

(12) INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(19) World Intellectual Property Organization

International Bureau



(43) International publication date

11 December 2003 (11.12.2003)

PCT

(10) International publication number

WO 03/102047 A1

(51) International patent classification⁷:
59/34, 59/14, B01D 17/04, C10G 33/04

C08G 65/26,

(74) Attorney: MIKULECKY, Klaus; Clariant Service GmbH, Patente, Marken, Lizenzen, Am Unisys-Park 1, 65843 Sulzbach (DE).

(21) International application number: PCT/EP03/05155

(22) International filing date: 16 May 2003 (16.05.2003)

(81) Designated states (*national*): ID, NO, SG, US.

(25) Language of filing: German

(84) Designated states (*regional*): European Patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR).

(26) Language of publication: German

(30) Data relating to the priority:

102 24 275.5 31 May 2002 (31.05.2002)

DE

Published:

- With International Search Report.

(71) Applicant (*for all designated States except US*): CLARIANT GMBH [DE/DE]; Brüningstrasse 50, 65929 Frankfurt am Main (DE). FREUNDL, Hildegard [DE/DE]; Burghauser Strasse 11, 84508 Burgkirchen (DE).

-For an explanation of the two-letter codes and the other abbreviations, reference is made to the explanations ("Guidance Notes on Codes and Abbreviations") at the beginning of each regular edition of the PCT Gazette.

(72) Inventors; and

(75) Inventors/Applicants (*US only*): LEINWEBER, Dirk [DE/DE]; Robert-Koch-Strasse 44, 84489 Burghausen (DE). FEUSTEL, Michael [DE/DE]; Auf der Nonnenwiese 34, 55278 Königernheim (DE). GRUNDNER, Heidi [DE/DE]; Kanalstrasse 14, 84518 Garching/Alz (DE).

As printed

(54) Title: DEMULSIFIERS

(54) Bezeichnung: EMULSIONSSPALTER

WO 03/102047 A1

(57) Abstract: The invention relates to polymers that can be obtained by: A) reacting an epoxidized ester, which is selected from one or more unsaturated fatty acids having 8 to 26 C atoms and a polyol having 2 to 6 OH groups, with a monoamine, diamine or polyamine; B) alkoxylation of the polyamine obtained hereby with a C₂ to C₄ alkylene oxide in molar excess so that the average degree of alkylation per OH group ranges from 1 to 100. The polymers have a numerical average molecular weight ranging from 500 to 100,000 g/mol. The invention also relates to the use of these polymers in quantities ranging from 0.0001 to 5 % by weight with regard to the oil as demulsifiers for oil-in-water emulsions.

(57) Zusammenfassung: Gegenstand der Erfindung sind Polymere, erhältlich durch A) Umsetzung eines epoxidierten Esters aus einer oder mehreren ungesättigten Fettsäuren mit 8 bis 26 C-Atomen und einem Polyol mit 2 bis 6 OH-Gruppen mit einem Mono-, Di- oder Polyamin B) Alkoxylierung des so erhaltenen Polyamins mit einem C₂- bis C₄-Alkylenoxid im molaren Überschuss, so dass der mittlere Alkoxyierungsgrad pro OH-Gruppe zwischen 1 und 100 liegt, wobei die Polymere zahlenmittlere Molekulargewichte von 500 bis 100.000 g/mol aufweisen, sowie deren Verwendung in Mengen von 0,0001 bis 5 Gew.-% bezogen auf das Öl, als Spalter für Öl/Wasser-Emulsionen.

Demulsifiers

The present invention relates to the use of polymers, preparable by reaction of epoxidized fatty acid esters with amines and subsequent
5 alkoxylation, for breaking 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 processed further, these crude oil emulsions have to be
10 broken into the oil and water constituents. For this purpose, use is generally made of petroleum breakers. Petroleum breakers are interface-active compounds which are able to effect the required separation of the emulsion constituents within a short time.

