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- (54) Benævnelse: **FREM GANGSMÅDE TIL FREMSTILLING AF POLYOXYALKYLEN POLYSILOXAN BLOKPOLYMERISATER**
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Description

The invention relates to a process for producing SiOC-linked, linear polydimethylsiloxane-polyoxyalkylene block copolymers of the structural type C-B-(AB)_a-Cl and also to the use thereof as constituents in interface-active substances, such as in PU foam stabilizers, defoamers, deaerating agents, emulsifiers, demulsifiers and paint and levelling additives.

10 The terms "siloxanes" and "polysiloxanes" are used as synonyms in the present invention.

The term "defoamer" in the present case encompasses both products and formulations that prevent foam and also those that destroy foam and enable deaeration. In practice, the transitions between these product properties are blurred, so that here the common collective term defoamer is used.

In many industrial processes, in particular when work is being carried out in aqueous media, it is necessary to repress or to completely prevent the undesired formation of foam during the production or processing operations, since foam or heads of foam which form during stirring and dispersing operations or form in the containers during the filling operation can lengthen the production times or reduce the effective volume of the plant or even prevent correct operation thereof, in that overflowing of the formulation out of the mixing tank cannot be avoided and a lack of colour transfer during the application thereof is unavoidable.

30 This can be achieved by adding defoamers which even at very low use concentrations of from approximately 0.001% by weight are capable of avoiding or destroying undesired foams and which at the same time do not cause any surface defects after application of the systems and suppress air inclusions in the paint. In practice, these aspects must be taken into account at least just as much as good defoaming.

Surface defects are to be understood to be features that are undesirable to the user such as for example pinholes, craters, loss of gloss, orange peel effect, wrinkling and loss of adhesion in the coating system. However, an appropriate long-term
5 stability of the defoamer in formulations is also of high importance to the user since products such as paints are often not used up immediately but instead sometimes only after a relatively long storage. In the case of storage under extreme climatic conditions (heat and solar irradiation), the efficacy
10 of a defoamer formulation can occasionally collapse after only a short time.

Defoamers according to the prior art are for example silicone oils, native oils, paraffin and mineral oils, but also
15 hydrophobic polyoxyalkylenes, long-chain alcohols and also mixtures of these products with one another and emulsions thereof.

Defoamers for defoaming aqueous and non-aqueous media and
20 comprising polyoxyalkylene polysiloxane polymers as the active agent with a crucial influence on the defoaming exhibit particular efficacy and storage stability. This includes foam inhibition, defoaming, very good long-term stability, and also outstanding compatibility in aqueous and non-aqueous media. All
25 of these properties are of high importance for modern paint applications.

For the purposes of increasing the efficacy, what are known as hydrophobic solids are frequently also added in amounts of 0.1%
30 to 10% by weight, which promote dewetting processes in a targeted manner at foam lamellae and hence assist the foam collapse very effectively. Suitable hydrophobic solids are corresponding hydrophobized or non-hydrophobized silicas, hydrophobized or non-hydrophobized precipitated silica, metal carboxylates such
35 as metal stearates, polyolefins and natural or synthetic waxes such as paraffin waxes, polyolefin waxes, amide waxes and urea or poly(ureas), such as described for example in DE 28 29 906 A1.

By means of addition of suitable emulsifiers or protective colloids, such defoamer formulations can also be converted into aqueous emulsions which can be additized more simply in paint formulations in terms of application. CN 101100515 A discusses a specific emulsification process, which can likewise be used for the emulsification of the polyether polysiloxane polymers.

It is likewise known to use polyoxyalkylene polysiloxane block copolymers as defoaming agents. For instance, DE 1 012 602 by way of example describes polyoxyalkylene polysiloxane polymers having an A'-B'-A' structure, where A' denotes the polyoxyalkylene blocks and B' denotes a polysiloxane block. These active agents are assigned to the so-called SiOC polyethersiloxane defoamer substance class.

DE 24 43 853 describes defoaming preparations which comprise not only linear but also branched polyoxyalkylene polysiloxane block copolymers.

US 4,028,218 describes a process for preventing or destroying foam in aqueous solutions or dispersions, which uses a similar preparation as that described in DE 24 43 853. The preparation essentially differs in an additional content of organic oil which likewise has a defoaming action. Suitable organic oils are the esters of alcohols and fatty acids, such as for example vegetable or animal oils, mineral oils, polybutadiene oils or polypropylene glycols.

According to the current state of the art, a plurality of process variants are used for the production of the economically important substance class of the SiOC-linked polyethersiloxanes, also referred to as silicone polyethers or polysiloxane polyether copolymers.

It is known to those skilled in the art that these SiOC-linked polyethersiloxanes are a product class which does not have a tendency to resinify. Even if SiOC-linked polyethersiloxanes

contain reactive groups such as hydroxy groups, they are not used for the targeted crosslinking. In contrast to silicone resins, they are not film-forming.

