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(54) **VINYLAMINE COMPOUNDS**

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(57) **ABSTRACT**

Compounds which contain one or more groups of the formula (I)



where

R¹ and R², independently of one another, are each hydrogen, C₁₋₂₀-alkyl, C₆₋₁₈-aryl, C₇₋₂₀-alkaryl, C₇₋₂₀-aralkyl or a polyamine radical,

are prepared by reductive amination of compounds which contain one or more groups of the formula (II)



where

R³ is hydrogen, C₁₋₂₀-alkyl, C₆₋₁₈-aryl, C₇₋₂₀-alkaryl or C₇₋₂₀-aralkyl, with amines of the formula (III)



and hydrogen.

VINYLAMINE COMPOUNDS

[0001] The present invention relates to compounds, in particular copolymers, which contain vinylamine building blocks. The present invention furthermore relates to a process for the preparation of such compounds of copolymers, their use as assistants in mineral oils, mineral oil distillates, combustion fuels and power fuels and in other areas, and concentrates and combustion fuel and power fuel compositions containing them.

[0002] Vinylamine polymers can be obtained only indirectly by polymer-analogous reactions since the base monomer, vinylamine, cannot be isolated. Vinylamine polymers are prepared, for example, by hydrolysis of poly-N-vinylamides, such as poly-N-vinylformamide or poly-N-vinylacetamide, poly-N-vinylimides, such as poly-N-vinylsuccinimide or poly-N-vinylphthalimide and by Hoffmann degradation of polyacrylamide under the action of basic hypochlorite. These synthesis routes start from poorly obtainable or expensive monomers and include complicated reaction or working-up steps. They have been used to date only in a few special applications, for example flocculants and retention aids.

[0003] Mineral oil distillates, in particular middle distillates, such as gas oils, diesel oils or heating oils, which are obtained from mineral oils by distillation and the further processing stages of the refineries, have, depending on the origin of the crude oil, different contents of n-paraffins, which may crystallize on cooling. This point is referred to as the cloud point (CP). On further cooling, the lamellar paraffin crystals form a sort of house-of-cards structure, so that a middle distillate (MD) sets although the predominant part is still liquid. This point is referred to as the pour point. The flowability, in particular of power fuels, is considerably impaired by the precipitated paraffins in the temperature range between cloud point and pour point. The paraffins block filters and, in the case of power fuels, cause an uneven fuel supply to the engine or completely stop said supply. Similar problems arise in the case of heating oils.

[0004] It is known that the crystal growth of the paraffins in middle distillates and kerosene middle distillate mixtures can be modified by introducing suitable additives into the mineral oil distillate. Effective additives prevent paraffins in middle distillates from forming such structures resembling a house of cards and the middle distillates from becoming solid at temperatures only a few ° C. below the temperature at which the first crystals are precipitated. They thus act as flow improvers. The improvement of the flow properties of middle distillates is frequently determined as a reduction of the cold filter plugging point (CFPP), for example according to DIN EN 116. On the other hand, these additives result in the formation of fine, well crystallized, separate paraffin crystals which do not settle out and which cannot pass through the filters, so that trouble-free fuel transport is ensured. Here, they act as wax-anti-settling additives (WASA).

[0005] Copolymers which are derived from ethylene and vinyl acetate have widely been described as flow improvers for mineral oil middle distillates (cf. for example DE-A-196 24 861). The copolymers described furthermore contain (meth)acrylate building blocks which are derived from amino alcohols which may be alkoxylated.

[0006] EP-A-0 964 052 relates to the use of nitrogen-containing ethylene copolymers for the preparation of fuel

oils having an improved lubricating effect. In addition to structural units which are derived from ethylene, the copolymers also contain those structural units which are derived from ethylenically unsaturated compounds which have at least one aromatically or aliphatically bonded nitrogen atom. Alkylamino (meth)acrylates, alkyl(meth)acrylamides, vinylamides, aminoalkyl vinyl ethers, allylamines and heterocycles containing a vinyl group are mentioned as such comonomers. In particular, terpolymers which are derived from ethylene, vinyl acetate and 1-vinyl-2-pyrrolidone, N-vinyl-N-methylacetamide or dimethylaminoethyl methacrylate are used.

[0007] The nitrogen-containing vinylic comonomers have in some cases a complicated structure and as a rule cannot be prepared in a simple manner and from economical raw materials.

