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(54) Title: DEMULSIFIERS FOR CRUDE OIL EMULSIONS

(57) Abstract: Complex polyesters based on polycarboxylic acids and polyalcohols derivable by reaction of: 1. A process for demulsification of a water-in-oil emulsion, especially a crude oil emulsion, wherein there is used a reaction product derivable by reaction of, 1. a carboxylic acid component comprising, (a) a poly-carboxylic acid having 2 to 30 carbon atoms and 2 to 5 carboxylic acid groups, and, if desired, (b) a C₁₋₂₄ monocarboxylic acid with, 2. an alcohol component comprising (a) (i) a polyhydric alcohol comprising 1 to 10 glycol units each having 2 to 4 carbon atoms and each glycol having 2 or 3 hydroxy groups, or, (ii) a sugar or polysaccharide, and, if desired, (b) a C_{1-C24} monohydric alcohol are efficient as demulsifiers for oil and water emulsions. The poly-carboxylic acid may be, for example, citric acid and the polyhydric alcohol may be, for example, di-propylene glycol, tri-ethylene glycol or tri-propylene glycol, or a sugar or polysaccharide.



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DEMULSIFIERS FOR CRUDE OIL EMULSIONS

5 FIELD OF THE INVENTION

This invention relates to demulsifiers for crude oil emulsions.

BACKGROUND OF THE INVENTION

10

Stable water-in-oil (W/O) emulsions are formed during the production and processing of crude oil. The emulsions are caused by associated water, gas, solids or naturally occurring surfactants in the crude oil. Films formed at the oil-water interface are thought to stabilise these emulsions. Prior to crude oil

15 processing, the associated water and emulsions must be removed. The characteristics of oil-in-water emulsions vary based on geological location, crude oil and formation water composition and production method of the crude oil.

Both chemical and physical techniques have traditionally been employed in order
20 to break the oil-water interfacial films. Chemicals may react chemically with stabilising components in the W/O emulsions, or may influence the interfacial tension of the W/O films. Demulsifier formulations are based on empirical testing and usually consist of a number of different components.

25 The majority of commercial demulsifiers, such as alkoxyated phenolic resins, diepoxides/epoxy-ethers, alkoxyated polyamines, polyacrylates, ethylene

oxide/propylene oxide block polyols and polyol esters, are biologically persistent. Recently, there has been a focus on the environmental impact of the demulsifier components discharged into the sea. Oil-soluble persistent chemicals may accumulate in the biological food chain. Hence, the demand for biodegradable
5 demulsifiers in the oil field industry is increasing.

SUMMARY OF THE INVENTION

We have prepared biodegradable complex polyesters based on polycarboxylic
10 acids and polyalcohols that have been found to be efficient as demulsifiers for oil and water emulsions.

The present invention provides a process for demulsification of an oil and water emulsion, especially a crude oil emulsion, wherein there is used a reaction product
15 derivable by reaction of

1. a carboxylic acid component comprising
 - (a) a poly-carboxylic acid having 2 to 30 carbon atoms and 2 to 5 carboxylic acid groups, and, if desired,
 - (b) a C₁₋₂₄ monocarboxylic acid
- 20 with
2. an alcohol component comprising
 - (a)(i) a polyhydric alcohol comprising 1 to 10 glycol units each having 2 to 4 carbon atoms and each glycol having 2 or 3 hydroxy groups, or
 - (ii) a sugar or polysaccharide, and, if desired,
 - 25 (b) a C_{1-C24} monohydric alcohol.

The use of an acid component comprising at least one acid other than an α , β -unsaturated carboxylic acid should especially be mentioned.

The present invention also provides the reaction product above, for use as a
5 demulsifier.