15 The petroleum breakers used are, inter alia, alkylphenol aldehyde resins, which are disclosed, for example, in US-4 032 514. These resins are obtainable from the condensation of a p-alkylphenol with an aldehyde, in most cases formaldehyde. The resins are often used in alkoxyated form, as is disclosed, for example, in DE-A-24 45 873. For this, the free phenolic
20 OH groups are reacted with an alkylene oxide.

Alkylphenol-free demulsifiers are described in WO-A-99/07808. Here, epoxidized fatty acid esters are opened with alcohols or carboxylic acids, and the resulting OH function is reacted with alkylene oxides. The
25 compounds prepared from this have good properties as demulsifiers.

The varying properties (such as, for example, asphaltene and paraffin content) and water fractions of different crude oils make it imperative to further develop the existing petroleum demulsifiers. In particular, a low
30 dosing rate of the demulsifier to be used besides the higher effectiveness which is to be strived for is at the front from an economic and ecological point of view.

It was therefore the object to develop novel petroleum breakers which are
35 superior in their effect to the products already known, and can be used in an even lower concentration.

Surprisingly, it has been found that products which are based on ring-opening products of epoxidized fatty acid esters with amines, diamines or polyamines, after subsequent alkoxylation, have an excellent breaking effect even at a very low concentration compared with known emulsion
5 breakers.

The invention provides polymers obtainable by

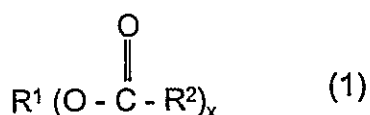
- A) reaction of an epoxidized ester of one or more unsaturated fatty acids having 8 to 26 carbon atoms and a polyol having 2 to 6 OH
10 groups with a monoamine, diamine or polyamine
- B) alkoxylation of the resulting polyamine with a C₂- to C₄-alkylene oxide in molar excess, such that the average degree of alkoxylation per OH group is between 1 and 100,
where the polymers have number-average molecular weights of from 500
15 to 100 000 g/mol.

The invention further provides the use of the polymers according to the invention in amounts of from 0.0001 to 5% by weight, based on the oil, as
20 breakers for oil/water emulsions.

The invention further provides a method of breaking oil/water emulsions by adding the polymers according to the invention to the emulsion in amounts of from 0.0001 to 5% by weight.

25 The first step (stage A) for the preparation of the polymers according to the invention consists in reacting an epoxidized fatty acid polyol ester with a monoamine, diamine or polyamine.

Epoxidized fatty acid polyol esters correspond generally to the formula 1



30

in which

R¹ is a hydrocarbon group having 2 to 6 carbon atoms which has x valences overall,

R² is a polymethylene group having 11 to 25 carbon atoms which carries at

least one epoxide group, and
x is a number from 2 to 6.

5 The esters of the formula 1 can be synthesized by esterifying a polyol of the formula $R^1(OH)_x$ with one or more carboxylic acids of the formula R^2COOH . R^1 , x and R^2 have the meaning given above.

10 The esters are preferably complete esters, although they can also have free OH groups. They are preferably based on naturally occurring glycerides, such as, for example, soybean oil, olive oil, sunflower oil or linseed oil.

x is preferably 2 or 3.

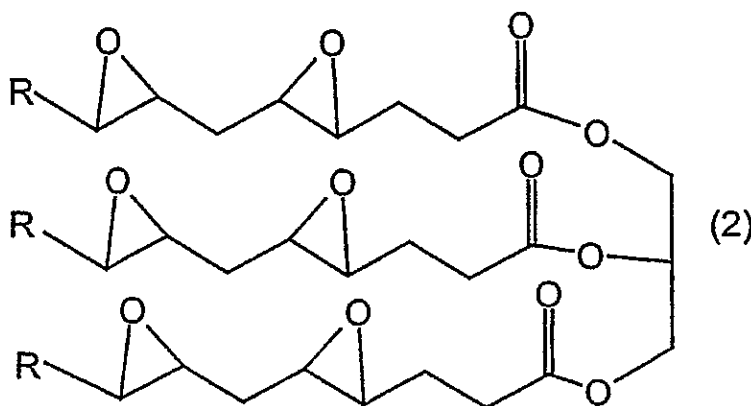
15 R^1 is preferably derived from ethylene glycol, propylene glycol, diethylene glycol, pentaerythritol, trimethylolpropane or glycerol. Particular preference is given to ethylene glycol and glycerol.

