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(71) Applicant *(for all designated States except US)*: **FORTUM OYJ** [FI/FI]; Keilaniemi, FIN-02150 Espoo (FI).

(72) Inventors; and

(75) Inventors/Applicants *(for US only)*: **HARJUHAHTO, Hannu** [FI/FI]; Edelfeltinbulevardi 11, FIN-06100 Porvoo (FI). **VIRTANEN, Esa** [FI/FI]; Eestinmäentie 5 B 8, FIN-06450 Porvoo (FI). **KARBASI, Amir, Kiumars** [FI/FI]; Vuokselantie 10 B 2, FIN-02140 Espoo (FI). **ROCKAS, Leif** [FI/FI]; Lyhdetie 22, FIN-06150 Porvoo (FI). **LAIHO, Tapani** [FI/FI]; Jaalakuja 2 A 3, FIN-06150 Porvoo (FI). **KARHU, Esa** [FI/FI]; Lyhdetie 11, FIN-06150 Porvoo (FI). **EKLUND, Mirja** [FI/FI]; Puistotie 7, FIN-06650 Hamari (FI).

(74) Agent: **BERGGREN OY AB**; P. O. Box 16, FIN-00101 Helsinki (FI).

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(54) Title: PROCESS FOR PREPARING AND METHOD OF USING A DRAG REDUCING AGENT

(57) Abstract: The invention relates to process for the production of a drag reducing agent wherein a monomer or monomer mixture comprising one or more C_4-C_{30} monoolefins, preferably C_6-C_{20} monoolefins, is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer in the presence of a polymerization catalyst system comprising a Group 4-6 (IUPAC 1990) transition metal compound and an organoaluminium compound. In order to obtain a shear force resistant drag reducing agent, said transition metal compound has been prepared by providing a support comprising an atomized complex of a magnesium halide and a monohydric C_1-C_4 alcohol and contacting the support with a halogenous titanium compound and a C_6-C_{18} alkyl carboxylic acid ester under conditions which deposit the halogenous titanium compound on the support and cause transesterification between the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester. The shear force resistance can further be improved by copolymerizing the C_4-C_{30} monoolefin(s) with 0.0001-10%, based on of the weight of the C_4-C_{30} monoolefin(s), of a polyunsaturated aliphatic hydrocarbon.

Process for preparing and method of using a drag reducing agent

Field of the invention

The invention relates to a process for the production of a drag reducing agent wherein a monomer or monomer mixture comprising one or more C_4-C_{30} monoolefins is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultra-high molecular weight drag reducing polymer in the presence of a polymerization catalyst system comprising a Group 4-6 (IUPAC 1990) transition metal compound and an organoaluminium compound. The invention also relates to a method for reducing the drag of hydrocarbon flowing by using said drag reducing agent, and the use of a catalyst of the above-mentioned type for improving the high shear force resistance of drag reducing polymers.

The prior art

When a fluid, such as a liquid hydrocarbon, is fed through a conduit, friction resulting from the fluid stream causes a pressure drop increasing with the distance from the point(s) of feeding. Such a friction loss, also called drag, causes very high fluid transportation costs.

In order to reduce drag, a variety of polymeric materials have been used as additives in the fluid to be transported. Suitable materials have been polymers (= homopolymers and copolymers) of olefins, in particular very high molecular weight, non-crystalline and hydrocarbon soluble polymers of C_4-C_{30}-α-olefins.

In order to reduce drag effectively, a drag reducing olefin polymer must be of very high molecular weight, but at the same time soluble in and compatible with the fluid to be transported. These properties are only achieved with the right kind of catalysts. Ziegler-Natta catalysts have been modified to produce polymers having said properties. In the methods of Mack and Mack *et al.*, see columns 11-18 of US 4,415,714, columns 7-10 of US 4,358,572 and column 4 of US 4,289,679, α-olefins are polymerized in the presence of a Ziegler-Natta system comprising titanium chloride, an electron donor, and an alkyl aluminium cocatalyst and the polymerization is stopped at below about 20% conversion. Such polymers are soluble in hydrocarbon fluids and act as drag reducing agents.