5 SiOC-linked polyethersiloxanes are classically formed by the reaction of a polysiloxane having a leaving group (e.g. halogen) bonded to the silicon atom and an alcohol or polyetherol. The latter is typically obtained beforehand by alkoxylation of hydroxy-functional starter compounds such as for example
10 methanol, butanol or glycol with alkylene oxides. Chlorine as leaving group on the silicon atom is in particular known and widespread as starting compounds for this type of reaction. However, chlorosiloxanes and chloropolysiloxanes are difficult to handle as they are extremely reactive. The use thereof is
15 additionally associated with the disadvantage that hydrogen chloride formed in the course of the reaction necessitates corrosion-resistant installations and results in both technical and environmental challenges. Moreover, organic chlorine compounds which are undesirable for toxicological reasons can
20 also be formed in the presence of chloropolysiloxanes and alcohols or polyetherols, such that in the production process there are the requirements of suppressing and destroying these. As is known to those skilled in the art, it is also necessary in the case of the reaction of a chlorosiloxane with an alcohol
25 or polyetherols to achieve and to ensure a quantitative conversion, with the result that the OH-functional component often needs to be used in a stoichiometric excess based on the chlorine leaving group of the polysiloxane component. In practice, the use of a polyether excess means that the
30 polyethersiloxanes thus produced unavoidably contain relatively large amounts of unreacted excess polyethers which lower the concentration of the active polyethersiloxane component and impair the performance properties of the polyethersiloxanes. It is frequently additionally necessary to use HCl scavengers in
35 the above-described process in order to achieve suitable quantitative conversions. The use of HCl scavengers results in the formation of large quantities of salt, the removal of which on an industrial scale causes problems.

Defoamers for defoaming aqueous and non-aqueous media and comprising linearly structured polyoxyalkylene polysiloxane block copolymers as the active agent with a crucial influence on the defoaming exhibit particular efficacy and stability. This includes foam inhibition, defoaming, very good long-term stability, and also outstanding compatibility in aqueous and non-aqueous media. All of these factors are of great importance for modern processes in the field of surface technology.

EP 2094761 B1 describes polyoxyalkylene-polysiloxane block polymers and a process for the production thereof by reaction of the alcohol components with chloropolysiloxanes.

The chloropolysiloxanes used in this document are linear structures with α,ω chlorine functionality, with the of the cycles D4 and D5 being mixed in a defined quantitative ratio with dimethyldichlorosilane, possibly with the addition of water to control the chain length, and being further equilibrated by means of addition of what is known as an equilibration catalyst, such as for example sulfuric acid, methanesulfonic acid, trifluoromethanesulfonic acid or iron(III) chloride. EP 2094761 B1 further states that in the case of the preferred use of iron(III) chloride as catalyst for the preparation of the linear α,ω -dichlorosiloxanes, prior removal of the catalyst using activated carbon is recommended in order to preclude undesired discolourations as a result of the presence of the iron catalyst.

One possible alternative to this process comprises reacting alcohols or polyetherols with hydrosiloxanes in which hydrogen is directly bonded to the silicon. Under suitable conditions the formation of the SiOC bond here results merely in elimination of hydrogen. This process, known as dehydrogenative condensation, can be performed exclusively only in the presence of a catalyst. US 5,147,965 refers to a process described in the Japanese patent publication JPS 4819941, in which a hydrosiloxane is reacted with an alcohol with the addition of alkali metal hydroxides or alkali metal alkoxides. A

disadvantage with this process is that the catalysts have to be neutralized after reaction is complete and the salt load formed in the process, although it is much lower than that of the chlorosiloxane process, nevertheless requires complicated removal by filtration.

EP 3 438 158 describes a process for producing SiOC-linked polyethersiloxanes by transesterification of alkoxysiloxanes with polyetherols in the presence of zinc acetylacetonate as catalyst.

EP 0 475 440 describes a process in which hydrosiloxanes are reacted with an alcohol with addition of an organic acid in the presence of a Pt salt. The reaction unavoidably requires the use of large amounts of organic acid (0.1 to 1 mol based on alcohol), toluene as solvent and a platinum salt. Since both toluene and acid are undesirable in the end product, they must be removed in turn after the end of the reaction. In addition, platinum salts are not only expensive but also not unproblematic from a physiological viewpoint. Specifically in the cosmetics industry sector, there is a demand for platinum-free products.

The process described in J. Boyer, R. J. P. Corriu, R. Perz, C. Reye, J. Organomet. Chem. 1978, 157, 153-162 does not require the use of heavy metals. Salts such as potassium tartrate, phthalate or formate for example are used as heterogeneous catalysts. However, the reactions require equimolar use of the salts based on the SiH units and are successful only at high temperatures of approx. 180°C. Both the drastic conditions and the large quantities of salt required render this process unattractive for the technical and industrial scale.

Patent applications DE 10 312 636 and DE 10 359 764 utilize boron-containing catalysts for the dehydrogenative condensation of hydrosiloxanes and alcohols. As much as these dehydrogenative processes for SiOC linking are attractive, specifically in relation to the avoidance of liquid and/or solid by-products, both the use of costly and toxic catalysts such as for example

tris(pentafluorophenyl)borane and the safe handling of the hydrogen gas formed in the synthesis stand in the way of widespread application of the technology on an industrial scale.

5 The present invention is therefore based on the object of providing a process for producing linear SiOC-linked polyethersiloxane block copolymers of the structural type C-B-(AB)_a-C1 which do not exhibit any of the disadvantages known from the prior art with respect to the use of the chlorosiloxane.