20 R^2 is preferably a polymethylene group having 9 to 21 carbon atoms, and is thus preferably derived from a C_{10} - to C_{22} -carboxylic acid. R^2 can carry 1, 2 or 3 epoxide groups.

The molecular weight of the polymers according to the invention is preferably at least 1000, for example 2000 g/mol, in particular from 1000 to 50 000 g/mol.

25

Formula 2 illustrates the ester structure of one example derived from glycerol



R is a hydrocarbon group which completes the fatty acid radical.

The epoxide ring opening may be carried out uncatalyzed (high nucleophilicity of the amines), with an acid catalyst or with a base catalyst. Base catalysis by means of sodium methoxide or potassium tert-butoxide has proven to be particularly preferred since it leads to more uniform products in significantly shorter reaction times.

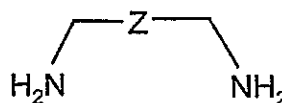
Suitable amines preferably correspond to the formulae 3 to 5



(3)



(4)



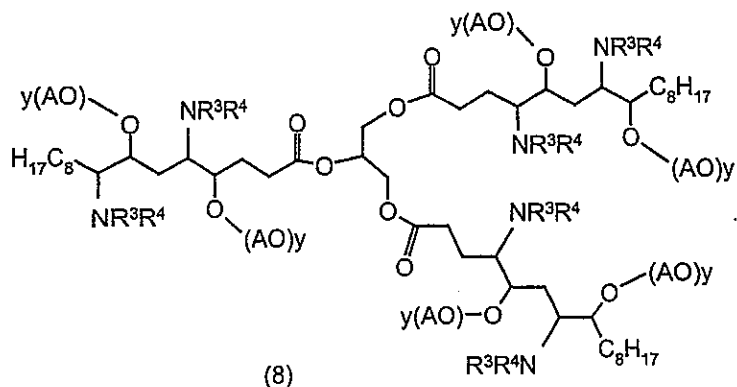
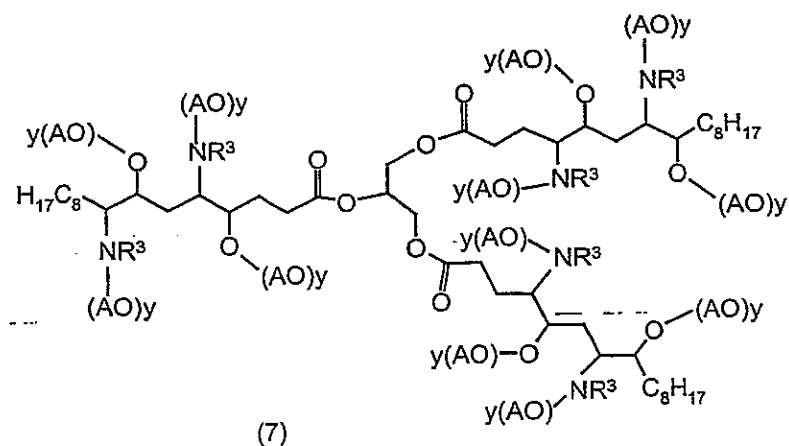
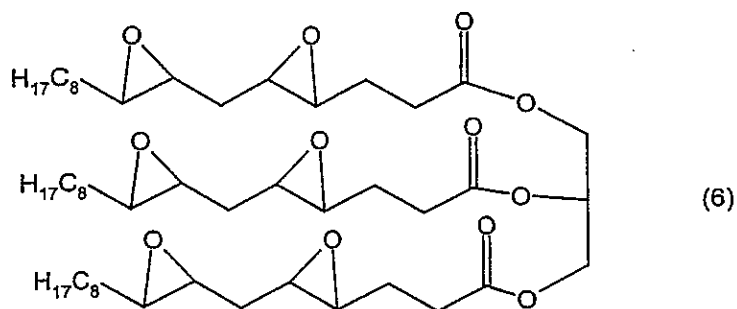
(5)

R^3 and R^4 , independently of one another, are C_1 - to C_{40} -alkyl, C_2 - to C_{40} -alkenyl, C_6 - to C_{18} -aryl or C_7 - to C_{30} -alkylaryl, in particular C_6 - to C_{22} , especially C_{10} - to C_{18} -alkyl or alkenyl, which may be straight-chain or branched.