DETAILED DESCRIPTION OF THE INVENTION

A poly-carboxylic acid component 1a may be aliphatic or cycloaliphatic or may
10 contain both aliphatic and cycloaliphatic moieties. An aliphatic group may be straight chain or branched. Aliphatic and cycloaliphatic groups may be saturated or unsaturated (non-vinylic groups should especially be mentioned), and, especially in the case of aliphatic groups, may be unsubstituted or substituted by one or more oxygen-containing groups, for example by one or more hydroxyl
15 groups, typically by 0 – 1 hydroxyl group, and may be uninterrupted or interrupted by one or more oxygen atoms. Poly-carboxylic acids containing at least one oxygen atom in the chain and/or at least one hydroxyl substituent should especially be mentioned. Generally the acid has up to 5 carboxyl groups and up to 30 carbon atoms. Di- and tri-carboxylic acids should especially be mentioned. The acid may
20 have, for example, 2 to 10 carbon atoms, especially 4 to 8, and typically 6, carbon atoms. Examples of suitable acids include citric acid and adipic acid, but acids with fewer carbon atoms, e.g. C₂, C₃, C₄ or C₅ acids, should also be mentioned.

The acid may alternatively contain a longer chain group, e.g. having up to 22 or up to 24 carbon atoms. Polycarboxylic acids having at least 8 carbon atoms and
25 those having from 6 to 22 carbon atoms should especially be mentioned. The component may comprise, for example, maleated tall oil. The use of a non-vinylic

acid should especially be mentioned. Mixtures of carboxylic acid components 1a may be used if desired.

A monocarboxylic acid component 1b may be used in conjunction with a

- 5 polycarboxylic acid component 1a but not alone. An acid which is an optional component 1b of the starting mixture also may be aliphatic or cycloaliphatic or may contain both aliphatic and cycloaliphatic moieties. An aliphatic group may be straight chain or branched. Aliphatic and cycloaliphatic groups may be saturated or unsaturated, and non-vinylic groups should especially be mentioned. Hydroxy-
- 10 substitution and/or interruption by oxygen may, for example, be possible, but more usually the acid is unsubstituted and is uninterrupted by oxygen atoms. Generally the acid has 1 to 24 carbon atoms, and for example at least 4 carbon atoms, especially at least 8 carbon atoms, and for example up to 22 carbon atoms. C₄-C₂₄ monocarboxylic acids, especially C₈-C₂₄, more especially C₈-C₂₂, fatty acids should
- 15 be mentioned, for example butyric acid, lauric acid, palmitic acid, stearic acid, oleic acid, linoleic acid or linolenic acid. Preferably, but not necessarily, the acid is branched-chain or cyclic and/or is unsaturated. The use of a non-vinylic acid should especially be mentioned. A preferred acid is tall oil fatty acid. Mixtures of monocarboxylic acid components 1b may be used if desired.

20

- The term "vinylic acid" is used herein to include not only acrylic acid and maleic acid, but also other related α , β -unsaturated acids, that is, more particularly, methyl-substituted or other C₁-C₄ alkyl-substituted acrylic and maleic acids. The use of at least one non-vinylic acid in the carboxylic acid component should be
- 25 mentioned, more especially when the alcohol component is a polyhydric alcohol component 2(a)(i).

A polyhydric alcohol component 2a may be aliphatic or cycloaliphatic or may contain both aliphatic and cycloaliphatic moieties. An aliphatic group may be straight chain or branched. Aliphatic and cycloaliphatic groups may be saturated or unsaturated and may be unsubstituted by one or more oxygen-containing groups and may be uninterrupted or interrupted by one or more oxygen atoms. Non-cyclic structures generally have 2 to 40 carbon atoms and 2 or 3 hydroxy groups, if desired with one or more oxygen atoms in the chain, being derivable from glycols having 2 or 3 OH groups each. Polyhydric alcohols containing 1 to 3 oxygen atoms in the chain should especially be mentioned. Thus, for example, there may be one or more units selected from alkyleneoxy and alkenyleneoxy groups, e.g. two or three such units, and generally no more than 10 such units, each containing, for example, 2 to 4, especially 2 or 3, carbon atoms. Examples of suitable di- or poly-ols include ethylene glycol, glycerol, and, especially, di-propylene glycol, tri-propylene glycol, di-ethylene glycol or tri-ethylene glycol. Di-propylene glycol, tri-ethylene glycol and tri-propylene glycol should especially be mentioned. Cyclic structures are, for example, C₃-C₆ sugars, usually C₅ or C₆ sugars, and polysaccharides, with hydroxyl groups being in free or protected form. Mixtures of components 2a may be used if desired.