However, none of these documents teach or suggest a method for obtaining an ultrahigh molecular weight polymer having all properties suitable for use as a drag reducing agent. Especially, the drag reducing agents of these documents tend to loose their effect when exposed to high shear forces caused e.g. by a centrifugal pump.

The purpose of the invention is to obtain a drag reducing agent, which in addition to reducing the fluid stream friction also retains that property when exposed to high shear forces.

The invention

The purpose of the invention has now been fulfilled by means of a new process for the production of a drag reducing agent wherein a monomer or monomer mixture comprising one or more C_4-C_{30} monoolefins, preferably C_6-C_{20} monoolefins, is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer in the presence of a polymerization catalyst system comprising a Group 4-6 (IUPAC 1990) transition metal compound and an organoaluminium compound.

In the process, said transition metal compound has been prepared by providing a support comprising an atomized complex of a magnesium halide and a monohydric C_1-C_4 alcohol and contacting the support with a halogenous titanium compound and a C_6-C_{18} alkyl carboxylic acid ester. The contacting takes place under conditions which deposit the halogenous titanium compound on the support and cause transesterification between the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester.

Detailed description of the invention

The support has preferably been prepared by contacting and heating magnesium chloride and ethanol to form a molten complex, preferably $MgCl_2 \cdot n\ C_2H_5OH$, wherein n is 2-6, and atomizing and solidifying the molten complex. The atomization can e.g. be accomplished by heating the components in a hot, inert liquid, whereby a dispersion of molten complex droplets is formed, after which the dispersion is poured into another cooled liquid for the precipitation of small complex particles. Preferably, however, $MgCl_2$ and C_2H_5OH are melted and reacted together and the molten complex is sprayed into a cooled gas medium (spray-crystallizing), whereby small support particles are formed having sufficient alcohol on their surface to adhere the transition metal compound thereto and engage in transesterification with the carboxylic acid ester.

Next, the contacting between the support and the transitional metal compound takes place under conditions, which deposit the transitional metal compound on the support and cause transesterification between the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester. This is preferably accomplished by preparing a hydrocarbon slurry of the support, adding titanium tetrachloride and a C_6-C_{18} alkyl phthalate to the slurry, preferably at a temperature below + 120°C, and heating the resulting mixture to an elevated temperature, preferably over +120°C, at which transesterification takes place.

The organoaluminium component of the polymerization catalyst system may be any compound known in the field of Ziegler-Natta catalysis for acting as a so called co-catalyst. It preferably has the following composition:

$$R_mAl_nX_{3n-m}$$

wherein R is a C_1-C_8 alkyl, X is a halogen, $m > 1$ and $n = 1$ or 2. Most preferably, the organoaluminium compound is a tri-C_1-C_2-alkyl aluminium such as triethyl aluminium or triisobutyl aluminium.

According to one embodiment of the invention, a so called external donor may be used with the organoalumonium compound. A preferred external donor is a di-C_1-C_{12} alkyl-di-C_1-C_6 alkoxy silane, e.g. cyclohexyl methyl dimethoxy silane.

The C_4-C_{30} monoolefins used in the production process of the invention are typically higher monoolefins capable of undergoing polymerization by a Ziegler-Natta catalyst system. There are tens of such polymerizable C_4-C_{30} monoolefins and their selection on the basis of the prior art is easy for a person skilled in the art. When selecting the monomers, they should be chosen on the basis of their capability to form high molecular weight non-crystalline and hydrocarbon soluble polymers.

Typical α-olefin monomers are hexene-1, octene-1, decene-1, dodecene-1, tetradecene-1, hexadecene-1 and eicosene-1. Preferably, the C_4-C_{30} monoolefin(s) of the invention is(are) selected from C_6-C_{12} alkene-1 compounds and their mixtures. Typical such α-olefin monomers and their combinations include propene-dodecene-1, butene-1-dodecene-1, butene-1-decene-1, hexene-1-dodecene-1, octene-1-tetradecene-1, butene-1-decene-1-dodecene-1, propene-hexene-1-dodecene-1, etc. Preferred monomers and monomer mixtures are hexene-1, octene-1, decene-1, dodecene-1, propene-dodecene-1, butene-1-decene-1, butene-1-dodecene-1 and hexene-1-dodecene-1. Especially preferred monomers are hexene-1 and octene-1.