10

It has now been found that, surprisingly, a simple chlorine-free route to polyoxyalkylene polysiloxane block copolymers of general formula (I)



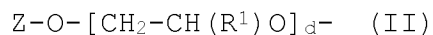
15 (I)

in which

A = a polyoxyalkylene block of the general formula $(\text{C}_n\text{H}_{2n}\text{O})_b-$,

20 B = a polysiloxane block of the general formula $(\text{SiR}_2\text{O})_c-$,

C, C1 = identical or different alkoxyalkylene radicals of general formula (II)



where Z = an alkyl, alkylene, aryl or alkylaryl radical,

25 or

C, C1 = an alkyl radical with the proviso that C or C1 possesses an alkoxyalkylene radical of general formula (II) where Z = hydrogen,

or

30 C, C1 = identical or different alkoxyalkylene radicals of general formula (II) where Z = a hydrogen with the proviso that C or C1 possesses an alkoxyalkylene radical of general formula (II) where Z = an alkyl, alkylene, aryl or alkylaryl radical,

35 R = identical or different C₁₋₄-alkyl radicals or phenyl radicals with the proviso that at least 90% of the radicals R are methyl radicals,

R^1 = identical or different hydrogen radicals, C_{1-12} -alkyl radicals or phenyl radicals,

a = 1 to 20,

b = an average value of from 10 to 130,

5 c = 3 to 100,

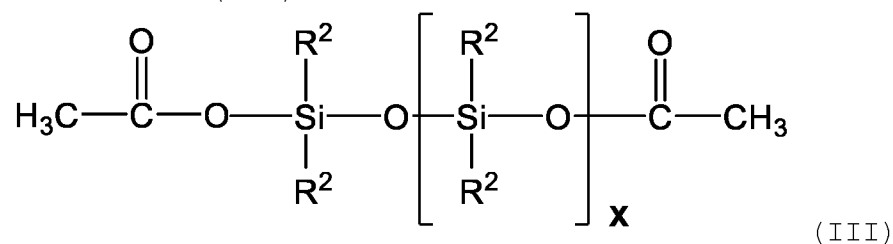
d = independently of one another in C/C1 values of from 2 to 20 with the proviso that the average value is in the range from 2 to < 15,

10 n = 2 to 12 with an average numerical value of from 2.7 to 4.0,

is opened up by reacting end-equilibrated α,ω -diacetoxypolydimethylsiloxanes with a mixture consisting of at least one polyether polyol, preferably a polyether diol, and at least one polyether monool or at least one monohydric alcohol.

15

Preferably, end-equilibrated α,ω -diacetoxypolydimethylsiloxanes of formula (III) below



where

20 R^2 is an alkyl radical having 1 to 4 carbon atoms or a phenyl radical, but preferably more than 90% of the radicals R^2 are methyl radicals and

$x = 2 \leq x \leq 250$, preferably $5 \leq x \leq 100$,

particularly preferably $10 \leq x \leq 30$,

25 are used.

Routes to acetoxy-functional polysiloxanes are described in the literature. The as-yet unpublished European patent applications having the application reference numbers EP 18172882.5, EP 18172876.7, EP 18189072.4, EP 17195510.7, EP 17204277.2, EP 18189073.2 and EP 18210035.4 address the preparation of trifluoromethanesulfonic acid-acidified, equilibrated acetoxysilanes of linear structural type.

Cited as a reference in relation to the M, D, T, Q nomenclature used in the context of this document to describe the structural units of organopolysiloxanes is W. Noll, Chemie und Technologie der Silicone [Chemistry and Technology of the Silicones], Verlag Chemie GmbH, Weinheim (1960), page 2 ff.

Following the teaching of EP 18189073.2, for example, cyclic polysiloxanes, in particular comprising D4 and/or D5, and/or mixtures of cyclic branched polysiloxanes of D/T type are reacted with acetic anhydride while using trifluoromethanesulfonic acid as catalyst and with addition of acetic acid. In addition, EP 18189073.2 states that both mixtures of cyclic branched polysiloxanes of D/T type, which consist exclusively of polysiloxanes having D and T units and whose cumulative proportion, determinable with ^{29}Si NMR spectroscopy, of D and T units present in the siloxane matrix and having Si-alkoxy and/or SiOH groups is less than 2 mole percent, preferably less than 1 mole percent, and that they additionally advantageously contain at least 5% by weight of siloxane cycles, such as preferably octamethylcyclotetrasiloxane (D4), decamethylcyclopentasiloxane (D5) and/or mixtures thereof, and also mixtures of cyclic branched siloxanes having exclusively D and T units, whose cumulative proportion, determinable with ^{29}Si NMR spectroscopy, of D and T units present in the siloxane matrix and having Si-alkoxy and/or SiOH groups is greater than 2 and less than 10 mole percent, are particularly well suited for the production of end-equilibrated polysiloxanes having acetoxy functions.

The as-yet unpublished European application document 18210035.4 likewise describes (i) reaction systems for the production of polysiloxanes bearing acetoxy functions, comprising a) silanes and/or polysiloxanes bearing alkoxy groups and/or b) silanes and/or polysiloxanes bearing acetoxy groups, c) silanes and/or polysiloxanes bearing hydroxy groups, d) optionally simple polysiloxane cycles and/or DT cycles, e) a reaction medium, comprising acetic anhydride, perfluoroalkanesulfonic acid and preferably acetic acid, (ii) a process for producing linear or

branched polysiloxanes bearing acetoxy functions. According to the application identified above, it is for example possible to arrive at a branched polysiloxane bearing terminal acetoxy groups by reacting a branched polysilicone equilibrate (= pre-equilibrate) bearing terminal alkoxy groups as sole reactant with a reaction medium consisting of acetic anhydride, trifluoromethanesulfonic acid and acetic acid.

