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(54) Title: ALKOXYLATED POLYGLYCEROLS AND THEIR USE AS DEMULSIFIERS

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

(57) Abstract: The invention relates to the use of alkoxyated polyglycerols as demulsifiers. The invention is characterized by the use of alkoxyated polyglycerols having a molecular weight of 250 to 100000 moieties which comprise 2 to 100 glycerol moieties whose free OH groups are alkoxyated with C₂-C₄ alkylene oxide groups or a mixture of such alkylene oxide groups so that the alkoxyated polyglycerol has an alkoxylation degree of 1 to 100 alkylene oxide moieties per free OH group. The inventive polyglycerols are used as demulsifiers for oil/water emulsions in an amount of from 0.0001 to 5 % by weight, based on the oil content of the emulsion to be demulsified.

(57) Zusammenfassung: Verwendung alkoxylierter Polyglycerine als Emulsionsspalter. Gegenstand der Erfindung ist die Verwendung alkoxylierter Polyglycerine mit einem Molekulargewicht von 250 bis 100.000 Einheiten, welche 2 bis 100 Glycerineinheiten umfassen, deren freien OH-Gruppen mit C₂-C₄- Alkylenoxidgruppen oder einer Mischung solcher Alkylenoxidgruppen alkoxyliert sind, so dass das alkoxylierte Polyglycerin eine Alkoxylierungsgrad von 1 bis 100 Alkylenoxidienheiten pro freier OH-Gruppe aufweist, zur Spaltung von Öl/Wasseremulsionen in Mengen von 0.0001 bis 5 Gew.-%, bezogen auf den Ölgehalt der zu spaltenden Emulsion.

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Alkoxylated polyglycerols and their use as demulsifiers

The present invention relates to the use of alkoxylated polyglycerols preparable by polycondensation of glycerol and subsequent alkoylation for demulsifying water-oil emulsions, in particular in the production of crude oil.

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 compounds which are able to effect the required separation of the emulsion constituents within a short time.

Disclosed petroleum demulsifiers are, in US-A 321 146, alkylene oxide block copolymers and, in US-5 445 765, alkoxylated polymines. These can be used as individual components, in mixtures with other demulsifiers, or else as crosslinked products. Crosslinkings are generally carried out by reactions of the individual demulsifier components with bifunctional compounds such as diepoxides or diisocyanates. Such crosslinked compounds are disclosed in US-5 759 409 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.

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 alkoxylated polyglycerols leads to substances which are used in hair shampoos, as disclosed in US-4 263 178. However, alkoxylated polyglycerols have still not been used as demulsifiers.

The various properties (e.g. asphaltene and paraffin content) and proportions of water in various crude oils make it imperative to further

develop the existing petroleum demulsifiers. In particular, a low dosing rate of the 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.

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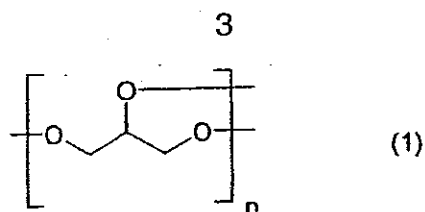
The object was thus to develop novel petroleum demulsifiers which are superior in their effect to the already known alkoxyated polyalkylene glycols or polyamines, and can be used in an even lower concentration.

- 10 Surprisingly, it has been found that alkoxyated polyglycerols exhibit an excellent effect as petroleum demulsifiers even at a very low concentration.

The invention therefore provides for the use of alkoxyated polyglycerols with a molecular weight of from 250 to 100 000 units which comprise 2 to
15 100 glycerol units whose free OH groups are alkoxyated with C₂-C₄-alkylene oxide groups or a mixture of such alkylene oxide groups so that the 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
20 emulsion to be demulsified.

These alkoxyated polyglycerols are obtainable from polyglycerols having 2 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
25 that the alkoxyated polyglycerol has said degree of alkoxylation.

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.
30 The reaction is normally carried out at atmospheric pressure. Examples of catalyzing acids are HCl, H₂SO₄, sulfonic acids or H₃PO₄, and bases 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
35 depicted by formula 1.