[0008] EP-A-0 405 270 relates to a process for improving the flowability of mineral oils and mineral oil distillates by adding a mixture of an ethylene/vinyl acetate copolymer and an ethylene/vinyl acetate/N-vinyl-pyrrolidone terpolymer.

[0009] WO 96/18706 relates to combustion and power fuel compositions which have a low sulfur content and whose flowability is increased by adding nitrogen-containing compounds. In particular, amine salts or amides, which are obtained by reacting hydrocarbon-substituted amines with alkanolic acids, are used.

[0010] It is an object of the present invention to provide a process for the preparation of compounds which contain structural elements derived from vinylamine, it being intended that the amino group be capable of being introduced simply and economically.

[0011] In addition, it is intended to provide copolymers which have a number of advantageous properties as assistants in mineral oil, mineral oil distillates and combustion and power fuels.

[0012] We have found that this object is achieved, according to the invention, by a process for the preparation of a compound which contains one or more groups of the formula (I)



[0013] where

[0014] R^1 and R^2 , independently of one another, are each hydrogen, C_{1-20} -alkyl, C_{6-18} -aryl, C_{7-20} -alkaryl, C_{7-20} -aralkyl or a polyamine radical, by reductive amination of compounds which contain one or more groups of the formula (II)



[0015] where

[0016] R^3 is hydrogen, C_{1-20} -alkyl, C_{6-18} -aryl, C_{7-20} -alkaryl or C_{7-20} -aralkyl,

[0017] with amines of the formula (III)



[0018] and hydrogen.

[0019] It was found, according to the invention, that structural elements derived from vinyl esters and present in chemical compounds, for example polymers, can be con-

verted into structures derived from vinylamine by reductive amination with amines and hydrogen.

[0020] The compounds which contain the structures of the formula (I) or (II) may be low molecular weight, oligomeric or polymeric structures. They may accordingly have 1, 2, 3, 4, 5, 6 or more of the structures of the formulae (I) and (II). Preferably, the compounds having the structures of the formula (I) have altogether 4 to 100,000, particularly preferably 10 to 10,000, in particular 10 to 1000, carbon atoms if they are low molecular weight or oligomeric compounds.

[0021] Particularly preferably, the compounds are polymers which contain vinylamine building blocks of the formula (I) in the main chain. The polymers contain 1 or 2, 3, 4, 5, 6 or more of the building blocks of the formula (I).

[0022] They may be completely composed of building blocks of the formula (I). In this case, they are homopolymers. Frequently, they are copolymers which contain unconverted structures of the formula (II) in addition to the structures of the formula (I). Moreover, further building blocks as described below may be present.

[0023] Preferably, the compounds are polymers which contain one or more vinylamine building blocks of the formula (I) in the main chain and are obtained by reductive amination of polymers which contain one or more vinyl ester building blocks of the formula (II) in the main chain.

[0024] Particularly preferably, the polymers to be aminated are copolymers which contain C_2 - C_{12} -olefin building blocks and vinyl esters of C_{1-12} -monocarboxylic acids as building blocks.

[0025] In particular, the copolymers to be aminated are ethylene/vinyl acetate copolymers.

[0026] In the groups of the formula (I) and in the amines of the formula (III), R^1 and R^2 , independently of one another, are each preferably hydrogen or C_{1-12} -alkyl, particularly preferably hydrogen or C_{1-4} -alkyl, in particular hydrogen. Particularly preferably, ammonia is used as a compound of the formula (III).

[0027] In the structures of the formula (II), R^3 is preferably hydrogen or C_{1-12} -alkyl, particularly preferably C_{1-4} -alkyl, in particular methyl. These are therefore in particular vinyl acetate building blocks.

[0028] Particularly preferred compounds which contain the structures of the formula (I) or (II) are polymers having a number average molecular weight of from 100 to 10,000, 000, particular preferably from 500 to 100,000.

[0029] The novel reductive amination can be carried out analogously to known processes for the reductive amination of, for example, aldehydes, ketones or esters and alcohols. It is preferably carried out using suitable catalysts. Suitable catalysts are known and are described, for example, in the non-prior-published DE-A-199 10 960 with the earlier priority.

[0030] Catalysts customary for the reductive amination are, for example, those based on Ni, Co, Cu, Fe, Pd, Pt, Ru, Rh, Al, Si, Ti, Zr, Nb, Mg, Zn or a combination thereof. Typical reaction conditions are temperatures of from 50 to 300° C. and pressures of up to about 600 bar.

