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(54) Title: ALKOXYLATED, CROSS-LINKED POLYGLYCEROLS AND USE THEREOF AS BIODEGRADABLE DEMULSIFIER

(54) Bezeichnung: ALKOXYLIERTE VERNETZTE POLYGLYCERINE UND IHRE VERWENDUNG ALS BIOLOGISCH ABBAUBARE EMULSIONSSPALTER

(57) Abstract: The invention relates to the use of alkoxylated cross-linked polyglycerols having multifunctional electrophilic compounds. Said polyglycerols have a molecular weight of between 1000 - 100.000 units and have between 5 - 100 glycerol units which are alkoxylated by C₂-C₄-alkylen oxide groups or a mixture of said type of alkylen oxide groups such that the cross-linked, alkoxylated polyglycerol has an alkoxylation degree of between 1 - 100 alkylen oxide units per free OH group. The invention also relates to the use of said polyglycerols for the demulsification of oil/water emulsions in amounts ranging from 0.0001 5 wt.-%, in relation to the oil content of the emulsion which is to be demulsified.

(57) Zusammenfassung: Verwendung alkoxylierter, mit multifunktionalen elektrophilen Verbindungen vernetzter Polyglycerine mit einem Molekulargewicht von 1000 bis 100.000 Einheiten, welche 5 bis 100 Glycerineinheiten umfassen, die mit C₂-C₄-Alkylenoxidgruppen oder einer Mischung solcher Alkylenoxidgruppen alkoxyliert sind, so dass das vernetzte, alkoxylierte Polyglycerin einen Alkoxyierungsgrad von 1 bis 100 Alkylenoxideinheiten pro freier OH-Gruppe aufweist, zur Spaltung von Öl/Wasser-Emulsionen in Mengen von 0,0001 bis 5 Gew.-%, bezogen auf den Ölgehalt der zu spaltenden Emulsion.

WO 2004/108863 A1

Description

Alkoxylated, cross-linked polyglycerols and use thereof as biodegradable demulsifiers

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The present invention relates to the use of alkoxylated, cross-linked polyglycerols for demulsifying water-oil emulsions, in particular in the production of crude oil.

10 During its recovery, crude oil is produced as an emulsion with water. Before the crude oil is further processed, these crude oil emulsions must be demulsified into the oil and water constituents. For this purpose, use is generally made of petroleum demulsifiers. Petroleum demulsifiers are interface-active polymeric compounds which are able to effect the required
15 separation of the emulsion constituents within a short time.

Disclosed petroleum demulsifiers are, in US-4 321 146, alkylene oxide block copolymers and, in US-5 445 765, alkoxylated polyethyleneimines. These can be used as individual components, in mixtures with other
20 demulsifiers, or else as crosslinked products. Crosslinkings are carried out, for example, by reactions of alkoxylated low molecular weight alcohols (such as, for example, glycerol or pentaerythrol) or alkoxylated alkylphenol formaldehyde resins with bifunctional compounds such as diepoxides or diisocyanates. Such crosslinked compounds are disclosed in US-5 759 409
25 and US-5 981 687.

The use of alkoxylated glycerol as demulsifying constituent in lubricating oils has been described in DD-229006. Here, glycerol is reacted with alkylene oxides either to give a block copolymer or a random copolymer.

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The use of alkoxylated di- and triglycerols as petroleum demulsifiers has likewise been described (US-3 110 737, US-2 944 982 and US-4 342 657).

35

Alkoxylated polyglycerols are known per se. They are described in the prior art for various applications. For example, in US-5 502 219, alkoxylated polyglycerols were esterified in order to prepare a low-calorie substitute for plant oils. In US-4 061 684, the alkoxylated polyglycerols were esterified and used as gels which swell in water. Alkoxylated polyglycerols which

have been reacted with alpha-olefin epoxides act, according to WO-98/03243, as antifoams. The sulfation of alkoxyated polyglycerols leads to substances which are used in hair shampoos, as disclosed in US-4 263 178.

5

Alkoxyated polyglycerols have been disclosed in DE 101 07 880 A1 as effective demulsifiers.