Z is $-(CH_2)_n-$ where $n = 0$ to 10 or $-(CH_2NHCH_2)_m-$ where $m = 1$ to 20.

Formulae 7 and 8 show particularly preferred compounds based on soybean oil epoxide. Soybean oil epoxide is the epoxidized form of the natural substance soybean oil, which is the triglyceride of a polyunsaturated C_{16} - C_{18} -fatty acid. An idealized chemical structure is given in formula 6. On average, soybean oil epoxide has 6 to 7 epoxide groups.

If R^3 and R^4 are an alkylaryl radical, the alkylaryl is preferably a radical bonded via the aromatic ring, the aromatic ring of which preferably comprises 6 carbon atoms, and which carries an alkyl radical with a chain length of from preferably 1 to 18, particularly preferably 4 to 16, in particular 6 to 12, carbon atoms in the o, m or p position relative to the abovementioned bond.



5

(AO)_yO is an alkoxyated OH radical, (AO)_yN is an alkoxyated NH radical in which AO is the alkylene oxide unit, and y gives the degree of alkoxylation. y is preferably between 2 and 80.

- 10 For use as petroleum breakers, the polymers are added to the water/oil emulsions, which preferably takes place in solution. Preferred solvents for the polymers are paraffinic or aromatic solvents. The polymers 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, of polymer based on the oil content of the emulsion to be broken.

5

As is known in the prior art, the alkoxylation takes place by reacting the ring-opening products with an alkylene oxide (preferably: ethylene oxide, propylene oxide or butylene oxide) under an increased pressure of generally from 1.1 to 20 bar at temperatures of from 50 to 200°C.

10

Examples

1. Reaction of soybean oil epoxide with coconut fatty amine (uncatalyzed)

15

194 g (1 mol) of coconut fatty amine were heated to 160°C under a nitrogen atmosphere. 235 g of soybean oil epoxide (1 eq. of epoxide/mol of amine) were added dropwise with stirring over the course of one hour. To conclude the reaction, the mixture was left to after-react for 10 h at 150°C.

20 This gave a clear-yellow slightly viscous product which was analyzed by means of NMR and GPC.

2. Reaction of soybean oil epoxide with coconut fatty amine (NaOMe-catalyzed)

25

194 g (1 mol) of coconut fatty amine and 1.8 g of sodium methoxide (1 mol%, 30% strength in methanol) were heated to 160°C under a nitrogen atmosphere. 235 g of soybean oil epoxide (1 eq. of epoxide/mol of amine) were added dropwise with stirring over the course of one hour. To conclude the reaction, the mixture was left to after-react for 4 h at 150°C. This gave a clear yellow slightly viscous product which was analyzed by means of NMR and GPC.

30

3. Reaction of soybean oil epoxide with dicoconut fatty amine (NaOMe-catalyzed)

35

405 g (1 mol) of dicoconut fatty amine and 4.5 g of sodium methoxide (2.5 mol%, 30% strength in methanol) were heated to 170°C under a

nitrogen atmosphere. 235 g of soybean oil epoxide (1 eq. of epoxide/mol of amine) were added dropwise with stirring over the course of one hour. To conclude the reaction, the mixture was left to after-react for 8 h at 170°C. This gave a clear yellow slightly viscous product which was analyzed by means of NMR and GPC.

4. Reaction of soybean oil epoxide with triethylenetetramine (NaOMe-catalyzed)

157 g (1 mol) of triethylenetetramine and 1.8 g of sodium methoxide (1 mol%, 30% strength in methanol) were heated to 80°C under a nitrogen atmosphere. 235 g of soybean oil epoxide (1 eq. of epoxide/mol of amine) were added dropwise with stirring over the course of one hour. To conclude the reaction, the mixture was left to after-react for 7 h at 80°C. This gave a clear yellow product which was solid at room temperature, which was analyzed by means of NMR and GPC.