Preferably, the monomer or monomer mixture is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer by carrying out the polymerization essentially in the absence of chain transfer agents, such as hydrogen, and/or stopping the reaction at a low conversion such as 10-30 mol-%, preferably 10-20 mol-%. The reaction can suitably be stopped by adding a substance, e.g. acetone, which deactivates the catalyst system. By using such a measure, ultra high molecular weight (UHMW, Mw > $_{\text{light scattering}}10^6$ g/mol) non-crystalline C_4-C_{30} α-olefin polymers are produced.

The above mentioned drag reducing properties and especially the good shear force resistance obtained with the above defined catalyst system can be further improved by polymerizing the C_4-C_{30} monoolefins in the presence of 0.0001-10%, based on of the weight of the C_4-C_{30} monoolefin(s), of a polyunsaturated aliphatic hydrocarbon which is copolymerized with the C_4-C_{30} monoolefin(s). By "aliphatic" is here meant non-aromatic. In the invention, preferably 0.001-1%, most preferably 0.01-0.1% of the polyunsaturated aliphatic hydrocarbon, based on the weight of the C_4-C_{30} monoolefin, is copolymerized with the C_4-C_{30} monoolefin(s).

Thanks to the polyunsaturation of the comonomer, some crosslinking takes place, which improves the high shear force resistance of the drag reducing agent. Thanks to the aliphatic character of the comonomer, the solubility of the drag reducing agent in the fluid to be transported is very high. A polymer is best dissolved by solvents having the same chemical structure as the polymer. Equally high solubilities are not to be expected of the drag reducing agents of Gessell *et al.* (US 5,276,116), which uses the non-aliphatic divinyl benzene or divinyl siloxane as polyunsaturated comonomers. Besides, Gessell *et al.* uses another catalyst system than the invention.

The polyunsaturated aliphatic hydrocarbon comonomer used to prepare the drag reducing agent of the invention may be any compound which copolymerizes and crosslinks either during or after the copolymerization. The art of olefin polymerization knows a large number of such polyunsaturated hydrocarbons which easily can be selected for the invention. Terpenes (isoprene oligomers and polymers) and related compounds such as dicyclopentadiene and 2-ethylidenenorborn-2-ene can be selected. According to a preferred embodiment of the invention, the polyunsaturated hydrocarbon is selected among linear C_4-C_{30} dienes, preferably linear non-conjugated C_6-C_{20} dienes. Typical such dienes are hexa-1,4-diene, octa-1,4-diene, octa-1,6-diene, octa-1,7-diene, and deca-1,9-diene.

In addition to one polyunsaturated aliphatic hydrocarbon comonomer, mixtures of two and more of such comonomers may also be used.

The copolymerization of the C_4-C_{30} monoolefin(s) and the polyunsaturated aliphatic hydrocarbons can be carried out at any convenient reaction conditions. As the drag reducing effect is better if the molecular weight of the copolymer is high, the copolymerization, just like the polymerization mentioned above, is preferably carried out at conditions which give high molecular weights. In the art of olefin homo- and copolymerization, the means for obtaining high molecular weight are generally known. Such means are, e.g., the elimination of all chain transfer agents, such as hydrogen, and impurities acting as chain transfer agents, see above.

More preferably, the copolymerization is carried out under conditions which produce ultrahigh molecular weight (Mw > 10^6 g/mol) polymer, most preferably by carrying out the copolymerization rapidly to a monomer conversion of only 10-30 mol-%, advantageously 10-20 mol-%. See above. Then, the copolymerization is preferably finished by adding a substance such as acetone, which deactivates the catalyst system. If an ultrahigh molecular weight copolymer of an olefin and a polyunsaturated aliphatic hydrocarbon is produced in this manner, a superior combination of drag reduction, solubility and high shear force resistance is achieved.

