



(86) Date de dépôt PCT/PCT Filing Date: 2003/06/17
(87) Date publication PCT/PCT Publication Date: 2004/01/22
(45) Date de délivrance/Issue Date: 2011/09/20
(85) Entrée phase nationale/National Entry: 2005/01/13
(86) N° demande PCT/PCT Application No.: SE 2003/001015
(87) N° publication PCT/PCT Publication No.: 2004/007630
(30) Priorité/Priority: 2002/07/15 (SE0202198-8)

(51) Cl.Int./Int.Cl. *C09K 3/00* (2006.01),
C09K 8/06 (2006.01), *C09K 8/584* (2006.01),
C10M 173/02 (2006.01), *E21B 43/22* (2006.01),
F17D 1/17 (2006.01)

(72) Inventeurs/Inventors:
HELLSTEN, MARTIN, SE;
OSKARSSON, HANS, SE

(73) Propriétaire/Owner:
AKZO NOBEL NV, NL

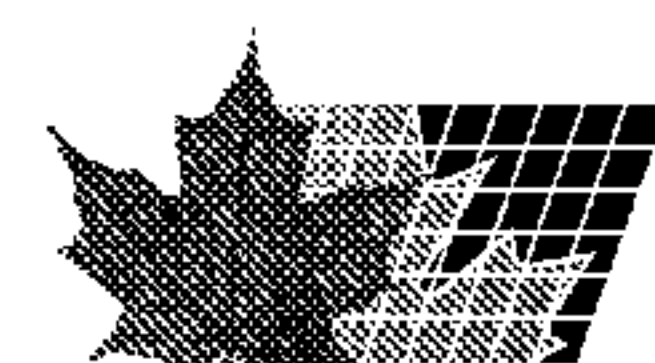
(74) Agent: NORTON ROSE OR S.E.N.C.R.L., S.R.L./LLP

(54) Titre : AGENT REDUCTEUR DE TRAINEE UTILISE DANS L'INJECTION D'EAU LORS DE LA RECUPERATION
D'HUILE SECONDAIRE

(54) Title: A DRAG-REDUCING AGENT FOR USE IN INJECTION WATER AT OIL RECOVERY

(57) Abrégé/Abstract:

The present invention relates to the use of a drag-reducing agent in an amount of 50-400 ppm in water having an electrolyte content of 0.01-7% by weight. The drag-reducing agent comprises two zwitterionics, each comprising acyl containing surfactant and an anionic surfactant, where the hydrophilic group is a sulphate, a sulphonate or an ether sulphate. The water containing the drag-reducing agent is suitable to be used in injection water at oil recovery.



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

(19) World Intellectual Property
Organization
International Bureau



(43) International Publication Date
22 January 2004 (22.01.2004)

PCT

(10) International Publication Number
WO 2004/007630 A1

(51) International Patent Classification⁷: **C09K 3/00**,
C10M 173/02, E21B 43/22, F17D 1/17

(74) Agent: **ANDERSSON, Rolf**; Akzo Nobel Surface Chem-
istry AB, S-444 85 Stenungsund (SE).

(21) International Application Number:
PCT/SE2003/001015

(81) Designated States (*national*): AE, AG, AL, AM, AT, AU,
AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU,
CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH,
GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC,
LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW,
MX, MZ, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RU, SC,
SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG,
US, UZ, VC, VN, YU, ZA, ZM, ZW.

(22) International Filing Date: 17 June 2003 (17.06.2003)

(25) Filing Language: English

(26) Publication Language: English

(30) Priority Data:
0202198-8 15 July 2002 (15.07.2002) SE

(84) Designated States (*regional*): ARIPO patent (GH, GM,
KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW),
Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM),
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), OAPI patent (BF, BJ, CF, CG, CI, CM,
GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

(71) Applicant (*for all designated States except US*): **AKZO
NOBEL NV** [NL/NL]; P.O. Box 9300, NL-6800 SB Arn-
hem (NL).

Published:

— with international search report

(72) Inventors; and

(75) Inventors/Applicants (*for US only*): **HELLSTEN, Mar-
tin** [SE/SE]; Vårsåddsvägen 4, S-444 05 Ödsmå (SE). **OS-
KARSSON, Hans** [SE/SE]; Egnahemsvägen 3a, S-444 41
Stenungsund (SE).

