 140 to 170°C serves as the suspending medium.

25 At a reaction temperature of 80°C and a yield, based on catalyst used, of 1.7 kg of PE/mmol of Ti, the resulting ethylene partial pressure is about 0.32 MPa. The hydrogen content of the gas phase is about 0.5% by volume. The ratio of suspending medium to polyethylene (in l/kg)

30 is 4.3. The activator (= IPRA) concentration in the reaction medium fed to the reactor is adjusted so that the molar ratio of aluminum to titanium component (based on the amount of titanium originally used as Ti(IV)



compound) in the reactor is about 10 : 1. The molecular weight of the polymer is controlled via the hydrogen content of the reactor gas phase. The following product properties are obtained in a reproducible manner in two parallel experiments (A and B):

		Experiment	Experiment
		A	B
10	Mean particle diameter [μm]	210	200
	s value	0.51	0.51
	Bulk density [g/l]	370	380
	ZST value [N/mm ²]	0.24	0.24

Example 2

2.1. Preparation of a catalyst according to the invention
 The catalyst (K0) described under 1.1 is diluted to a concentration of about 40 mmol of titanium component/l and treated at room temperature with IPRA (K1 to K6). A deepening of color from reddish brown to dark brown occurs, depending on the amount of alkylaluminum used. The degree of reduction remains unchanged. On the other hand, the content of chemically fixed aluminum in the catalyst solid increases from 0.2-0.33 : 1 to 0.6 : 1. To determine these values by atomic absorption spectroscopy, the catalyst is filtered under an inert gas and washed twice with gasoline.

25	Catalyst designation	Catalyst treatment	Bound Al
		Ti total : Al	Ti : Al
30	K0	0	1 : 0.32
	K1	1 : 0.05	1 : 0.21
	K2	1 : 0.1	1 : 0.23
	K3	1 : 0.5	1 : 0.55
	K4	1 : 1	1 : 0.45
	K5	1 : 2	1 : 0.5
	K6	1 : 5	1 : 0.4

35

After a reaction time of 24 hours, the catalyst is used



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for the polymerization. K6 shows that, under otherwise identical conditions, the use of larger amounts of the organic aluminum compound does not lead to an increase in the proportion of aluminum in the titanium component.

5 2.2. Polymerizations using the catalyst prepared according to 2.1.

2.2.1. Use of catalysts not separated off

10 For the synthesis of UHMW-PE, the catalyst types K3 and K5 are used directly after the preparation, i.e. neither filtered off nor washed, analogously to the process described under 1.1. Compared with the reference catalyst K0, the reaction temperature is reduced to about 78°C and the molar ratio of aluminum (IPRA) to titanium component in the reactor to about 3.0, in order to

15 establish an ethylene partial pressure of about 0.25 MPa. The hydrogen content is adjusted as under 1.2.

2.2.2. Use of a catalyst separated off beforehand

20 The polymerization is carried out as described under 2.2.1. A catalyst type K4, which is filtered off and washed with the suspending agent before being used, is employed.

Results of the polymerization experiments:

25	Catalyst type	Yield	Mean particle diameter [μm]	s value	Bulk density [g/l]	ZST [N/mm²]
		[kg of PE/ mmol of Ti]				
30	K3	1.1	150	0.43	450	0.24
	K4	2.8	160	0.39	460	0.24
	K5	3.3	180	0.43	445	0.24

Reference experiment 1.2.

K0	1.7	210	0.51	370	0.24
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Patent Claims

1.) A process for the preparation of pulverulent poly-ethylenes having a viscometrically measured molecular weight of at least 10^6 g/mol and a bulk density of 350 to 460 g/l, in particular 430 to 460 g/l, by polymerization of ethylene at temperatures of 30 to 130°C and pressures of 0.05 to 4 MPa in the presence of a mixed catalyst, comprising a titanium component and an organic aluminum compound, and a molecular weight regulator, which comprises obtaining the titanium component by reaction in two stages, in a first stage a Ti(IV) compound being reacted with an organic aluminum compound at -40 to 140°C in a molar ratio of titanium to aluminum of 1 : 0.1 to 1 : 0.6 to give a titanium(III) compound and, in a second stage, the reaction product of the first stage being aftertreated with an organic aluminum compound at -10 to 150°C in a molar ratio of titanium to aluminum of 1 : 0.01 to 1 : 5 and the titanium component being formed into the mixed catalyst with an organic aluminum compound in a molar ratio of titanium to aluminum of 1 : 1 to 1 : 15.

2.) The process as claimed in claim 1, wherein the titanium compound used in the first stage is of the formula $Ti(OR^1)_nX_n$, where n is an integer of from 1 to 4 and R^1 are identical or different hydrocarbon radicals, in particular alkyl radicals having 1 to 18, preferably 2 to 8, carbon atoms, and the organic aluminum compound is of the formula $AlR^2_mX_n$, where m is 0, 1 or 2, R^2 are identical or different alkyl radicals having 1 to 12, in particular 2 to 6, carbon atoms and X is halogen, in particular chlorine or bromine, or is a polymeric organic aluminum compound, in particular isoprenylaluminum.

3.) The process as claimed in claim 1 or 2, wherein the reaction between the titanium(IV) compound and the



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aluminum compound is carried out at temperatures of
-20 to 120°C.

- 4.) The process as claimed in one or more of claims 1 to
3, wherein 0.3 to 0.5 mol of aluminum in the form of
an organic aluminum compound is used per mol of
titanium(IV).
- 5.) The process as claimed in one or more of claims 1 to
4, wherein the titanium(III) compound obtained in
the first stage is aftertreated in the second stage
with mononuclear or polynuclear mono- or dialkyl-
aluminum halides or with trialkylaluminum compounds.
- 6.) The process as claimed in one or more of claims 1 to
5, wherein the titanium(III) compound of the first
stage is filtered off and washed with an inert
solvent before the aftertreatment.
- 7.) The process as claimed in one or more of claims 1 to
6, wherein the molar ratio of titanium to aluminum
in the second stage is 1 : 0.01 to 1 : 5, preferably
1 : 0.4 to 1 : 1.2.
- 8.) The process as claimed in one or more of claims 1 to
7, wherein the titanium component obtained in the
second stage is formed into the mixed catalyst with
an organoaluminum compound, in particular with tri-
isobutylaluminum or isoprenylaluminum.
- 9.) The process as claimed in claim 8, wherein the
organoaluminum compound and the titanium component
are used in a molar ratio of 1 : 1 to 15 : 1,
preferably 2 : 1 to 10 : 1.

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