It is preferably conceivable for polysiloxanes having Q units to also be used in addition to polysiloxanes having D and T units, with the proviso that in these mixtures the proportion of Si atoms coming from Q units amounts to $\leq 10\%$ by mass to $\geq 0\%$ by mass, preferably $\leq 5\%$ by mass to $\geq 0\%$ by mass, wherein the lower limit may be > 0 or $= 0\%$ by mass, but is especially $> 0\%$ by mass, in each case based on the entirety of all Si atoms.

The provision of mixtures of cyclic branched polysiloxanes of D/T type, which in addition to polysiloxanes having D and T units also contain those having Q units, is readily possible for those skilled in the art for example in analogy to the teaching of the documents mentioned using for example silicic esters yielding Q units (Si(OR)_4).

The end-equilibrated α,ω -diacetoxypolydimethylsiloxanes of formula (III) below are preferably obtainable from the reaction of

- silanes and/or siloxanes bearing alkoxy groups, and/or
- silanes and/or siloxanes bearing hydroxy groups, and/or
- simple siloxane cycles and/or DT cycles,
- with acetic anhydride, superacid, in particular trifluoromethanesulfonic acid, and acetic acid.

Preferably, for the production of the end-equilibrated α,ω -diacetoxypolydimethylsiloxanes of formula (III), a silane and/or siloxane bearing alkoxy groups and containing at least one T and/or Q group, and/or DT cycles can be used.

In a preferred embodiment of the invention, acetic acid is added in amounts of 0.4 to 3.5 per cent by weight, with preference 0.5 to 3 per cent by weight, preferably 0.8 to 1.8 per cent by weight, particularly preferably in amounts of 1.0 to 1.5 per cent by weight, based on the reaction matrix consisting of acetic anhydride and cyclic polysiloxanes, comprising D4 and/or D5, or consisting of acetic anhydride and mixtures of cyclic branched polysiloxanes of D/T type, optionally also having Q units, or consisting of cyclic polysiloxanes, comprising D4 and/or D5, and mixtures of cyclic branched polysiloxanes of D/T type.

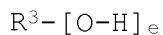
In a preferred embodiment of the invention, the catalyst trifluoromethanesulfonic acid is used in amounts of 0.1 to 1.0 per cent by mass, preferably 0.1 to 0.3 per cent by mass, based on the reaction matrix consisting of acetic anhydride and cyclic polysiloxanes, especially comprising D4 and/or D5, and/or cyclic branched polysiloxanes of D/T type, optionally also having Q units.

The term "end-equilibrated" is to be understood as meaning that the equilibrium established at a temperature of 23°C and a pressure of 1013.25 hPa has been reached. The indicator of attaining the equilibrium employed may be the total cycles content determined by gas chromatography and defined as the sum total of the D4, D5, and D6 contents, based on the siloxane matrix and ascertained after derivatization of the α,ω -diacetoxypolydimethylpolysiloxanes to give the corresponding α,ω -diisopropoxypolydimethylpolysiloxanes or after the derivatization of the branched acetoxypolysiloxanes to give the corresponding branched isopropoxysiloxanes. The inventive use of the acetic acid makes it possible here to undershoot without problems otherwise customary equilibrium proportions of about 8 per cent by weight for the total cycles content in the branched acetoxypolysiloxanes. It accordingly corresponds to a preferred embodiment when equilibrium proportions of the total cycles content of less than 8, preferably less than 7 per cent by weight are undershot in the branched acetoxypolysiloxanes. The derivatization to give the branched isopropoxypolysiloxanes is

chosen here deliberately in order to prevent a thermally induced redissociation reaction of the α,ω -diacetoxypolydimethylpolysiloxanes or of the branched acetoxypolysiloxanes which may take place under the conditions of analysis by gas chromatography (regarding the redissociation reaction, see *inter alia* J. Pola et al., Collect. Czech. Chem. Commun. 1974, 39(5), 1169-1176 and also W. Simmler, Houben-Weyl, Methods of Organic Chemistry, Vol. VI/2, 4th Edition, O-Metal Derivates of Organic Hydroxy Compounds p. 162 ff.).

Preferably, for component A of formula (I), polyether polyols selected from polyether diols, polyether polyols or mixtures of polyether diols and polyether polyols are used.

The polyether polyols are preferably prepared by addition of alkylene oxides, according to the invention preferably ethylene oxide, propylene oxide, butylene oxide, styrene oxide, preferably mixed products composed of at least two monomer units, especially of ethylene oxide and propylene oxide, onto polyhydric starter alcohols of the general formula



in which

R^3 = an e-valent hydrocarbon radical and $e = 2$ to 6 , preferably can be 2 to 3 , according to the alkoxylation methods known in the prior art. Starter alcohols that can be used are in principle all straight-chain or branched alcohols that are at least dihydric. According to the invention, preference is given to di- and/or trihydric alcohols such as in particular ethanediol, propanediol, butanediol, hexanediol, trimethylolpropane, which can be used alone or as a mixture.

In a preferred embodiment, the polyether polyols essentially consist of oxyethylene units or oxypropylene units, preference being given to mixed oxyethylene and oxypropylene units with an oxyethylene content of about 1 to 70 per cent by weight and 99 to 30 per cent by weight oxypropylene content, based on the total content of oxyalkylene units in the block.

According to the invention, preference is given to polyether diols in which ethylene oxide (EO) and propylene oxide (PO) are present as copolymers. Particular preference is given to EO/PO copolymers having a block-type construction and containing an
5 EO content of about 1% to 30% by weight based on the total content of oxyalkylene units.