Further, it is preferable, if the homo- or copolymerization of the invention to a ultrahigh molecular weight polymer is carried out in a hydrocarbon solvent. The homo- or copolymerization can e.g. be carried out at a starting temperature of between −30°C and +20°C, preferably about −10°C to −5°C and a final temperature of between −5°C and +30°C, preferably about +10°C to +15°C. Then, the pressure is preferably 1-20 bar, most preferably 2-5 bar.

After the copolymerization, the product is preferably recovered as a gel containing the copolymer, the solvent and/or unreacted monomer. The gel may then be added as such to the hydrocarbon fluid, the drag of which is to be reduced. Advantageously, the gel contains 4-10% by weight of the polymer or the copolymer, 30-50% by weight of the monomer and 50-65% by weight of the solvent. Alternatively, the monomer may be removed and recovered for reuse.

The gel may also be transformed into a drag reducing powder, slurry, solution or dispersion, which is then added to the conduit or fluid to be transported.

In addition to the above described process for preparing a drag reducing agent, the invention also relates to a method for reducing the drag of hydrocarbon flowing.

In the claimed drag reducing method, (a) a drag reducing agent prepared of the above described type is provided, and (b) the drag reducing composition is fed into a conduit or the like, in which the hydrocarbon is or will be flowing, or, alternatively to a fluid to be transported in the conduit or the like. Preferably, the drag reducing composition is fed in an amount of 1-200 ppm, preferably 10-100 ppm, most preferably 20-80 ppm, based on the amount of the flowing hydrocarbon.

The invention also relates to the use of a transition metal compound, which has been prepared by contacting an atomized solid complex of a magnesium halide and a monohydric C_1-C_4 alcohol with a halogenous titanium compound and a C_6-C_{18} alkyl carboxylic acid ester under conditions depositing the halogenous titanium compound on the complex and transesterifying the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester, in the polymerisation of one or more C_4-C_{30}-monoolefins for improving the high shear force resistance of resulting drag reducing polymers. In the use according to the invention, essentially the same parameters are used as described in connection with the claimed production process.

The following examples, in which the parts and percentages are on a weight basis, unless otherwise indicated, are merely provided to illustrate the invention.

Examples

Measuring methods

The methods used for characterizing the drag reducing agents (compositions), henceforth called DRA, can crudely be subdivided into the physical properties (dry matter, viscosity) and the actual performance properties (DPT, Visko 50).

The dry matter of a gel sample is determined by removing the gel solvent(s) by evaporating in a heating chamber. In addition to the polymer, the gel hardly contains other solids, so, the dry matter gives the polymer content of the product. The dry matter of the gel is a remarkable physical property in so far as the performance reached at the site of use depends on the amount of polymer dissolved in the fluid, i.e. when feeding to the fluid equal masses or volumes of different products, most effective agent is fed with the product having the larges dry matter.

The viscosity is the dynamic viscosity (cP) was measured by a Brookfield viscometer using different shear rates (e.g. 0.5, 1, 2.5, 5, 10, 20, 50 and 100 rpm).

The DPT (= delta pressure vs. time) is a kind of life span analysis. The sample to be tested is fed to a solvent circulation system maintained by a gear pump. By measuring the productivity pressure, the dissolution of the sample can be followed and thereafter the gradual disappearance of the drag reducing effect can be followed as the sample one time after another passes the pump. In DPT measurements, attention is especially paid to the percent DPT, which is obtained as an integral by summing up the differences between the reference pressure and the momentary pressures during the measurement. The drag reduction can be calculated using the following equation:

$$\% \text{ drag reduction} = (p_0 - p_S)/p_0 \times 100$$

wherein p_0 is the measured drop occurring when hexane without drag reducing agent was pumped through the test line, and p_S is the measured pressure drop occurring when hexane containing the drag reducing agent was pumped through the test line.