*For two-letter codes and other abbreviations, refer to the "Guid-
ance Notes on Codes and Abbreviations" appearing at the begin-
ning of each regular issue of the PCT Gazette.*

(54) Title: A DRAG-REDUCING AGENT FOR USE IN INJECTION WATER AT OIL RECOVERY

(57) Abstract: The present invention relates to the use of a drag-reducing agent in an amount of 50-400 ppm in water having an electrolyte content of 0.01-7% by weight. The drag-reducing agent comprises two zwitterionics, each comprising acyl containing surfactant and an anionic surfactant, where the hydrophilic group is a sulphate, a sulphonate or an ether sulphate. The water containing the drag-reducing agent is suitable to be used in injection water at oil recovery.

WO 2004/007630 A1

A DRAG-REDUCING AGENT FOR USE IN INJECTION WATER AT OIL RECOVERY

The present invention relates to the use of a drag-reducing agent containing a zwitterionic surfactant and an anionic surfactant in waters containing electrolytes. The agent is very efficient at low contents even in waters having a high electrolyte content and is suitable to be utilized in injection waters at oil recovery.

A crude oil reservoir is formed by a stratum of porous rock or sand covered by a rock layer difficult for the crude oil to penetrate. When the pressure in an oil reservoir declines, it is quite common to inject water, for example sea-water, into the oil well to maintain the pressure and the recovery of oil on a high level. However, the injection of water is hampered by the flow resistance (drag) in the conduits and in the oil reservoir and in order to reduce the drag, it has been suggested to add a drag-reducing additive to the injection water.

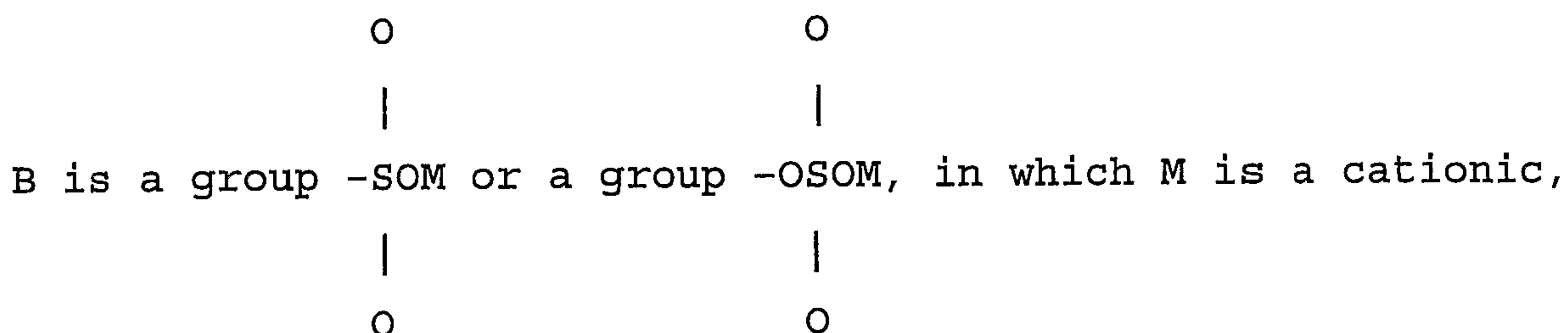
Thus, EP 116 779 discloses that copolymers of acrylamide and alkylpoly(etheroxy)acrylate have drag-reducing properties in brine solution. In US 4 489 180 it is described a drag-reducing agent comprising of a complex polymer of a mixture of a cationic polymer and an anionic polymer. The addition of the drag-reducing additive is in Example 2 is 500 ppm. Although poly(amide acrylate) polymers may have good drag-reducing effect at a low concentration, it has also been observed that the polymers have a tendency to form aggregates in the oil reservoir, which causes a substantial drop of the flow of injection water.

It is also known, e.g. from WO 92/13925 and WO 96/28527, that surfactants forming rod-like micelles have good drag-

reducing effects. Thus, WO 96/28527 describes a drag-reducing agent comprising at least one betaine surfactant having an alkyl or acyl group with 10-24 carbon atoms in combination with an anionic surfactant having the general structure

5 R_1-B

where R_1 is a hydrocarbon group with 10-24 carbon atoms and



preferably monovalent group, in a proportion between the betaine surfactant and the anionic surfactant of from 20:1 to 1:2. Preferably the betaine surfactant has the general

15 formula



where R is the alkyl group or the group $R'NC_3H_6-$ where R' is the acyl group. However, the amount of the surfactant necessary to obtain an essential reduction of the drag has shown to be above 500 ppm of the water. In addition, the

25 formation of micelles and therewith the reduction of drag is expected to be negatively affected by the presence of large amounts of electrolytes. Thus, this type of drag-reducing agents has not at all been regarded as suitable to be used in injection waters, especially not when the injection water is

30 based on sea-water.