Preferably, for component C, C1 of formula (I), a polyether monool or a monohydric C1 - C18 alcohol selected from methanol,
10 ethanol, propanol, isopropanol, butanol and isobutanol is used.

The polyether monools can in principle be prepared in the same way as the polyether polyols, with the modification that the starter alcohols used are monofunctional compounds Z^1 -OH, in
15 which Z^1 can be an alkyl, alkylene, alkylaryl, aryl radical which optionally is branched and/or contains multiple bonds and which has 1 to 18 carbon atoms, preferably 1 to 10 carbon atoms.

Preferably, the molar ratio of end-equilibrated α,ω -diacetoxypolydimethylsiloxanes to the mixture consisting of at least one polyether polyol, preferably a polyether diol, and at least one polyether monool or at least one monohydric alcohol is in the range from 1.01 to 3.00, preferably in the range from 1.01 to 2.00, very particularly preferably in the range 1.01 to
25 1.50.

Preferably, the reaction, that is to say the reaction of end-equilibrated α,ω -diacetoxypolydimethylsiloxanes of formula (III) with a mixture consisting of at least one polyether polyol, preferably a polyether diol, and at least one polyether monool or at least one monohydric alcohol, is conducted at temperatures of 20°C to 180°C, preferably at temperatures of 60°C to 150°C.
30

In a preferred embodiment, the bases to be used are selected from the alkali metal and/or alkaline earth metal carbonates and/or hydrogencarbonates and/or amines, very particularly preferably gaseous ammonia.
35

As known to those skilled in the art, the use of simple solid bases is also envisaged. Taking the poor solubility of the alkali metal/alkaline earth metal carbonates and/or hydrogencarbonates in the reaction system into account, according to the invention
5 relatively high excesses of these are selected which correspond at least to a 2000-fold stoichiometric equivalent of the trifluoromethanesulfonic acid present in the α,ω -diacetoxypolydimethylsiloxane.

10 A known technical alternative for conducting the SiOC linking reaction is that of using buffer mixtures consisting of sodium trichloroacetate and trichloroacetic acid, or sodium acetate and trichloroacetic acid, both in each case dissolved in acetic acid. Here too, the amount of bases present in the buffer
15 mixtures is typically such that it corresponds at least to the stoichiometric equivalent, preferably to a 2- to 3-fold stoichiometric equivalent of the trifluoromethanesulfonic acid present in the α,ω -diacetoxypolydimethylsiloxane used.

20 With respect to the amount of the acetic acid used for dissolving the buffer mixture, the from the unpublished inventions state that it is preferably selected such that it is sufficient to produce a clear buffer solution that is free of solid salt contents and which can be metered into the reaction matrix in a
25 loss-free manner. Use amounts of acetic acid exceeding this are in contrast less critical for the successful performance of the process according to the invention, however large amounts are also not advantageous since they must then be removed again from the reaction matrix.

30 Taking account of the known tendency to condensation of acetoxysiloxanes, very particular preference is given to those bases which on account of their chemical composition do not introduce any water into the reaction system. Thus anhydrous
35 carbonates are preferred over hydrogencarbonates and bases free from water of hydration are preferred over bases containing water of hydration.

In a preferred embodiment of the invention, inert solvents that can be used are alkanes, cycloalkanes, alkylaromatics, end-capped polyethers and/or emollient esters, such as the esters derived from lauric acid, myristic acid, palmitic acid, stearic acid, oleic acid, isostearic acid, ricinoleic acid and behenic acid combined with cetyl, stearyl, isostearyl, oleyl, octyldodecyl, myristyl and behenyl alcohol or glycerol, preferably myristyl myristate.

10 In a preferred embodiment, the reaction with a mixture consisting of at least one polyether polyol, preferably a polyether diol, and at least one polyether monool or at least one monohydric alcohol is effected solventlessly.

15 Preferably, the weight-average molecular weight of each polysiloxane block (B) is between 650 to 6500 g/mol, preferably 800 to 1500 g/mol, particularly preferably 1000 to 1200 g/mol.

The polydimethylsiloxane-polyoxyalkylene block copolymer produced by the process according to the invention has a weight-average molecular weight of at least 2000 g/mol to approx. 160 000 g/mol, preferably 4000 g/mol to approx. 50 000 g/mol, in particular 5000 g/mol to approx. 36 000 g/mol. The determination of the average molecular weights is based on the known methods of GPC analysis.

In order to guarantee increased storage stability, the linear SiOC-linked polyethersiloxanes produced by the process according to the invention can additionally also be admixed with small amounts of organic amines, such as for example N-methylmorpholine, triisopropanolamine or triethanolamine. This corresponds to a preferred embodiment of the invention.

The invention also further provides for the use of the SiOC-linked, linear polydimethylsiloxane-polyoxyalkylene block copolymers of formula (I) according to the invention, produced by the process according to the invention, as interface-active additives for the production of PU foam stabilizers, defoamers,

deaerating agents, emulsifiers, demulsifiers and paint and levelling additives.

It is likewise conceivable to use the SiOC-linked, linear polydimethylsiloxane-polyoxyalkylene block copolymers produced by the process according to the invention for the production of diesel defoamers, of hydrophobizing agents, of polymer dispersions, of adhesives or sealants, of paper towels; of cleaning and care formulations for the household or for industrial applications, in particular for the production of fabric softeners, of cosmetic, pharmaceutical and dermatological compositions, in particular cosmetic cleansing and care formulations, hair treatment agents and hair aftertreatment agents; of construction material compositions, of thermoplastic shaped bodies.