20

A monohydric alcohol which is an optional component 2b of the starting mixture also may be aliphatic or cycloaliphatic or may contain both aliphatic and cycloaliphatic moieties. An aliphatic group may be straight chain or branched. Aliphatic and cycloaliphatic groups may be saturated or unsaturated. Primary alcohols are preferred. Interruption by oxygen may, for example, be possible, but more usually the alcohol is uninterrupted by oxygen atoms. Generally, the alcohol

25

has 1 to 24 carbon atoms, for example 1 to 20 carbon atoms, and for example at least 4, especially at least 8, carbon atoms. C₈-C₂₀, especially C₁₂ or C₁₃, fatty alcohols should be mentioned, for example oleyl alcohol, linoleyl alcohol, linolenyl alcohol, octyl alcohol, decyl alcohol, lauryl alcohol, myristyl alcohol, cetyl alcohol or stearyl alcohol, and, more especially, isododecanol, although alcohols having a lower number of carbon atoms are also possible. Cyclohexanol should also be mentioned. Preferably, but not necessarily, the alcohol is branched-chain or cyclic and/or is unsaturated. Mixtures of fatty alcohol components 2b may be used if desired.

10

As indicated, starting materials may contain straight or branched chains and/or cyclic structures and may contain saturated or unsaturated hydrocarbon groups; branched chains and aliphatic cyclic structures as well as unsaturated hydrocarbon groups should especially be mentioned as in general these assist with biodegradability.

15

The esterification reaction is generally carried out by heating with or without application of a vacuum and usually with stirring. A catalyst, e.g. para-toluenesulphonic acid, may be added if desired. The temperature may be, for example, substantially 220°C, and generally in the range of from 20 to 260°C, the lower temperatures usually requiring a vacuum and/or catalyst. Any suitable solvent for the esterification reaction may be used, although it is preferable to use a biodegradable organic solvent which can also be used as solvent during subsequent use for the demulsification. Examples are, for example Esticlean AS-OF (available from Estichem, Denmark) and Solvesso 150 (available from Esso). Water may be removed, for example by a Dean Stark trap.

20

25

A starting material may, for example, be in protected form. An acid, for example, may be used in the form of a simple derivative, e.g. an ester, halide or anhydride; chlorides and C₁-C₄ alkyl esters should especially be mentioned.

5

Acid and alcohol may, for example, be used in substantially stoichiometric proportions, or there may be excess OH or COOH groups. Esterification may be substantially complete, and there may be no or few OH or COOH groups remaining. Alternatively, excess OH or excess COOH groups may be present.

- 10 The esterification range may be, for example, from 20 to 100% of the acid groups, typically 80%. The use of a molar excess of the alcohol should especially be mentioned.

- The reaction may, for example, be carried out in one step or, when a component
- 15 1(b) or 2(b) is used, the reaction may, for example, be a two-step process, with the additional component(s) 1(b) and/or 2(b) being added in the second step, monohydric alcohol being added, for example in an amount sufficient to esterify any remaining acid groups present, and monocarboxylic acid being added, for example, to esterify any remaining OH, e.g. OH substituent on the polycarboxylic
- 20 acid. Thus, if used, a monocarboxylic acid component 1b may be, for example, up to one mole per mole of the hydroxyl groups. A monohydric alcohol component 2b, if used, may be, for example, up to one mole per mole of the carboxylic acid groups

- 25 Both hydrophilic and hydrophobic properties should be present, but the degree of hydrophilicity/hydrophobicity will vary according to the compounds and ratios used.