The Visko 50 test is based on measuring the kinematic viscosity of the sample. A 50 ppm solution of the DRA is prepared, the viscosity of which is compared to the viscosity of pure solvent. The result of a Visko 50 test contains information about the solubility of the DRA as well as its ability to alter the viscoelastic properties of the hydrocarbon fluid. The DRA is considered the better, the larger the Visko 50 value is.

Preparation

1. General

The process is based on batch polymerization of a mixture of C_6 , C_8 and C_{12} linear alpha olefins using a saturated hydrocarbon as solvent and Ziegler-Natta catalyst as a polymerization catalyst system. The used catalyst system has been prepared by reacting and heating $TiCl_4$ and C_2H_5OH to produce a molten complex and spray crystallizing the complex (see below). The polymerization process is a rapid one, partly because only about 15% of monomers will polymerize. When the proper molecular weight has been obtained, the polymerization product is pumped out of the reactor injecting simultaneously acetone to it for "killing" the catalyst. A monomer recovery process may eventually be included in the unit to improve the production economics.

2. Catalyst preparation

The catalyst was prepared essentially as follows:

102 kg of spray-chrystallized solid complex $MgCl_2 \cdot nC_2H_5OH$ wherein n = 2-4, containing 438 mol of Mg, was mixed in a reactor under inert conditions with 600 l of hydrocarbon medium (LIAV 110, Neste Oy) having a boiling point of 110°C. The obtained slurry was cooled to −15°C. Then, 1200 l of cold $TiCl_4$ was added and the temperature was allowed to rise gradually to 20°C. Next, 24.8 kg (63.6 mol) of dioctyl phthalate (DOP) was charged to the reactor. The temperature was elevated to 130°C for transesterification between the C_2H_5OH and the DOP, and the solution was removed from the reactor after half an hour. Next, 1200 l of fresh $TiCl_4$ was charged to the reactor for a second titanation. Subsequently, the mixture was thermostated at 120°C. After one hour, the solid catalyst was washed three times with hot hydrocarbon (LIAV 1110) and dried under nitrogen at 50-60°C. The analyzed composition was Ti 2.0 wt-%, Mg 15.2 wt-%, DOP 0.1 wt-%, DEP 14.3 % and Cl 50.3 wt-%.

3. Raw material supply and specifications

The monomers C_6, C_8 and C_{12} alpha olefins as well as 1,9-decadiene can be purchased as ready made blends or as such. They have the following specifications:

Monomer	1-hexene	1-octene	1-dodecene	1,9-decadiene
Average molecular weight	84	112	168	138
Density at 20 °C, kg/l	0.673	0.715	0.758	0.750
Purity, alpha olefin content, wt-%	98.5	98.5	>96	>95

A non-aromatic hydrocarbon solvent distillate is the solvent used in the production of the DRA gel.

Distillation, °C	Specification	Typical Value
IBP	min 200	200-205
95 %	reported	239-241
FBP	max 250	246-250
Dry point	reported	244-249
Density, 15 °C	reported	800-810

A Ziegler-Natta catalyst is used for the polymerization. Its specifications are:

Magnesium chloride, wt-%	40-60
$TiCl_4$, wt-%	5-16
Hydrocarbon distillate, wt-%	10-25
Dialkyl esters of 1,2-benzene dicarboxylic acid, wt-%	5-15

4. Cocatalyst

Aluminium alkyl is used as a cocatalyst with Ziegler catalyst. The DRA polymerization uses TIBA (triisobutyl aluminium) as a 25 wt-% solution in heptane as a cocatalyst. The cocatalyst has the following specifications:

Chemical Name	Triisobutylaluminium
Abbreviation	TIBA
Concentration, wt-% in heptane	25
Density, kg/l	0.7248

5. External donor

The external donor is cyclohexyl methyl dimetoxy silane. The donor is diluted with a solvent (bp. 250 °C) for a 15 wt-% solution.

6. Quencher

Any catalyst deactivating compound, e.g. acetone, can be used for stopping the polymerization reaction. The quencher is mixed with the polymerized product when the polymerized DRA product is transferred from the reactor to the storage tank.