The SiOC-linked, linear polydimethylsiloxane-polyoxyalkylene block copolymers produced by the process according to the invention can also be used as processing aid in the extrusion of thermoplastics, as adjuvant in crop protection, as additive for the cleaning and care of hard surfaces, for the surface treatment of fibres, particles or fabrics, in particular for the finishing or impregnation of textiles, or in the coating of fillers.

25

Methods

The following examples serve only to elucidate this invention for those skilled in the art and do not constitute any restriction whatsoever of the claimed subject matter. The inventive determination of the water contents is in principle performed by the Karl Fischer method based on DIN 51777, DGF E-III 10 and DGF C-III 13a.

35 In the context of the present invention, the ^{29}Si NMR samples are analysed at a measurement frequency of 79.49 MHz in a Bruker Avance III spectrometer equipped with a 287430 sample head with gap width of 10 mm, dissolved at 22°C in CDCl_3 and against a

tetramethylsilane (TMS) external standard [$d(^{29}\text{Si}) = 0.0$ ppm].
 ^{29}Si NMR spectroscopy was used for reaction monitoring in all examples.

5 The gas chromatograms are recorded on a GC instrument of the GC 7890B type from Agilent Technologies, equipped with a column of the HP-1 type; 30 m x 0.32 mm ID x 0.25 μm dF (Agilent Technologies no. 19091Z-413E) and hydrogen as carrier gas, with the following parameters:

10 Detector: FID; 310°C

Injector: split; 290°C

Mode: constant flow, 2 ml/min

Temperature programme: 60°C at 8°C/min -150°C at 40°C/min - 300°C 10 min.

15

The indicator of attaining the equilibrium employed is the total cycles content determined by gas chromatography and defined as the sum total of the D4, D5, and D6 contents, based on the siloxane matrix and ascertained after derivatization of the α,ω -diacetoxypolydimethylsiloxanes to give the corresponding α,ω -diisopropoxypolydimethylsiloxanes. The derivatization to give the α,ω -diisopropoxypolydimethylsiloxanes is chosen here deliberately in order to prevent a thermally induced redissociation reaction of the α,ω -diacetoxypolydimethylsiloxanes which may take place under the conditions of analysis by gas chromatography (regarding the redissociation reaction, see *inter alia* J. Pola et al., Collect. Czech. Chem. Commun. 1974, 39(5), 1169-1176 and also W. Simmler, Houben-Weyl, Methods of Organic Chemistry, Vol. VI/2, 4th Edition, O-Metal Derivates of Organic Hydroxy Compounds p. 162 ff.).

30

The polyether diols used have water contents of approx. 0.2% by mass and are used without further pre-drying. Employed toluene and, respectively, alkylbenzene (C_{10} - C_{13}) have a water content of 0.03% by mass and are likewise used without pre-drying.

35

The OH number of the polyether diols is determined according to DGF C-V 17 a (53) or according to Ph. Eur. 2.5.3 Method A, wherein the hydroxyl groups of the sample to be analysed are firstly acetylated with acetic anhydride in the presence of pyridine and then within the scope of a differential titration (blank sample, accounting for acetic anhydride excess) the liberated acetic acid is titrated as the consumption of KOH in mg per gram of polyether diol.

10 Example

a) Production of an end-equilibrated, acetoxy-terminated, linear polydimethylsiloxane

15 A 1000 ml four-neck flask equipped with a precision glass stirrer, an internal thermometer, and a reflux condenser on top is initially charged with 77.3 g (0.757 mol) of acetic anhydride together with 732.8 g (1.98 mol) of decamethylcyclopentasiloxane (D₅) and 24.3 g of acetic acid (3.0 per cent by weight based on the total mass of the reactants) while stirring and this is admixed with 1.62 g (0.88 ml) of trifluoromethanesulfonic acid (0.2 per cent by mass based on the total mixture) and swiftly heated to 150°C. The initially slightly cloudy reaction mixture is left at this temperature for 25 4 hours with continued stirring.

After cooling the mixture, a colourless, clear, mobile liquid is isolated, the ²⁹Si NMR spectrum of which demonstrates the presence of Si-acetoxy groups in a yield of approx. 93% based on acetic anhydride used, corresponding to an α,ω-diacetoxypolydimethylsiloxane having an average total chain length of approx. 14.

35 Conversion of the α,ω-diacetoxypolydimethylsiloxane into the corresponding α,ω-diisopropoxypolydimethylsiloxane for analytical characterization

Immediately after the synthesis, in a 250 ml four-neck round-bottom flask equipped with a precision glass stirrer, an internal thermometer, and a reflux condenser on top, 50.0 g of this trifluoromethanesulfonic acid-acidified, equilibrated α,ω -diacetoxypolydimethylsiloxane are mixed together with 11.3 g of a molecular sieve-dried isopropanol at 22°C with stirring. Gaseous ammonia (NH₃) is then introduced to the reaction mixture until alkaline reaction (moist universal indicator paper) and the mixture is then stirred at this temperature for a further 45 minutes. The precipitated salts are separated off using a fluted filter.

A colourless, clear liquid is isolated, whose accompanying ²⁹Si NMR spectrum demonstrates the quantitative conversion of the α,ω -diacetoxypolydimethylsiloxane into an α,ω -diisopropoxypolydimethylsiloxane.