From 1 to 5 of the carboxylic acid groups on the polycarboxylic acid may be esterified. Any hydroxyl group on the polyacid may be esterified or unesterified.

As mentioned, the polyester may be produced and applied in a biodegradable organic solvent. The solution used for demulsification may contain, for example, 5-80% of polyester by weight. A demulsifier of the present invention may be applied at the well-head, at a suitable injection point downstream, or at any stage of crude oil processing, for example in an amount of from 2 to 200 ppm, e.g. from 5 to 25 ppm, of the polyester in the oil. Mixtures of demulsifiers of the invention may be used, and a demulsifier or demulsifier mixture of the invention may, if desired, be used with a different biodegradable demulsifier.

The following Examples illustrate the invention.

15 Preparation of demulsifiers

Example 1

Starting materials:

		<u>wt %</u>	<u>wt % calc on reactants</u>
20	Citric acid	83.73 g	26.45
	TEG	129.06 g	40.78
	Nafol 1214*	87.21 g	27.55
25	Solvesso 150**	50 g	12.78
	Water removed		-7.56

* Nafol 1214 is a C12 + C14 fatty acid product available from Sasol

**Solvesso 150 is a petroleum distillate (naphtha based) solvent available from Esso

5

Citric acid (CA) and tri-ethylene glycol (TEG) were added to a 500ml round-bottomed flask fitted with a Dean Starks trap. The mixture was heated to 100°C with continuous stirring. The solution became clear and colourless at this point. Nafol 1214 and Solvesso 150 were added, the solution becoming cloudy white.

- 10 The mixture was then heated further, with water starting to be removed at 150°C. Heating was continued to 216°C for 2.5-3 hours, no more water being recovered (a total of 27.3 g liquid being recovered). The solution was clear and light yellow.

- The Solvesso 150 was added as solvent to prevent possible gelling of the product;
15 it plays no role in the reaction.

- The total liquid recovered (27.3g) should be compared with the theoretical amount of water recovered (23.55g). The actual liquid recovered had a distinctive ester (sweet) smell, indicating some low molecular weight esters were pulled off as well.
20

This product was made as a 1:3:1 molar ratio of CA:TEG:C-12,14 alcohol.

Subsequent samples were prepared in the same way:

- 25 The starting materials are mixed, heating and stirring is started, and the mixture/

solution is heated to 215-220°C while removing water.

Example 2

	<u>wt %</u>
5 CA	26.23%
TEG	41.42%
Di-propylene glycol (DPG)	32.35%

This product was designed with a 0.95:1.5:1.5 ratio of CA:TEG:DPG; no
10 monohydric alcohol was used.

Example 3

	<u>wt %</u>
CA	26.16%
15 TEG	26.16%
DPG	20.44%
C-12,14 alcohol	27.24%

This product was designed with a 1:1:1:1 ratio of all starting materials.

20 Example 4

	<u>wt %</u>
CA	29.56%
TEG	70.44%

This was a 1:3 ratio of citric acid and TEG.

Example 5

- 5 Maleated tall oil acid (C22, 3 acid groups, unsaturated, 126 g) was blended with tri-propylene glycol (74 g) and heated to 200°C. The mixture was kept at high temperature until about 80% of the acid groups had esterified, water being distilled off.

10 Demulsifier bottle test results

An oil-in-water emulsion of crude oil containing no demulsifier components was sampled downstream of the 1st stage separator. Crude oil, 100 ml, was measured into demulsifier testing shaking bottles. The samples were placed in a waterbath at 15 60 °C. Demulsifier bases were added to the crude oil samples prior to a predefined procedure for manual agitation of the test bottles. After agitation the test bottles were placed in a waterbath at 60 °C. Water drop in the test bottles was recorded every 2, 4, 6, 10 and 20 minutes. Finally, residual water in the oil phase was determined by use of Karl Fisher titration.

20

The test results are presented in Table 1.