5. Reaction of soybean oil epoxide with tetraethylenepentamine (NAOMe-catalyzed)

222 g (1 mol) of tetraethylenepentamine and 1.8 g of sodium methoxide (1 mol%, 30% strength in methanol) were heated to 80°C under a nitrogen atmosphere. 235 g of soybean oil epoxide (1 eq. of epoxide/mol of amine) were added dropwise with stirring over the course of one hour. To complete the reaction, the mixture was left to after-react for 7 h at 80°C. This gave a clear yellow product which was solid at room temperature, which was analyzed by means of NMR and GPC.

Alkoxylation of the amine-opened epoxidized carboxylic esters

Ethylene oxide

The above-described ring-opening products were introduced into a 1 l glass autoclave and the pressure in the autoclave was adjusted to about 0.2 bar above atmospheric pressure using nitrogen. It was heated slowly to 140°C and, after this temperature had been reached, the pressure was again adjusted to 0.2 bar above atmospheric pressure. Subsequently, at 140°C, the desired amount of EO 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

5

The above-described ring-opening products were introduced into a 1 l glass autoclave and the pressure in the autoclave was adjusted to about 0.2 bar above atmospheric pressure using nitrogen. It was heated slowly to 130°C and, after this temperature had been reached, the pressure was again
10 adjusted to 0.2 bar above atmospheric pressure. Subsequently, at 130°C, the desired amount of EO was metered in, during which the pressure should not exceed 4.0 bar. When the addition of EO was complete, the mixture was left to after-react for a further 30 minutes at 130°C.

15 Determination of the breaking 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, the demulsifying glasses (tapered, graduated
20 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 breaker was mixed into the emulsion by intensive shaking. The demulsifying glasses were then placed in a conditioning bath (30°C and
25 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
30 the salt content was determined conductometrically. In this way, it was possible to assess the novel breakers according to water separation and also dewatering and desalting of the oil.

Breaking action of the demulsifiers described

35

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

Concentration : 20 ppm

5

Water separation [ml] per time [min]	5	20	30	60	90	180	Water in the top oil [%]	Salt in the top oil (ppm)
Alkoxylated product from Example 1	2	10	30	41	43	45	0.45	28
Alkoxylated product from Example 2	8	16	37	44	46	46	0.15	20
Alkoxylated product from Example 3	10	19	38	45	45	46	0.11	16
Alkoxylated product from Example 4	9	17	38	46	46	46	0.12	15
Dissolvan 3245 (standard)	1	8	27	37	40	41	0.97	87

Claims:

1. A polymer obtainable by
 - A) reaction of an epoxidized ester of one or more unsaturated fatty acids having 8 to 26 carbon atoms and a polyol having 2 to 6 OH groups with a monoamine, diamine or polyamine
 - B) alkoxylation of the resulting polyamine with a C₂- to C₄-alkylene oxide in molar excess, such that the average degree of alkoxylation per OH group is between 1 and 100,where the polymer has a number-average molecular weight of from 500 to 100 000 g/mol.
2. The polymer as claimed in claim 1, wherein the polyol is ethylene glycol, propylene glycol, diethylene glycol, pentaerythritol, trimethylolpropane or glycerol.
3. The polymer as claimed in claim 1 and/or 2, wherein the epoxidized esters are derived from naturally occurring glycerides, preferably soybean oil, olive oil, sunflower oil or linseed oil.
4. The polymer as claimed in one or more of claims 1 to 3, which has a number-average molecular weight of from 1000 to 50 000 g/mol.
5. The polymer as claimed in one or more of claims 1 to 4, wherein the esters are derived from a C₁₀- to C₂₂-carboxylic acid.
6. The use of the polymers as claimed in one or more of claims 1 to 5 in amounts of from 0.0001 to 5% by weight, based on the oil, as breakers for oil/water emulsions.