An aliquot of this α,ω -diisopropoxypolydimethylsiloxane is withdrawn and analysed by gas chromatography. The gas chromatogram shows the following contents (reported in per cent by mass):

D ₄	D ₅	D ₆	Sum total (D ₄ - D ₆)	Isopropanol content
4.09%	2.62%	0.86%	7.57%	4.60%

b) Production of an SiOC-linked, linear polydimethylsiloxane-polyoxyalkylene block copolymer of the structural type C-B-(AB)_a-C1

In a 250 ml four-neck flask equipped with a precision glass paddle stirrer, an internal thermometer, and a reflux condenser on top, a mixture of 67.9 g of a polyether diol having an average molar mass of 2671 g/mol (determined according to OH number) and having a ratio by mass of ethylene oxide to propylene oxide of 60:40 and 4.0 g of a butanol-started polyetherol (propylene oxide content of 100%) having a molar mass of 600 g/mol (molar mass determined according to OH number) is admixed while

stirring with a solution of sodium acetate and trichloroacetic acid (0.06 g of sodium acetate (0.2% by weight based on the acetoxysiloxane) and 0.21 g of trichloroacetic acid (0.2% by weight based on the total mixture consisting of the polyether mixture and acetoxysiloxane)) in 5 g of acetic acid. This is followed by the addition of 28.0 g of the trifluoromethanesulfonic acid-acidified α,ω -diacetoxypolydimethylsiloxane from step a). The reaction mixture is heated to 70°C and is held at this temperature for 3 hours while stirring vigorously. The reflux condenser on top is replaced by a short distillation bridge and the reaction mixture is freed of volatiles at 100°C bottom temperature and an applied auxiliary vacuum of 1 mbar.

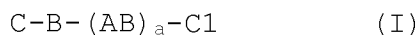
After cooling down to 70°C, 17 g of isopropanol are added while stirring and the mixture is allowed to react at this temperature for 3 hours, and subsequently 2.4 g of sodium carbonate (2.0% by weight based on the total mixture) are added and the mixture is stirred for a further 2 hours.

After cooling to 25°C, the solid constituents are separated off using a fluted filter and excess isopropanol is removed from the clear filtrate by means of distillation on a rotary evaporator at 70°C/1 mbar auxiliary vacuum.

A colourless copolymer having a viscosity of 1750 mPas is isolated, the accompanying ²⁹Si NMR spectrum of which confirms the target structure (20% isopropoxy-substituted Si end groups based on 80% of the SiOC bonds originating from the polyether Si linkage).

Patentkrav

1. Fremgangsmåde til fremstilling af SiOC-bundne, lineære polydimethylsiloxan-polyoxyalkylen-blokcopolymerer med den generelle formel (I)



hvor i betyder

A = en polyoxyalkylenblok med den generelle formel $(\text{C}_n\text{H}_{2n}\text{O})_b-$,

B = en polysiloxanblok med den generelle formel $(\text{SiR}_2\text{O})_c-$, C, C1

= ens eller forskellige alkoxyalkylenradikaler med den generelle formel (II)



med Z = et alkyl-, alkylen-, aryl- eller alkylarylradikal, eller

C, C1 = et alkylradikal med det forbehold, at C eller C1 har et alkoxyalkylenradikal med den generelle formel (II) med Z = hydrogen, eller

C, C1 = ens eller forskellige alkoxyalkylenradikaler med den generelle formel (II) med Z = et hydrogen med det forbehold, at C eller C1 har et alkoxyalkylenradikal med den generelle formel (II) med Z = et alkyl-, alkylen-, aryl- eller alkylarylradikal,

R = ens eller forskellige $\text{C}_1 - 4$ -alkylradikaler eller phenylradikaler med det forbehold, at i det mindste 90 % af radikalerne R er methylradikaler,

R^1 = ens eller forskellige hydrogen-, C_{1-12} -alkylradikaler eller phenylradikaler,

a = 1 til 20,

b = en gennemsnitlig værdi på 10 til 130,

c = 3 til 100,

d = uafhængigt af hinanden i C/C1 værdier på 2 til 20 med det forbehold, at middelværdien ligger i området 2 til < 15,

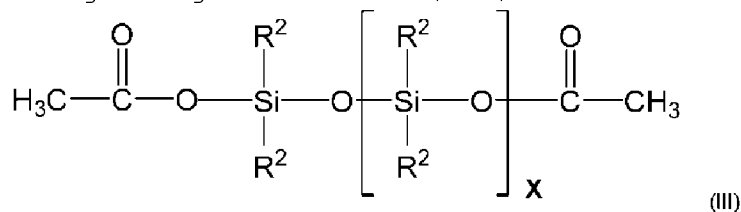
n = 2 til 12 med en gennemsnitlig talværdi på 2,7 til 4,0

kendetegnet ved, at

man omdanner ende-ækvilibrerede α, ω -diacetoxy-polydimethylsiloxaner med en blanding bestående af i det mindste en polyetherpolyol, foretrukket en polyetherdiol, og i det

mindste en polyethermonool eller i det mindste en monovalent alkohol.

2. Fremgangsmåde ifølge krav 1, kendetegnet ved, at der anvendes ende-ækvilibrerede α, ω -diacetoxy-polydimethylsiloxaner ifølge følgende formel (III)



hvorved

- R^2 er et alkylradikal med 1 til 4 carbonatomer eller et phenylradikal, dog er foretrukket mere end 90 % af radikalerne R^2 methylradikaler, og
 $x = 2 \leq x \leq 250$, foretrukket $5 \leq x \leq 100$, særligt foretrukket $10 \leq x \leq 30$.