10

The various properties (e.g. asphaltene, paraffin and salt content, chemical composition of the natural emulsifiers) and proportions of water in various crude oils make it imperative to further develop the existing petroleum demulsifiers. In particular, a low dosing rate and broad applicability of the petroleum demulsifier to be used as well as the relatively high effectiveness to be strived for is at the forefront from an economic and ecological point of view. There is also an increasing need for demulsifiers which have good biodegradability and low bioaccumulation in order to replace the alkylphenol-based products under discussion.

15

The object was thus to develop novel petroleum demulsifiers which are superior in their effect to the already known alkoxyated polyglycerols, can be used in an even lower concentration and have better biodegradability.

20

Surprisingly, it has been found that alkoxyated, cross-linked polyglycerols exhibit an excellent effect as petroleum demulsifiers even at a very low concentration. In addition, they exhibited markedly better biodegradabilities (according to OECD 306) in comparison with customary commercial demulsifiers and alkoxyated, uncrosslinked polyglycerols.

25

The invention therefore provides for the use of alkoxyated polyglycerols crosslinked with multifunctional electrophilic compounds with a molecular weight of from 1000 to 100 000 units which comprise 5 to 100 glycerol units which are alkoxyated with C₂-C₄-alkylene oxide groups or a mixture of such alkylene oxide groups so that the crosslinked alkoxyated polyglycerol has a degree of alkoxylation of from 1 to 100 alkylene oxide units per free OH group, for demulsifying oil/water emulsions in amounts of from 0.0001 to 5% by weight, based on the oil content of the emulsion to be demulsified.

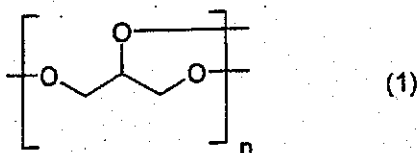
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These alkoxyated, crosslinked polyglycerols are obtainable from crosslinked polyglycerols having 5 to 100 glycerol units by alkoxylation of

the free OH groups with a C₂-C₄-alkylene oxide or a mixture of such alkylene oxides in molar excess, such that the alkoxyated crosslinked polyglycerol has said degree of alkoxylation.

- 5 The preparation of polyglycerol is known in the prior art and takes place generally by acid- or alkali-catalyzed condensation of glycerol. The reaction temperature is generally between 150 and 300°C, preferably 200 to 250°C. The reaction is normally carried out at atmospheric pressure. Examples of catalyzing acids are HCl, H₂SO₄, sulfonic acids or H₃PO₄, and bases
 10 which may be mentioned are NaOH or KOH, which are used in amounts of from 0.1 to 50% by weight, based on the weight of the reaction mixture. The condensation generally requires 3 to 10 hours. Polyglycerols can be depicted by formula 1.



15

In formula 1, n is the degree of condensation, i.e. the number of glycerol units. n increases with increasing reaction time and is determined by means of the OH number.

- 20 In the next step, the polyglycerols prepared in this way are crosslinked with di- or multifunctional, electrophilic compounds. This achieves a very easily controllable increase in the molecular weight of the polyglycerols. The crosslinkers used are, inter alia, di- and polyglycidyl ethers, di- and polyepoxides, di- and polycarboxylic acids, carboxylic anhydrides, di- and
 25 polyisocyanates, dialkoxydialkylsilanes, trialkoxyalkylsilanes, and tetra-alkoxysilanes. The crosslinking is carried out as known in the prior art.

The following crosslinkers are particularly preferred:

- bisphenol A diglycidyl ether, butane-1,4-diol diglycidyl ether,
 30 hexane-1,6-diol diglycidyl ether, ethylene glycol diglycidyl ether, cyclohexanedimethanol diglycidyl ether, resorcinol diglycidyl ether, glycerol diglycidyl ether, glycerol triglycidyl ether, glycerol propoxylate triglycidyl ether, polyglycerol polyglycidyl ether, p-aminophenol triglycidyl ether, polypropylene glycol diglycidyl ether, pentaerythritol tetraglycidyl ether,
 35 sorbitol polyglycidyl ether, trimethylolpropane triglycidyl ether, castor oil triglycidyl ether, diaminobiphenyl tetraglycidyl ether, soya oil epoxide,

adipic acid, maleic acid, phthalic acid, maleic anhydride, succinic anhydride, dodecylsuccinic anhydride, phthalic anhydride, trimellitic anhydride, pyromellitic anhydride, dimethoxydimethylsilane, diethoxydimethylsilane, tetraalkoxysilane, toluene diisocyanate, diphenylmethane diisocyanate.