Table 1

Product	Dosage of 2 wt% active demulsifier solution* (microlitre)	Water drop (%)					Residual water/oil
		2 min	4 min	6 min	10 min	20 min	(%) -
Blank	-	0.05	0.05	0.05	0.1	0.1	0.55
Example 2	10	0.1	0.1	0.1	0.1	0.4	0.35

Example 3	10	0.05	0.1	0.1	0.1	0.1	0.24
Example 4	10	0.05	0.1	0.1	0.1	0.2	0.23

Total watercut in crude oil prior to demulsification was determined by use of Karl Fisher titration to be in the range 2.3 to 2.53 %.

5 **Biodegradation and Bioaccumulation Test Procedure and Results**

- The potential for bioaccumulation of a chemical substance is related to the solubility properties of the material. Lipophilic chemicals may migrate passively into the oil-soluble bodies of marine organisms if discharged into the sea. Actual
- 10 bioaccumulation in the ecosystem will occur when a lipophilic and non-biodegradable chemical is discharged into the sea. Biodegradation can be defined as when a component is available for living organisms, and can be used as a energy source. It will be oxidised and mineralised throughout metabolism. Several test methods are approved for offshore industry, such as OECD 306, OECD
- 15 BODIES and Marine CO₂-release.

Biodegradation for chemicals in this present invention is determined by use of test method OECD 306.

Biodegradation = BOD/COD,

20 where

BOD = Biological Oxygen demand: (the amount of oxygen (mg/l) required for complete oxidation of a substance).

and

COD = Chemical Oxygen Demand: (the amount of oxygen (mg/l) required for

25 complete oxidation of a substance).

Biodegradation of a chemical is divided into the following three categories:

- Readily degradable : >60% degraded within 28 days
Inherently degradable : 20-60% degraded within 28 days
Persistent : <20% degraded within 28 days

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Bioaccumulation measurement is carried out by OECD method 107/117, or if not applicable measurement is based on water-solubility properties.

Biodegradation and Bioaccumulation test results

10

	<u>Biodegradation</u>	<u>Bioaccumulation</u>
Example 1	20-60% after 28 days	3-5
Example 2	20-60% after 28 days	>3
Example 3	20-60% after 28 days	>3
15 Example 4	40% after 28 days	>3

Toxicity

All samples tested for toxicity (LC₅₀ of *skeletoma costatum*, *alega*) had levels about 1000ppm (least toxic level for reporting)

CLAIMS

1. A process for demulsification of a water-in-oil emulsion, especially a
5 crude oil emulsion, wherein there is used a reaction product derivable by reaction
of
1. a carboxylic acid component comprising
- (a) a poly-carboxylic acid having 2 to 30 carbon atoms and 2 to 5
carboxylic acid groups, and, if desired,
- 10 (b) a C₁₋₂₄ monocarboxylic acid
with
2. an alcohol component comprising
- (a)(i) a polyhydric alcohol comprising 1 to 10 glycol units each having 2 to
4 carbon atoms and each glycol having 2 or 3 hydroxy groups, or
- 15 (ii) a sugar or polysaccharide, and, if desired,
- (b) a C_{1-C24} monohydric alcohol.
2. A process as claimed in claim 1, wherein component 1(a) comprises
a C_{6-C22} carboxylic acid which is unsubstituted or substituted by one or more
20 hydroxyl groups and uninterrupted or interrupted by one or more oxygen atoms.
3. A process as claimed in claim 1, wherein component 1(a) comprises
a carboxylic acid having up to 10 carbon atoms which is unsubstituted or
substituted by one or more hydroxyl groups and uninterrupted or interrupted by one
25 or more oxygen atoms.

4. A process as claimed in any one of claims 1 to 3 wherein component 1(a) comprises a carboxylic acid having at least 8 carbon atoms.

5. A process as claimed in any one of claims 2 to 4, wherein the acid
5 contains one or more hydroxyl groups and/or is interrupted by one or more oxygen atoms.