3. Fremgangsmåde ifølge krav 1 eller 2, kendetegnet ved, at de ende-ækvilibrerede, α, ω -diacetoxy-polydimethylsiloxaner ifølge formel (III) kan opnås fra omdannelsen af
- alkoxygrupper bærende silaner og/eller siloxaner, og/eller
 - hydroxygrupper bærende silaner og/eller siloxaner, og/eller
 - simple siloxancykler og/eller DT-cykler,
 - med acetanhydrid, supersyre, især trifluormethansulfonsyre, samt eddikesyre.

4. Fremgangsmåde ifølge et af kravene 1 til 3, kendetegnet ved, at der til fremstillingen af de ende-ækvilibrerede α, ω -diacetoxy-polydimethylsiloxaner ifølge formel (III) anvendes en silan og/eller siloxan, der bærer alkoxygrupper og indeholder i det mindste en T- og/eller Q-gruppe, og/eller DT-cykler.

5. Fremgangsmåde ifølge et af kravene 1 til 4, kendetegnet ved, at man til komponent A med formel (I) anvender polyetherpolyoler udvalgt fra polyetherdioler, polyetherpolyoler eller blandinger af polyetherdioler og polyetherpolyoler.

6. Fremgangsmåde ifølge et af kravene 1 til 4, kendetegnet ved, at man til komponent C, C1 med formel (I) anvender en polyethermonool eller en monovalent C1 - C18 - alkohol udvalgt fra methanol, ethanol, propanol, isopropanol, butanol, isobutanol.
7. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at det molære forhold af ende-ækvilibrerede α,ω -diacetoxy-polydimethylsiloxaner til blandingen bestående af i det mindste en polyetherpolyol, foretrukket en polyetherdiol, og i det mindste en polyethermonool eller i det mindste en monovalent alkohol ligger i området fra 1,01 til 3,00, foretrukket i området 1,01 til 2,00, helt særligt foretrukket i området 1,01 til 1,50.
8. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at omdannelsen gennemføres med en blanding bestående af i det mindste en polyetherpolyol, foretrukket en polyetherdiol, og en polyethermonool eller en monovalent alkohol ved temperaturer fra 20 °C til 180 °C, foretrukket ved temperaturer fra 60 °C til 150 °C.
9. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at de baser, der skal anvendes, er udvalgt fra alkali- og/eller jordalkali-carbonaterne og/eller -hydrogencarbonater og/eller aminer, ganske særligt foretrukket gasformig ammoniak.
10. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at der som inerte opløsningsmidler anvendes alkaner, cycloalkaner, alkylaromater, endelukkede polyethere og/eller emollientestere, såsom de af laurinsyre, myristinsyre, palmitinsyre, stearinsyre, oliesyre, isostearinsyre, ricinolsyre og behenilsyre afledte estere kombineret med cetyl-, stearyl-, isostearyl-, oleyl-, octyldodecyl-, myristyl- og behenyl-alkohol eller glycerin, fortrinsvis myristylmyristat.
11. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at omdannelsen sker opløsningsmiddelfrit med en blanding bestående af i det mindste en polyetherpolyol, foretrukket en

polyetherdiol, og en polyethermonool eller en monovalent alkohol.

12. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at den vægtgennemsnitlige molekylvægt, bestemt på grundlag af de kendte metoder i GPC-analysen, for hver polysiloxanblok (B) ligger mellem 650 og 6500 g/mol, fortrinsvis 800 til 1500 g/mol, særligt foretrukket ved 1000 til 1200 g/mol.

13. Fremgangsmåde ifølge et af de foregående krav, kendetegnet ved, at polydimethylsiloxan-polyoxyalkylen-blokcopolymeren har en vægtgennemsnitlig molekylvægt, bestemt på grundlag af de kendte metoder i GPC-analysen, på i det mindste 2.000 g/mol til ca. 160.000 g/mol, fortrinsvis 4.000 g/mol til ca. 50.000 g/mol, især 5.000 g/mol til ca. 36.000 g/mol.

14. Anvendelse af de SiOC-bundne, lineære polydimethylsiloxan-polyoxyalkylen-blokcopolymerer, fremstillet efter en fremgangsmåde ifølge et af kravene 1 - 13, til fremstilling af diesel-skumdæmpere, af hydrofoberingsmidler, af polymerdispersioner, af klæbestoffer eller tætningsstoffer, af papirklude; af rengørings- og plejeformuleringer til husholdningen eller til industrielle anvendelser, især til fremstilling af blødgøringsmidler, af kosmetiske, farmaceutiske og dermatologiske sammensætninger, især kosmetiske rense- og plejeformuleringer, hårbehandlingsmidler og hårefterbehandlingsmidler; af byggematerialsammensætninger, af termoplastiske formlegemer.

15. Anvendelse af de SiOC-bundne, lineære polydimethylsiloxan-polyoxyalkylen-blokcopolymerer, fremstillet efter en fremgangsmåde ifølge et af kravene 1 - 13, som proceshjælpemiddel ved ekstruderingen af termoplaster, som adjuvans i plantebeskyttelsen, som additiv til rengøring og pleje af hårde overflader, til overfladebehandling af fibre, partikler eller fladedannelser, især til udrustning eller imprægnering af tekstiler, eller ved belægningen af fyldstoffer.