The specified crosslinkers and chemically related compounds are used preferably in the range from 0.1-10% by weight, particularly preferably 0.5-5% by weight and specifically 1.0-2.5% by weight, based on the polyglycerol.

It is usual and particularly preferred to carry out the crosslinking step after the glycerol condensation and before the alkoxylation. Crosslinking after glycerol condensation and its subsequent alkoxylation can likewise be carried out according to the invention.

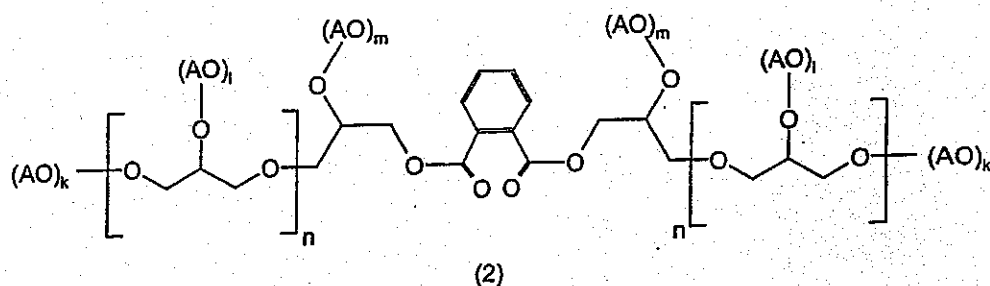
The crosslinked polyglycerols obtained from the glycerol condensation and subsequent crosslinking are then alkoxyated with one or more C₂-C₄-alkylene oxides, preferably ethylene oxide (EO) or propylene oxide (PO). The alkoxyating agent is used in molar excess. The alkoxylation takes place, as known in the prior art, by reaction of the polyglycerols with an alkylene oxide under an increased pressure of generally 1.1 to 20 bar at temperatures of from 50 to 200°C. The alkoxylation takes place on the free OH groups of the polyglycerols. The amount of alkylene oxide used is sufficient for the average degree of alkoxylation to be between 1 and 100 alkylene oxide units per free OH group. Average degree of alkoxylation is understood here as meaning the average number of alkoxy units which is positioned on each free OH group. It is preferably 2 to 70, in particular 5 to 50, especially 20 to 40.

Preferably, the alkoxylation is carried out firstly with PO and then with EO. The ratio of EO to PO in the alkoxyated polyglycerol is preferably between 1:1 and 1:10. Though, according to the invention, the alkoxylation can also take place in reverse order, first ED then PO or with a mixture of PO and EO.

The polyglycerol obtained following condensation, subsequent crosslinking and alkoxylation preferably has a molecular weight of from 3000 to 50 000 units, in particular from 5000 to 30 000 units, especially from 8000 to

25 000.

The alkoxyated, crosslinked polyglycerols prepared by the described process are depicted by way of example, in the case of the crosslinker phthalic anhydride, by the following structure (formula 2):



(AO)_{k,l,m}O are the alkoxyated OH radicals in which AO is a C₂-C₄-alkylene oxide unit and k, l, m are the degrees of alkoxylation. n is the degree of condensation of the glycerol. n is preferably a number from 5 to 50, particularly preferably 8 to 30, especially 10 to 20.

The present invention preferably provides for the use of the alkoxyated polyglycerol as demulsifiers for oil/water emulsions in the recovery of petroleum.

For use as petroleum demulsifiers, the crosslinked alkoxyated polyglycerols are added to the water-oil emulsions, which preferably takes place in solution. Preferred solvents for the crosslinked alkoxyated polyglycerols are paraffinic or aromatic solvents. The crosslinked alkoxyated polyglycerols are used in amounts of from 0.0001 to 5% by weight, preferably 0.0005 to 2% by weight, in particular 0.0008 to 1% by weight and specifically 0.001 to 0.1% by weight, based on the oil content of the emulsion to be demulsified.