6. A process as claimed in any one of claims 1 to 5, wherein component 1(a) comprises a C₁₂-C₂₄ carboxylic acid .

10

7. A process as claimed in any one of claims 1 to 6, wherein component 1(a) comprises a saturated carboxylic acid.

8. A process as claimed in any one of claims 1 to 7, wherein component
15 1(a) comprises a di- or tri-carboxylic acid.

9. A process as claimed in claim 8, wherein component 1a comprises a tri-carboxylic acid.

20 10. A process as claimed in claim 9, wherein component 1(a) comprises citric acid.

11. A process as claimed in any one of claims 1 to 10, wherein component 1(a) comprises a branched chain carboxylic acid.

25

12. A process as claimed in any one of claims 1 to 11, wherein component 1 includes an unsaturated or saturated monocarboxylic acid 1(b) having from 4 to 24 carbon atoms.

5 13. A process as claimed in claim 12, wherein the acid has from 8 to 24 carbon atoms.

14. A process as claimed in claim 12 or claim 13, wherein the monocarboxylic acid is branched or cyclic and/or unsaturated.

10

15. A process as claimed in claim 1 to 14, wherein component 1(b) comprises a saturated carboxylic acid.

16. A process as claimed in claim 1 to 15, wherein component 1
15 comprises a saturated or non-vinylic unsaturated carboxylic acid.

17. A process as claimed in any one of claims 1 to 16, wherein component 2(a) comprises a dihydric or trihydric alcohol containing up to 10 alkyleneoxy or alkenyleneoxy units.

20

18. A process as claimed in claim 17, wherein each alkyleneoxy or alkenyleneoxy unit has 2 or 3 carbon atoms.

19. A process as claimed in claim 17 or claim 18, wherein there are 2 or
25 3 alkyleneoxy or alkenyleneoxy groups.

20. A process as claimed in claim 19, wherein component 2(a) comprises di-propylene glycol, tri-ethylene glycol or tri-propylene glycol.

21. A process as claimed in any one of claims 1 to 20, wherein
5 component 2(a) comprises a branched chain polyhydric alcohol.

22. A process as claimed in any one of claims 1 to 21, wherein component 2(a) comprises a sugar or polysaccharide.

10 23. A process as claimed in any one of claims 1 to 22, wherein component 2 includes an unsaturated or saturated monohydric alcohol having from 1 to 24 carbon atoms.

24. A process as claimed in claim 23, wherein the monohydric alcohol
15 has at least 8 carbon atoms.

25. A process as claimed in claim 24, wherein the monohydric alcohol has up to 20 carbon atoms.

20 26. A process as claimed in any one of claims 23 to 25, wherein the monohydric alcohol is branched and/or unsaturated.

27. A process as claimed in claim 26, wherein component 2 includes isododecanol.

28. A process as claimed in any one of claims 1 to 27, wherein at least one starting material is unsaturated.

29. A process as claimed in any one of claims 1 to 28, wherein at least
5 one acid starting material is other than an α , β -carboxylic acid.

30. A process as claimed in any one of claims 1 to 29, wherein at least one starting material is branched or cyclic.

10 31. A process as claimed in any one of claims 1 to 30, wherein a mixture of reaction products is used.

32. A process as claimed in any one of claims 1 to 31, wherein the emulsion is a crude oil emulsion.

15

33. Crude oil which has been demulsified by a process as claimed in claim 32.

34. A reaction product or product mixture as specified in any one of
20 claims 1 to 31, for use as a demulsifier.

INTERNATIONAL SEARCH REPORT

International Application No

GB 03/05283

A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C10G33/04

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10G

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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X	US 2 599 538 A (BLAIR JR CHARLES M) 10 June 1952 (1952-06-10) column 1, line 16 - line 23; claim 1	1-34
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Further documents are listed in the continuation of box C.



Patent family members are listed in annex.

* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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INTERNATIONAL SEARCH REPORT

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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