7. Polymerization

The polymerization of C_6, C_8 and C_{12} monomer blend is performed in said saturated hydrocarbon solvent with said Ziegler-Natta catalyst in a series of two batch reactors. Chilled monomer blend, solvent, initiator and catalyst are charged into the first prepolymerization reactor with an agitator running in order to obtain a homogeneous mixture at all times. The initial temperature is –5 °C to –10 °C. The first 15 most crucial minutes of the polymerization process take place in the prepolymerization reactor. After these initial 15 minutes of the polymerization process when the temperature has risen to about 0 °C, the contents of a batch are still quite easily flowing and the batch is then transferred to the actual polymerization reactor where the final part of the polymerization takes place in an hour during which the temperature rises to about +10 °C to +15 °C. The amounts of monomer are adjusted to obtain the following product composition.

8. Product specifications

The obtained product, DRA gel, is a mixture of monomers, solvent and 7 wt-% of polymer with the following properties:

Composition, wt-%	
- polymer	5-7
- monomer	40-42
- solvent	52-54
- acetone	0.08
Average molecular weight	> 5 000 000 (typical)
Viscosity (Brookfield 7/20) at 20 °C, cP	> 20 000

The amounts of used reactants and the analytical results of the examples are given in the following table.

Table

The results of the reference and working examples

	Bench scale		Pilot scale					
Formulation	**Ex. 1**	**Ex. 2**	**Ex. 3**	**Ex. 4**	**Ex. 5**	**Ex. 6**	**Ex. 7**	**Ex. 8**
Solvent	1400 ml	1400 ml	1750 kg	1750 kg	0	0	1500 kg	1750 kg
C6	700 ml	700 ml	875 kg	875 kg	650 kg	650 kg	750 kg	875 kg
C8	350 ml	350 ml	437.5 kg	437.5 kg	0	0	375 kg	438 kg
C12	350 ml	350 ml	437.5 kg	437.5 kg	0	0	375 kg	438 kg
Catalyst	0.3 g	0.36 g	340 ml	460 ml	125 ml	125 ml	195 ml	380 ml
TIBA	10.4 ml	10.4 ml	7110 ml	7200 ml	1263 ml	1263 ml	4331 ml	7146 ml
Donor	0.4 ml	0.4 ml	1065 ml	1150 ml	188 ml	188 ml	427 ml	1100 ml
1,9-decadiene	0	0.84 g	0	2000 ml	0	560 ml	0	2000 ml
Analysis								
Visko 50	0.227	0.263	0.175	0.17	0.229	0.307	0.182	0.199
DPT %	5.69	9.03	7.8	9.7	9.3	10.1	6	9.1
Dry matter	4.1	4.7	6.9	6.8	9.9	6.5	6.6	7.8

Claims

1. A process for the production of a drag reducing agent, wherein a monomer or monomer mixture comprising one or more C_4-C_{30} monoolefins, preferably C_6-C_{20} monoolefins, is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer in the presence of a polymerization catalyst system comprising a Group 4-6 (IUPAC 1990) transition metal compound and an organoaluminium compound, **characterized** in that said transition metal compound has been prepared by providing a support comprising an atomized complex of a magnesium halide and a monohydric C_1-C_4 alcohol and contacting the support with a halogenous titanium compound and a C_6-C_{18} alkyl carboxylic acid ester under conditions which deposit the halogenous titanium compound on the support and cause transesterification between the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester.

2. A process according to claim 1, **characterized** in that the support has been prepared by contacting and heating magnesium chloride and ethanol to form a molten complex $MgCl_2 \cdot n\ C_2H_5OH$, wherein n is 2-6, and atomizing and solidifying the molten complex, preferably by spraying into cooled gas (spray-crystallizing).

3. A process according to claim 1 or 2, **characterized** in that the support has been contacted with the halogenous titanium compound and the C_6-C_{18}-alkyl carboxylic acid ester by preparing a hydrocarbon slurry of the support, adding titanium tetrachloride and a C_6-C_{18} alkyl phthalate to the slurry, preferably at a temperature below + 120°C, and heating the resulting mixture to an elevated temperature, preferably over +120°C.