Examples

Example 1

30 Preparation of pentadecaglycerol

100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a 250 ml three-necked flask fitted with contact thermometer, stirrer and water

separator. With stirring and nitrogen blanketing, the reaction mixture was heated rapidly to 240°C. At this temperature, the water of reaction was distilled off over 8 h. The product was evaporated to dryness on a rotary evaporator (yield: 67.3 g) and the molar mass was analyzed by GPC ($M^* \approx$
5 1100 g/mol, standard polyethylene glycol). The chain length n was determined via the OH number.

Example 2

Crosslinking of pentadecaglycerol with bisphenol A diglycidyl ether

10

250.0 g of pentadecaglycerol were heated to 80°C under gentle nitrogen blanketing in a 500 ml three-necked flask fitted with contact thermometer, stirrer and reflux condenser. At this temperature, 13.2 g of bisphenol A diglycidyl ether (80% strength solution in an aromatic solvent) were quickly
15 added dropwise. The reaction temperature was then increased to 120°C and the reaction mixture was stirred for 8 h until unreacted diglycidyl ether could no longer be detected by means of titration of the epoxy number. The product was evaporated to dryness on a rotary evaporator (yield: 260.0 g) and the molar mass was analyzed by GPC ($M^* \approx$ 2600 g/mol, standard
20 polyethylene glycol).

Example 3

Crosslinking of pentadecaglycerol with dodecylsuccinic anhydride

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100.0 g of pentadecaglycerol, 1.5 g of alkylbenzenesulfonic acid and 2.7 g of dodecylsuccinic anhydride were initially introduced at room temperature into a 250 ml three-necked flask fitted with contact thermometer, stirrer and water separator. The reaction mixture was then heated to 165°C and stirred for a further 8 h at this temperature until no more water of reaction formed
30 in the water separator (reaction control: acid number). The product was evaporated to dryness on a rotary evaporator (yield: 102.0 g) and the molar mass was analyzed by GPC ($M^* \approx$ 2450 g/mol, standard polyethylene glycol).

35

Example 4

Crosslinking of pentadecaglycerol with toluene 2,4-diisocyanate

100.0 g of pentadecaglycerol were heated to 60°C under gentle nitrogen blanketing in a 250 ml three-necked flask fitted with contact thermometer,

- stirrer and reflux condenser. At this temperature, 2.4 g of toluene 2,4-diisocyanate were then slowly added dropwise. The reaction temperature was increased to 100°C and the reaction mixture was stirred for a further 8 h until at this temperature (reaction control: isocyanate number). The product was evaporated to dryness on a rotary evaporator (yield: 102.2 g) and the molar mass was analyzed by GPC ($M^* \approx 2380$ g/mol, standard polyethylene glycol).

Example 5

10 Preparation of decaglycerol

- 100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a 250 ml three-necked flask fitted with contact thermometer, stirrer and water separator. With stirring and nitrogen blanketing, the reaction mixture was heated rapidly to 240°C. At this temperature, the water of reaction was distilled off over 5 h. The product was evaporated to dryness on a rotary evaporator (yield: 74.9 g) and analyzed by GPC ($M^* \approx 730$ g/mol). The chain length n was determined via the OH number.

20 Example 6

Crosslinking of decaglycerol with bisphenol A diglycidyl ether

- 100.0 g of decaglycerol were heated to 80°C under gentle nitrogen blanketing in a 250 ml three-necked flask fitted with contact thermometer, stirrer and reflux condenser. At this temperature, 3.0 g of bisphenol A diglycidyl ether (80% strength solution in an aromatic solvent) were quickly added dropwise. The reaction temperature was then increased to 120°C and the reaction mixture was stirred for 8 h until unreacted diglycidyl ether could no longer be detected by means of titration of the epoxy number. The product was evaporated to dryness on a rotary evaporator (yield: 102.3 g) and the molar mass was analyzed by GPC ($M^* \approx 1530$ g/mol, standard polyethylene glycol).