[0031] A preferred catalyst contains as catalytically active material, before the reduction with hydrogen,

[0032] from 20 to 85, preferably from 20 to 65, particularly preferably from 25 to 49.7, % by weight of oxygen-containing compounds of zirconium, calculated as ZrO_2 ,

[0033] from 1 to 30, preferably from 5 to 25, particularly preferably from 10 to 25, % by weight of oxygen-containing compounds of copper, calculated as CuO,

[0034] from 14 to 70, preferably from 29.7 to 70, particularly preferably from 40 to 60, % by weight of oxygen-containing compounds of nickel, calculated as NiO,

[0035] from 0 to 5, preferably from 0.3 to 3.5, % by weight of oxygen-containing compounds of molybdenum, calculated as MoO_3 , and

[0036] from 0 to 10, particularly preferably from 0 to 5, % by weight of oxygen-containing compounds of aluminum, calculated as Al_2O_3 ,

[0037] the total amount of which is 100% by weight.

[0038] A particularly preferred catalyst is composed of 51% by weight of NiO, 17% by weight of CuO, 30.5% by weight of ZrO_2 and 1.5% by weight of MoO_3 .

[0039] The catalyst is preferably composed only of catalytically active material and, if required, a molding assistant, such as graphite or stearic acid. The catalyst may be used in any suitable form, for example as pellets, beads, rings or extrudates.

[0040] The catalytically active material can, if required, furthermore contain one or more elements, or inorganic or organic compounds thereof, selected from groups IA to IVA and IB to VIIB and VIII of the Periodic Table of the Elements. Catalysts which, after the final heat treatment and before the reduction with hydrogen, contain less than 20, preferably less than 10, in particular less than 5, very particularly less than 1, % by weight of cobalt, calculated as CoO, are particularly preferred. Very particularly preferably, the catalytically active material contains no catalytically active amounts of cobalt or compounds thereof.

[0041] The catalysts can be prepared by various processes, for example by peptization of pulverulent mixtures of the hydroxides, carbonates, oxides and/or other salts of the components with water and subsequent extrusion and heating of the material thus obtained. In general, however, known precipitation methods are used for preparing the catalysts. In said methods, the individual components can be precipitated individually or together as a coprecipitate.

[0042] The precipitation products are dried in general at from 80 to 200° C., preferably from 100 to 150° C. and then calcined at from 300 to 800° C., preferably from 400 to 600° C., in particular from 450 to 500° C.

[0043] The amines of the formula (III) can be used in stoichiometric amounts, based on the ester groups to be reacted. Preferably, however, an excess of the amines is used, for example more than a 5 molar excess. In particular, ammonia is generally used in a 5- to 250-fold, preferably 10- to 100-fold, in particular 25- to 80-fold, molar excess.

[0044] The novel process can be carried out batchwise or continuously, the catalyst preferably being arranged as a

fixed bed in the reactor. The reaction can be carried out in the liquid phase or in the gas phase.

[0045] Usually, the reaction is effected at from 50 to 300° C., preferably from 80 to 250° C., particularly preferably from 80 to 230° C., in particular from 100 to 220° C.

[0046] In general, the reaction is carried out at from 1 to 400, preferably from 10 to 250, in particular from 20 to 200, bar.

[0047] In the reaction, the hydrogen is generally introduced in an amount of from 5 to 400, preferably from 50 to 250, (S.T.P.) per mol of ester component to be reacted.

[0048] The reaction may be carried out without additional solvent. The reaction involving high molecular weight starting compounds or products which are highly viscous or which are solid at room temperature is advantageously effected in a solvent which is inert under reaction conditions, for example in tetrahydrofuran, dioxane, N-methylpyrrolidone, mihagol, ethylene glycol dimethyl ether, cyclohexane or hexane or generally aliphatic or aromatic solvents.