4. A process according to claim 1, 2 or 3, **characterized** in that the organoaluminium compound is a compound of the composition:

$$R_mAl_nX_{3n-m}$$

wherein R is a C_1-C_8-alkyl, X is a halogen, $m > 1$ and $n = 1$ or 2, preferably triethyl aluminium or triisobutyl aluminium.

5. A process according to any preceding claim, **characterized** in that the polymerization catalyst system comprises a di-C_1-C_{12} alkyl-di- C_1-C_6 alkoxy silane.

6. A process according to any preceding claim, **characterized** in that the C_4-C_{30} monoolefin is selected from C_6-C_{12} alkene-1 compounds.

7. A process according to any preceding claim, **characterized** in that the monomer or monomer mixture is polymerized into an essentially non-crystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer by carrying out the polymerization essentially in the absence of chain transfer agents, such as hydrogen, and/or stopping the reaction at a low conversion such as 10-30 mol-%, preferably 10-20 mol-%.

8. A process according to any preceding claim, **characterized** in that, in order to improve the high shear force resistance of the drag reducing agent, the monomer mixture contains 0.0001-10%, preferably 0.001-1%, most preferably 0.01-0.1%, based on of the weight of the C_4-C_{30} monoolefin(s), preferably C_6-C_{20} monoolefin(s), of a polyunsaturated aliphatic hydrocarbon, which is copolymerized with the said monoolefin(s).

9. A process according to claim 8, **characterized** in that the polyunsaturated aliphatic hydrocarbon is a C_4-C_{30} diene, preferably a non-conjugated C_6-C_{20} diene, such as hexadiene, octadiene, decadiene, dodecadiene, tetradecadiene including any of their isomers such as hexa-1,4-diene, octa-1,4-diene, octa-1,7-diene, deca-1,7-diene, deca-1,9-diene, dodeca-1,11-diene, tetradeca-1,13-diene or hexadeca-1,15-diene, or a mixture thereof.

10. A process according to any of claims 8 or 9, **characterized** in that after the copolymerization, the product is recovered as a gel containing the copolymer, the solvent and/or unreacted monomer, preferably 4-10% by weight of the copolymer, 30-50% by weight of the monomer and 50-65% by weight of the solvent.

11. A method for reducing the drag of hydrocarbon flowing, **characterized** by

(a) providing a drag reducing agent prepared according to any of claims 1-15,

(b) feeding the drag reducing composition onto a conduit or the like in which the hydrocarbon is or will be flowing.

12. A method according to claim 11, **characterized** in that the drag reducing composition is fed in an amount of 1-200 ppm, preferably 10-100 ppm, most preferably 20-80 ppm, based on the amount of the flowing hydrocarbon.

13. **Use** of a transition metal compound, which has been prepared by contacting an atomized solid complex of a magnesium halide and a monohydric C_1-C_4 alcohol with a halogenous titanium compound and a C_6-C_{18} alkyl carboxylic acid ester under

conditions depositing the halogenous titanium compound on the complex and trans-esterifying the monohydric C_1-C_4 alcohol and the C_6-C_{18} alkyl carboxylic acid ester, in the polymerization of one or more C_4-C_{30} monoolefins for improving the high shear force resistance of resulting drag reducing polymers.

14. A process according to claim 13, **characterized** in that the solid complex has been prepared by contacting and heating magnesium chloride and ethanol to form a molten complex $MgCl_2$?n C_2H_5OH, wherein n is 2-6, and atomizing and solidifying the molten complex, preferably by spraying into cooled gas (spray-chrystallizing).

15. A process according to claim 13 or 14, **characterized** in that the solid complex has been contacted with halogenous titanium compound and the C_6-C_{18} alkyl carboxylic acid ester by preparing a hydrocarbon slurry of the solid complex, adding titanium tetrachloride and a C_6-C_{18} alkyl phthalate to the slurry, preferably at a temperature below +120°C, and heating the resulting mixture to an elevated temperature, preferably over +120 °C.