Example 7

35 Crosslinking of decaglycerol with dodecylsuccinic anhydride

100.0 g of decaglycerol, 1.5 g of alkylbenzenesulfonic acid and 2.5 g of dodecylsuccinic anhydride were initially introduced at room temperature into a 250 ml three-necked flask fitted with contact thermometer, stirrer and

water separator. The reaction mixture was then heated to 165°C and stirred for a further 8 h at this temperature until no more water of reaction formed in the water separator (reaction control: acid number). The product was evaporated to dryness on a rotary evaporator (yield: 101.8 g) and the molar mass was analyzed by GPC ($M^* \approx 1420$ g/mol, standard polyethylene glycol).

Example 8

Crosslinking of decaglycerol with toluene 2,4-diisocyanate

10

100.0 g of decaglycerol were heated to 60°C under gentle nitrogen blanketing in a 250 ml three-necked flask fitted with contact thermometer, stirrer and reflux condenser. Then, at this temperature, 2.4 g of toluene 2,4-diisocyanate were slowly added dropwise. The reaction temperature was increased to 100°C and the reaction mixture was stirred for a further 8 h at this temperature (reaction control: isocyanate number). The product was evaporated to dryness on a rotary evaporator (yield: 102.1 g) and the molar mass was analyzed by GPC ($M^* \approx 1650$ g/mol, standard polyethylene glycol).

20

Alkoxylation of the crosslinked polyglycerols

Ethylene oxide

25 The crosslinked polyglycerols described above were introduced into a 1 l glass autoclave and the pressure in the autoclave was adjusted to about 0.2 bar above atmospheric pressure with nitrogen. Heating was slowly carried out to 140°C and, after this temperature had been reached, the pressure was again adjusted to 0.2 bar above atmospheric pressure. Then, at 140°C, the desired amount of EO (see table 1) was metered in, during which the pressure should not exceed 4.5 bar. When the addition of EO was complete, the mixture was left to after-react for a further 30 minutes at 140°C.

Propylene oxide

The crosslinked polyglycerols described above were introduced into a 1 l glass autoclave and the pressure in the autoclave was adjusted to about 0.2 bar above atmospheric pressure with nitrogen. Heating was slowly carried out to 130°C and, after this temperature had been reached, the pressure was again adjusted to 0.2 bar above atmospheric pressure. Then, at 130°C, the desired amount of PO was metered in (see table 1), during which the pressure should not exceed 4.0 bar. When the addition of PO was complete, the mixture was left to after-react for a further 30 minutes at 130°C.

The degree of alkoxylation was determined by means of ^{13}C -NMR

15 Determination of the demulsifying effectiveness of petroleum demulsifiers

To determine the effectiveness of a demulsifier, the water separation from a crude oil emulsion per time, and also the dewatering and desalting of the oil were determined. For this, demulsifying glasses (tapered, graduated glass bottles with screw lids) were charged in each case with 100 ml of the crude oil emulsion, in each case a defined amount of the demulsifier was metered in just below the surface of the oil emulsion using a micropipette, and the demulsifier was mixed into the emulsion by intensive shaking. The demulsifying glasses were then placed in a conditioning bath (30°C and 50°C) and water separation was monitored.

During demulsification and after it had finished, samples were taken from the oil from the upper section of the demulsifying glass (so-called top oil), and the water content was determined in accordance with Karl Fischer and the salt content was determined conductometrically. In this way, it was possible to assess the novel demulsifiers according to water separation and also dewatering and desalting of the oil.

35 Demulsifying action of the demulsifiers described

Origin of the crude oil emulsion: Holzkirchen sonde 3, Germany

Water content of the emulsion: 46%

Salt content of the emulsion: 5%

Demulsification temperature: 50°C

Table 1: Effectiveness of alkoxyated crosslinked polyglycerols as demulsifiers compared with the corresponding alkoxyated uncrosslinked polyglycerol and Dissolvan 4738 (dosing rate 20 ppm)