[0049] The present invention also relates to the copolymers prepared by the novel process, particularly preferably a copolymer containing copolymerized vinylamine building blocks of the formula (I)



[0050] where

[0051] R^1 and R^2 , independently of one another, are each hydrogen, C_{1-20} -alkyl, C_{6-18} -aryl, C_{7-20} -alkaryl, C_{7-20} -aralkyl or a polyamine radical,

[0052] and, if required, different, polymerized vinyl comonomer building blocks of the formula (IV)



[0053] where

[0054] R^4 is hydrogen or C_{1-4} -alkyl,

[0055] R^5 is R^6 or

[0056] $-\text{O}-\text{C}(\text{O})-\text{R}^6$,

[0057] $-\text{O}-\text{R}^6$,

[0058] $-\text{C}(\text{O})-\text{R}^6$,

[0059] $-\text{C}(\text{O})-\text{O}-\text{R}^6$,

[0060] $-\text{CN}$,

[0061] -halogen,

[0062] $-(\text{O}-\text{CH}_2-\text{CHR}^7)_n-\text{O}-\text{R}^6$,

[0063] where R^7 is hydrogen or C_{1-4} -alkyl and n has a mean value of 1 to 100,

[0064] $-\text{C}(\text{O})-\text{NHR}^6$,

[0065] where R^6 is hydrogen, C_{1-20} -alkyl, C_{6-18} -aryl, C_{7-20} -alkaryl, C_{7-20} -aralkyl, which may be unsubstituted or substituted by

[0066] $-\text{OR}^8$,

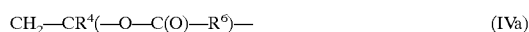
[0067] $-\text{NR}^8\text{R}^9$,

[0068] where R^8 and R^9 , independently of one another, are each hydrogen or C_{1-4} -alkyl.

[0069] Here, R^1 and R^2 have the preferred meanings stated above. In the structure $-\text{O}-\text{C}(\text{O})-\text{R}^6$, R^6 has the preferred meanings stated above for R^3 .

[0070] In the building blocks of the formula (IV), R^4 is preferably hydrogen or methyl, in particular methyl. R^5 is preferably R^6 or $-\text{O}-\text{C}(\text{O})-\text{R}^6$. If R^1 is R^6 , R^6 is preferably hydrogen, C_{1-12} -alkyl, phenyl or C_{7-10} -alkaryl, particularly preferably hydrogen, methyl, ethyl or phenyl.

[0071] In addition to the polymerized vinylamine building blocks of the formula (I), the copolymer particularly preferably contains building blocks of the formula (IVa)



[0072] and/or of the formula (IVb)



[0073] where R^5 is hydrogen, C_{1-20} -alkyl or C_{6-18} -aryl.

[0074] In particular, the copolymers have the building blocks of the formulae (I), (IVa) and (IVb).

[0075] Such copolymers may also contain up to 20% by weight, based on the total copolymer, of further building blocks; particularly preferably, they are composed essentially or only of the building blocks of the formulae (I), (IVa) and (IVb). Particularly preferably, they are ethylene/vinyl acetate/vinylamine terpolymers. The copolymers or terpolymers preferably have a number average molecular weight of from 100 to 10,000,000, particularly preferably from 500 to 100,000.

[0076] The novel copolymers can be prepared by any desired suitable process. Particularly preferably, the preparation of the copolymers is carried out by free radical copolymerization of vinyl esters of the formula (V)



[0077] where R^3 is hydrogen, C_{1-20} -alkyl, C_{6-18} -aryl, C_{7-20} -alkaryl or C_{7-20} -aralkyl,

[0078] if required different vinyl comonomers of the formula (VI)



[0079] where R^4 and R^5 have the stated meanings, and, if required, further vinylic comonomers to give a copolymer and subsequent reductive amination by the above process.

[0080] The ethylene/vinyl acetate copolymers are prepared, for example, by free radical polymerization by the high-pressure mass polymerization method, alternatively in stirred autoclaves, tubular reactors or segmented tubular reactors. Such processes are described, for example, in DE-A-197 54 039, DE-A-197 19 689 and M. Rätzsch, Erdöl und Kohle-Erdgas-Petrochemie in combination with Brennstoff-Chemie, 42(4) 1989.