16. A process according to claim 13, 14 or 15, **characterized** in that the transition metal is used together with an organoaluminium compound having the composition:

$$R_mAl_nX_{3n-m}$$

wherein R is a C_1-C_8 alkyl, X is a halogen, m > 1 and n = 1 or 2, preferably triethyl aluminium or triisobutyl aluminium.

17. A process according to any one of claims 13 to 16, **characterized** in that the transition metal is used together with a di-C_1-C_{12} alkyl-di-C_1-C_6 alkoxy silane.

18. A process according to any one of claims 13 to 17, **characterized** in that the C_4-C_{30} monoolefin is selected from C6-C_{12} alkene-1 compounds.

19. A process according to any one of claims 13 to 18, **characterized** in that the one or more C_4-C_{30} monoolefin is polymerised into an essentially non-chrystalline, hydrocarbon-soluble, ultrahigh molecular weight drag reducing polymer by carrying out the polymerization essentially in the absence of chain transfer agents, such as hydrogen, and/or stopping the reaction at a low conversion such as 10-30 mol-%, preferably 10-20 mol-%.

20. A process according to any one of claims 13 to 19, **characterized** in that, in order to further improve the high shear force resistance of the drag reducing polymer, the one or more C_4-C_{30} monoolefin contains 0.0001-10%, preferably 0.001-1%,

most preferably 0.1-1%, based on the weight of the C_4-C_{30} monoolefin(s), preferably C_6-C_{20} monoolefin(s), of a polyunsaturated aliphalic hydrocarbon, which is copolymerized with the said monoolefin(s).

21. A process according to claim 8, **characterized** in that the polyunsaturated aliphatic hydrocarbon is a C_4-C_{30} diene, preferably a non-conjugated C_6-C_{20} diene, such as hexadiene, octadiene, decadiene, dodecadiene, tetradecadiene including any of their isomers such as hexa-1,4-diene, octa-1,4-diene, octa-1,7-diene, deca-1,7-diene, deca-1,9-diene, dodeca-1,11-diene, tetradeca-1,13-diene or hexadeca-1,15-diene, or a mixture thereof.

22. A process according to any of claims 20 or 21, **characterized** in that after the copolymerization, the drag reducing polymer is recovered as a gel containing the copolymer, the solvent and/or unreacted monomer, preferably 4-10% by weight of the copolymer, 30-50% by weight of the monomer and 50-65% by weight of the solvent.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/FI 01/00926

A. CLASSIFICATION OF SUBJECT MATTER

IPC7: C08F 10/00, C08F 4/64
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)

IPC7: C08F

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

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

WPI DATA, EPO INTERNAL, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0627449 A1 (NESTE OY), 7 December 1994 (07.12.94), page 2, line 6 - line 35; page 3, line 22 - line 58; page 4, line 1 - line 20, page 5, line 21 - line 37; claims 1-15; abstract --	1-22
X	WO 9219653 A1 (NESTE OY), 12 November 1992 (12.11.92), claims 1-4,6-7,10-12 --	1-5,13-17
A	US 4289679 A (MARK P. MACK), 15 Sept 1981 (15.09.81), claims 1-5 --	1-22

[X] Further documents are listed in the continuation of Box C. [X] See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
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Date of the actual completion of the international search	Date of mailing of the international search report
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Name and mailing address of the International Searching Authority European Patent Office P.B. 5818 Patentlaan 2 NL-2280 HV Rijswijk Tel(+31-70)340-2040, Tx 31 651 epo nl, Fax(+31-70)340-3016	Authorized officer MONIKA BOHLIN/Els Telephone No.

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International application No.
PCT/FI 01/00926

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4358572 A (MARK P. MACK ET AL), 9 November 1982 (09.11.82), column 1, line 10 - line 24; column 2, line 25 - line 53; column 3, line 23 - line 37 -- --------	1-22

INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No.
PCT/FI 01/00926

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US 4358572 A	09/11/82	NONE	