Water separation [ml] per time [min]	5	10	20	30	45	60	90	120	180	Water in the top oil [%]	Salt in the top oil [ppm]
Product from 1 + 30 PO + 20 EO (comparison)	2	6	12	21	28	36	40	42	43	0.85	156
Product from 2 + 30 PO + 20 EO	4	10	22	30	38	43	46	46	46	0.15	35
Product from 3 + 30 PO + 20 EO	6	13	27	35	42	45	46	46	46	0.13	25
Product from 4 + 30 PO + 20 EO	4	11	24	33	40	44	45	46	46	0.31	56
Product from 5 + 40 PO + 30 EO (comparison)	0	4	10	19	26	34	40	42	42	0.92	189
Product from 6 + 40 PO + 30 EO	3	12	25	33	40	44	46	46	46	0.11	12
Product from 7 + 40 PO + 30 EO	2	5	12	26	37	42	45	45	46	0.19	21
Product from 8 + 40 PO + 30 EO	5	14	28	35	42	43	45	46	46	0.15	19
Standard: Dissolvan 4738 (comparison)	0	0	0	5	11	25	32	38	39	0.97	220

Table 2:

- 10 Biodegradability of alkoxyated, crosslinked polyglycerols (closed bottle test according to OECD 306) compared with the corresponding alkoxyated uncrosslinked polyglycerol and Dissolvan 4738

Biodegradability [%] after	14 days	28 days
Product from 1 + 30 PO + 20 EO (comparision)	16.5	22.4
Product from 2 + 30 PO + 20 EO	33.5	46.1
Product from 3 + 30 PO + 20 EO	40.6	50.3
Product from 4 + 30 PO +20 EO	38.5	53.4
Product from 5 + 40 PO + 30 EO (comparision)	10.5	19.5
Product from 6 + 40 PO + 30 EO	42.7	63.5
Product from 7 + 40 PO + 30 EO	38.2	58.3
Product from 8 + 40 PO + 30 EO	33.5	54.7
Standard: Dissolvan 4738 (comparision)	20.5	27.5
Reference (sodium benzoate) (comparision)	62.5	81.4

Patent claims

1. The use of alkoxylated polyglycerols, crosslinked with multifunctional electrophilic compounds with a molecular weight of from 1000 to 100 000 units which comprise 5 to 100 glycerol units which are alkoxylated with C₂-C₄-alkylene oxide groups or a mixture of such alkylene oxide groups so that the crosslinked alkoxylated polyglycerol has a degree of alkoxylation of from 1 to 100 alkylene oxide units per free OH group, for demulsifying oil/water emulsions in amounts of from 0.0001 to 5% by weight, based on the oil content of the emulsion to be demulsified.
2. The use as claimed in claim 1, in which the number of glycerol units is between 5 and 50.
3. The use as claimed in claim 1 and/or 2, where the alkoxylated, crosslinked polyglycerols have a molecular weight of from 3000 to 50 000 units.
4. The use as claimed in one or more of claims 1 to 3, in which the average degree of alkoxylation is between 1 and 70 alkylene oxide units per free OH group.
5. The use as claimed in one or more of claims 1 to 4, in which the alkylene oxide is ethylene oxide or propylene oxide.
6. The use as claimed in one or more of claims 1 to 5, in which a coalkoxylation with ethylene oxide and propylene oxide in the ratio of from 1:2 to 1:10 is present.
7. The use as claimed in one or more of claims 1 to 6, where the crosslinking of the polyglycerols takes place by means of bisphenol A diglycidyl ether, butane-1,4-diol diglycidyl ether, hexane-1,6-diol diglycidyl ether, ethylene glycol diglycidyl ether, cyclohexanedimethanol diglycidyl ether, resorcinol diglycidyl ether, glycerol diglycidyl ether, glycerol triglycidyl ether, glycerol propoxylate triglycidyl ether, polyglycerol polyglycidyl ether, p-aminophenol triglycidyl ether, polypropylene glycol diglycidyl ether, pentaerythritol tetraglycidyl ether, sorbitol polyglycidyl ether,

trimethylolpropane triglycidyl ether, castor oil triglycidyl ether, diaminobiphenyl tetraglycidyl ether, soya oil epoxide, adipic acid, maleic acid, phthalic acid, maleic anhydride, succinic anhydride, dodecylsuccinic anhydride, phthalic anhydride, trimellitic anhydride, pyromellitic anhydride,
5 dimethoxydimethylsilane, diethoxydimethylsilane, toluene diisocyanate, diphenylmethane diisocyanate.

8. The use as claimed in one or more of claims 1 to 7, where the crosslinking step is carried out after the alkoxylation of the polyglycerols.