[0081] The novel copolymers can be used in a large number of applications. The use as assistants in mineral oils, mineral oil distillates and combustion and power fuels, in chromatography, as ion exchangers, in dispersions, as emulsifiers, in papermaking (Wochenbl. Papierfabr. (1999) 127, 511 to 518), in membranes, in adhesives (WO 00/01783), in the production of cellulose fibers (WO 99/36604), in printing inks and papers for these (EP-A-0 878 323, EP-A-0 911 374, WO 98/42787, for the coating of fibers (U.S. Pat. No. 6,077,794), as fixing compositions (U.S. Pat. No. 6,039,

768), as mold release agents, for wastewater treatment (WO 96/38493), in detergent compositions, in particular as dye transfer inhibitors (U.S. Pat. No. 5,863,879), for decolorizing paper mill wastewaters (U.S. Pat. No. 5,476,594), for modifying metal surfaces (U.S. Pat. No. 5,494,535), in films (U.S. Pat. No. 5,492,765), in coating compositions and in other applications is preferred.

[0082] Examples of specific applications are as follows:

[0083] (1) The copolymers are suitable for optimizing the retention and drainage and for fixing anionic substances in papermaking (retention aids, drainage aids, flocculants and fixing compositions). In addition, the polymers improve the dry and wet paper strength (cf. also *Wochenbl. Papierfabr.* (1999), 127(8), 511-518).

[0084] (2) The copolymers are suitable for colorizing wastewaters from papermaking or for removing dye from said wastewaters (according to U.S. Pat. No. 5,476,594).

[0085] (3) In completely or partly protonated form, the polymers are suitable as water-soluble or water-swelling, cationic polyelectrolytes for aqueous adhesive dispersions for the production of multilayer paper or paper materials (according to DE 198 29 757).

[0086] (4) The copolymers are suitable for modifying cleaned or chemically pretreated metal surfaces, which are then suitable in particular for electrocoat coating (according to EP 0 672 467).

[0087] (5) The copolymers are suitable as dye transfer inhibitors for detergents (according to DE 441 3 720).

[0088] (6) The copolymers are suitable as a starting substance for the preparation of polymers containing carbamate units. These polymers are suitable as retention aids, drainage aids and flocculants and as fixing compositions in the production of paper, as protective colloids for the preparation of aqueous alkyldiketene dispersions and as dispersants for the preparation of aqueous filler suspensions (according to WO 98/35999).

[0089] (7) The copolymers are suitable for the treatment and preparation of viscose products with cationic polymers (according to WO 99/36604).

[0090] (8) The copolymers are suitable as water-soluble amine-based polymer components in multilayer membranes for separating acidic gases from gaseous mixtures (according to DE 196 00 954).

[0091] (9) The copolymers are suitable for the preparation of aqueous and organic dispersions, emulsions or solutions of amine-based polymers. The amine-based polymers, dispersions, emulsions or solutions are particularly suitable for coating and imparting water repellency to surfaces (finish surfaces, packaging coating, building material impregnation, particle boards, stone, metal, textiles, plastics, leather, wood, paper), for the treatment of various materials (stone, metal, textiles, plastics, leather, wood, paper), as process chemicals in the textile industry, as additives in printing inks and finishes, and as mold release agents.

[0092] (10) The copolymers are suitable as effective corrosion inhibitors in radiation protection mixtures.

[0093] The copolymers are particularly preferably used as flow improvers, wax-anti-settling-additives and lubricity

additives, for reducing fretting, as corrosion inhibitors and/or as internal combustion engine intake system cleaners in mineral oils, mineral oil distillates and combustion and power fuels.

[0094] When used as flow improvers, the novel copolymers are preferably employed in combustion and power fuel compositions, in particular in middle distillates, such as diesel fuels and light heating oils. They can be used together with further conventional additives.

[0095] The novel copolymers can be incorporated into the mineral oils, mineral oil distillates and combustion and power fuels, in particular into a middle distillate, directly but preferably as 20 to 70% strength by weight solutions. Preferably used solvents are hydrocarbon solvents. Suitable solvents are described, for example, in DE-A-196 24 861 and DE-A-43 41 528. The novel copolymers may be dissolved in a large amount in a hydrocarbon solvent; preferably, the solutions contain from 5 to 80, particularly preferably from 20 to 70, particularly from 40 to 60, % by weight of one or more novel copolymers alone or together with other assistants, for example according to the abovementioned applications. The present invention also relates to such concentrates or mixtures.

[0096] The concentrates may be further used, for example, for the preparation of combustion and power fuel compositions (cf. DE-A-196 24 861).

[0097] The present invention also relates to combustion and power fuel compositions which contain from 5 to 5000, preferably from 10 to 500, ppm by weight, based on the total weight of the composition, of the copolymer, alone or together with other assistants.

[0098] The Examples which follow illustrate the invention.