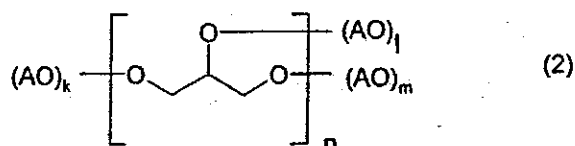
In formula 1, n is the degree of condensation, i.e. the number of glycerol units. n increases with increasing reaction time and is determined by means of the OH number.

The polyglycerols obtained from the condensation 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.

Preferably, the alkoxylation is carried out with a mixture of EO and PO. The ratio of EO to PO in the alkoxyated polyglycerol is preferably between 1:2 and 1:10.

The alkoxyated polyglycerol obtained following condensation and alkoxylation preferably has a molecular weight of from 500 to 50 000 units, preferably from 1 000 to 10 000 units.

The alkoxyated polyglycerols prepared by the described process can be depicted 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 3 to 50, particularly preferably 4 to 30.

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

For use as crude oil demulsifiers, the alkoxyated polyglycerols are added
10 to the water-oil emulsions, which preferably takes place in solution. Preferred solvents for the alkoxyated polyglycerols are paraffinic or aromatic solvents. The 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,
15 based on the oil content of the emulsion to be demulsified.

Examples

Example 1

20 Preparation of pentadecaglycerol

100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a 500 ml three-necked flask fitted with contact thermometer, stirrer and water separator. With stirring and nitrogen blanketing, the reaction mixture was
25 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 (with standard polyethylene glycol). The chain length n was determined via the OH number.

30

Example 2

Preparation of decaglycerol

100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a
35 500 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. The chain length n was

determined via the OH number.

Example 3

Preparation of pentaecicosaglycerol

5

100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a 500 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
10 distilled off over 12 h. The product was evaporated to dryness on a rotary evaporator (yield: 58.4 g) and analyzed by GPC. The chain length n was determined via the OH number.

Example 4

15 Pentacontanglycerol

100.0 g of glycerol and 3.7 g of NaOH (18% strength) were mixed in a 500 ml three-necked flask fitted with contact thermometer, stirrer and water separator. With stirring and nitrogen blanketing, the reaction mixture was
20 heated rapidly to 240°C. At this temperature, the water of reaction was distilled off over 20 h. The product was evaporated to dryness on a rotary evaporator (yield: 54.9 g) and analyzed by GPC. The chain length n was determined via the OH number.

25 Alkoxylation of the polyglycerols

Ethylene oxide

The polyglycerols described above were introduced into a 1 l glass
30 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 was metered in, during which the pressure should
35 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 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, 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

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.

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 polyglycerols as demulsifiers

Water separation [ml] per time [min]	Concentration [ppm]	Time/min										Water in the top oil [%]	Salt in the top oil [ppm]
		5	10	20	30	45	60	90	120	180			
Product from 1 + 40 mol of PO	30	3	15	30	33	41	45	46	46	46		0.35	64
Product from 1 + 50 mol of PO	30	1	17	24	29	37	46	46	46	46		0.24	52
Product from 2 + 40 mol of PO	30	2	9	16	23	28	40	45	46	46		0.32	43
Product from 2 + 50 mol of PO	30	1	10	19	32	40	45	46	46	46		0.41	81
Product from 3 + 40 mol of PO + 5 mol EO	30	4	15	27	39	44	44	45	45	46		0.38	71
Product from 3 + 50 mol of PO + 8 mol EO	30	3	12	24	36	42	44	45	44	46		0.47	88
Product from 4 + 40 mol of PO + 7 mol of EO	30	2	14	27	35	43	43	45	45	46		0.26	33
Product from 4 + 50 mol of PO + 10 mol of EO	30	1	9	16	22	29	38	44	44	46		0.31	32
Standard: Dissolvan 4738	80	1	3	10	15	21	30	39	39	40		0.95	104

CLAIMS

1. The use of alkoxyated polyglycerols with a molecular weight of from 250 to 100 000 units which comprise 2 to 100 glycerol units whose free OH
5 groups are alkoxyated with ethylene oxide and propylene oxide in the ratio of from 1:2 to 1:10 so that the 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.
- 10 2. The use as claimed in claim 1, in which the number of glycerol units is between 3 and 50.
3. The use as claimed in claim 1 and/or 2, where the alkoxyated
15 polyglycerols have a molecular weight of from 500 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.