EXAMPLES

[0099] Preparation of the Amination Catalyst:

[0100] An aqueous solution of nickel nitrate, cobalt nitrate and zirconium acetate, which contained 4.48% of NiO, 1.52% of CuO and 2.82% of ZrO₂, was precipitated simultaneously in a stirred vessel in a constant stream with a 20% strength aqueous sodium carbonate solution at 70° C. so that the pH of 7.0, measured using a glass electrode, was maintained.

[0101] The suspension obtained was filtered and the filter cake was washed with demineralized water until the electrical conductivity of the filtrate was about 20 mS. 1.5% of MoO₃ in the form of an aqueous solution of ammonium heptamolybdate were then stirred in. The filter cake was then dried at 150° C. in a drying oven or in a spray dryer. The basic carbonate mixture obtained in this manner was heated at 500° C. over a period of 4 hours.

[0102] The catalyst thus obtained had the following composition:

[0103] 51% by weight of NiO, 17% by weight of CuO, 30.5% by weight of ZrO₂ and 1.5% by weight of MoO₃. The catalyst powder was mixed with 3% by weight of graphite and molded to give 6x3 mm pellets.

[0104] Preparation of an Ethylene/vinyl Acetate/vinylamine Terpolymer:

[0105] First, an ethylene/vinyl acetate copolymer which was composed of 70.3% by weight of ethylene and 29.7% by weight of vinyl acetate was prepared. The melt viscosity at 120° C. was 65 mm²/s. The preparation was carried out as described in DE-A-197 54 039.

[0106] 75 g of this copolymer were mixed with 75 g of cyclohexane as a solvent, and 850 g of liquid ammonia were added in an autoclave. They were then heated at 200° C. for 16 hours at a hydrogen pressure of 200 bar in the presence of 50 g of the catalyst described above. Thereafter, cooling was carried out, the pressure was let down and the autoclave content was removed. After the catalyst had been filtered off and the cyclohexane separated off, 80 g of a liquid, colorless product were obtained.

[0107] The content of ethylene, vinyl acetate and vinylamine was determined by NMR spectroscopy. The terpolymer contained 75.6% by weight of ethylene, 14.7% by weight of vinyl acetate and 9.7% by weight of vinylamine. The kinematic melt viscosity, determined using a rotational viscometer at 120° C., was 70 mm²/S.

[0108] Test Oils

[0109] The novel terpolymer described above was used as an additive in various test oils. The test oils had the following characteristic data.

TABLE 1

	Test oil 1	Test oil 2	Test oil 3	Test oil 4	Test oil 5
Initial boiling point [° C.]	173	182	168	195	178
5% [° C.]	206	223	186	222	194
10% [° C.]	219	236	192	233	200
50% [° C.]	285	287	233	275	243
95% [° C.]	369	354	353	343	343
Final boiling point [° C.]	380	365	367	354	355
90%-20% [° C.]	115	87	127	80	115
FPB-90% [° C.]	27	25	39	27	30
Cloud point [° C.]	2.8	2	-6.4	-8.9	-7.7
CFPP [° C.]	0	0	-9	-12	-9
Sulfur [ppm]	2000	1800	450	310	45

[0110] The novel terpolymers were introduced into the test oils, and the cold filter plugging point (CFPP) was determined according to EN 116. In addition, the cloud point (CP) was determined according to ISO 3015. The CFPP is shown in Table 2 below.

TABLE 2

Test oil	Dose/ppm	CFPP [° C.]
1	100	-7
2	250	-2
3	50	-11
3	125	-18
4	25	-15

[0111] Lubricating Effect:

[0112] The lubricating effect of the ethylene/vinyl acetate/vinylamine terpolymer (II) described was determined in test

oil 5 according to DIN ISO 121546-1 (HFRR measurement). The results in Table 3 are specified as a wear scar diameter (WS 1.4). A lower wear scar indicates a good lubricating effect. A commercial lubricity additive Kerokorr® LA 99 (K) was used in comparison with the novel ethylene/vinyl acetate/vinylamine terpolymer (T).

TABLE 3

Additive	Dose/ppm	Wear scar diameter/ μm
No additive	—	590
T	50	483
T	75	304
K	50	516
K	75	421
K	100	333

[0113] Paraffin Sedimentation:

[0114] The effect on the paraffin sedimentation (wax-anti-settling) in test oil 3 was determined by an ARAL method (cf. Table 4). 500 ml of the diesel fuel were stored at -13° C. for 16 hours. The additives tested were the ethylene/vinyl acetate copolymer (C) described and the novel vinyl acetate/vinylamine terpolymer (T). The quality of the effect on the

paraffin sedimentation (wax-anti-settling) is determined by visual assessment:

[0115] Case (A): the sample is uniformly turbid and the paraffins are completely dispersed.

[0116] Case (B): the sample consists of two phases having different turbidities.

[0117] Case (C): the sample consists of two phase, the lower phase being turbid and the upper phase being clear.

[0118] Substances which lead to the results of case (A) and case (B) in the test are efficient wax-anti-settling additives. In addition, the cloud point (CP) and the CFPP are determined for the lower 20%. A positive effect on the low-temperature behavior of the test oil is present when the cloud point of the 20% lower phase is slightly (1-2° C.) above the cloud point before the storage test at -13° C.

Test oil 3 without additive CP: -6.4° C.		Visual assessment		20% lower phase	
CFPP: -9° C.	CFPP° C.	Lower phase	Upper phase	CP° C.	CFPP° C.
60 ppm of additive (C)	-20	42% paraffins settled out	58% clear phase	-0.0	-17
60 ppm of additive (C)	-27	28% paraffins settled out	72% turbid due to dispersed paraffins	-5.3	-27
75 ppm of additive (I)					

[0119] Table 4 shows that the ethylene/vinyl acetate copolymer used for the preparation of the ethylene/vinyl acetate/vinylamine terpolymer has no effect on the paraffin sedimentation. A positive effect on the paraffin sedimentation is achieved by adding the ethylene/vinyl acetate/vinylamine terpolymer to the ethylene/vinyl acetate copolymer.

We claim:

1. A process for the preparation of polymers which contain six or more vinylamine building blocks of the formula (I) in the main chain



where

R¹ and R², independently of one another, are each hydrogen, C₁₋₂₀-alkyl, C₆₋₁₈-aryl, C₇₋₂₀-alkaryl, C₇₋₂₀-aralkyl or a polyamine radical,

by reductive amination of copolymers which consist of C₂₋₁₂-olefin building blocks and vinyl esters of C₁₋₁₂-monocarboxylic acids as building blocks,

with amines of the formula (III)



and hydrogen.

2. A process as claimed in claim 1, wherein the copolymers to be aminated are ethylene/vinyl acetate copolymers.

3. A copolymer consisting of polymerized C₂₋₁₂-olefin building blocks, vinyl esters of C₁₋₁₂-monocarboxylic acids and six or more vinylamine building blocks of the formula (I)



where

R¹ and R², independently of one another, are each hydrogen, C₁₋₂₀-alkyl, C₆₋₁₈-aryl, C₇₋₂₀-alkaryl, C₇₋₂₀-aralkyl or a polyamine radical.

4. A copolymer as claimed in claim 3, consisting of polymerized ethylene, vinyl acetate and vinylamine building blocks.

5. The use of a copolymer as claimed in claim 3 or 4 as an assistant in mineral oils, mineral oil distillates and combustion and power fuels, in chromatography, as an ion exchanger, in dispersions, as an emulsifier, in papermaking, in inks, membranes, adhesives, detergents, mold release agents, in wastewater treatment, for coating and imparting water repellency to surfaces, for the treatment of materials, as a process chemical in the textile industry, and as an additive in printing inks and finishes.

6. The use as claimed in claim 5, as a flow improver, a wax-anti-settling additive or a lubricity additive, for reducing fretting, as a corrosion inhibitor and/or as an internal combustion engine intake system cleaner in mineral oil distillates.

7. A concentrate containing a mineral oil, a mineral oil distillate or a combustion or power fuel and from 5 to 80% by weight, based on the total amount of the concentrate, of at least one copolymer as claimed in either of claims 3 and 4.

8. A mixture of at least one concentrate as claimed in claim 7 and further assistants which are used according to the applications stated in claim 6.

9. A combustion or power fuel composition containing a combustion or power fuel and from 5 to 5000 ppm by weight, based on the total amount of the combustion or power fuel composition, of a copolymer as claimed in claim 3 or 4, alone or as a mixture with other mineral oil assistants.

10. A copolymer, obtainable by a process as claimed in claim 1 or 2.

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