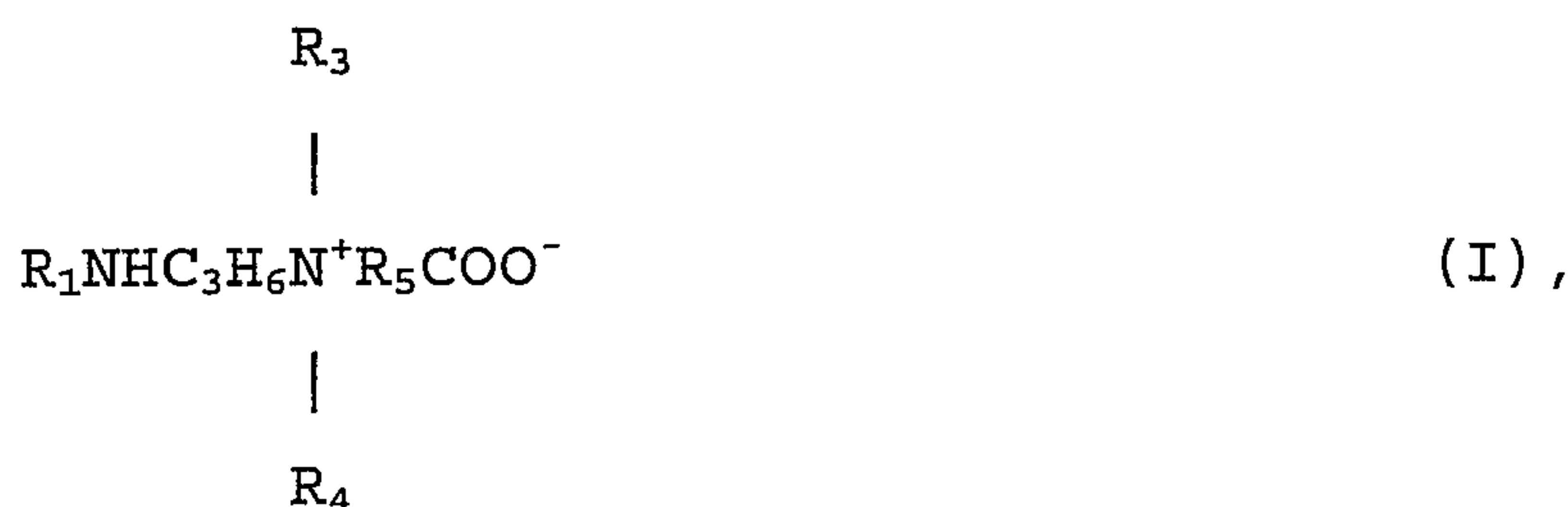
It has now been found that a drag-reducing agent containing certain types of zwitterionic surfactants has a

remarkably good drag-reducing effect at a concentration of 50-400 ppm, preferably 60-300 ppm, at large temperature intervals within the range of 2-70°C even in water with an electrolyte content of 0.01-7%, suitably 0.05-6% by weight.

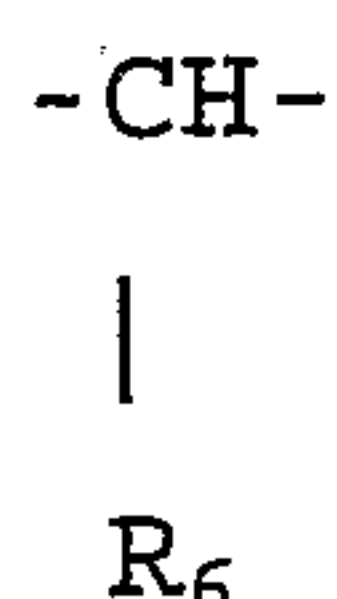
Thus, the drag-reducing agent according to the invention can also with a high efficacy and in low amounts be used in brackish water and sea-water with an electrolyte content of 0.3 to 6% by weight. The surfactants in the drag-reducing agent are also readily soluble in the water at the temperatures in the oil reservoir and do not cause any reduction of the injection water flow due to reduced permeability. On the contrary, tests have shown that the presence of the drag-reducing agents of the inventions in the injection water reduces the pressure drop with about 10%, when measured over a plug of calcium carbonate with a permeability of 1.3 mDarcy at a constant flow rate.

The drag-reducing agent for use according to the invention comprises

a) a zwitterionic surfactant of the formula



where R_1 is acyl group with 12-16 carbon atoms, R_3 and R_4 are independently of each other an alkyl group of 1-4 carbon atoms or an hydroxyalkyl group of 2-4 carbon atoms and R_5 is an alkylene group of 1-4 carbon atoms, preferably CH_2 or a group



where R_6 is an alkyl group of 1-3 carbon atoms, and

b) a zwitterionic surfactant of the formula



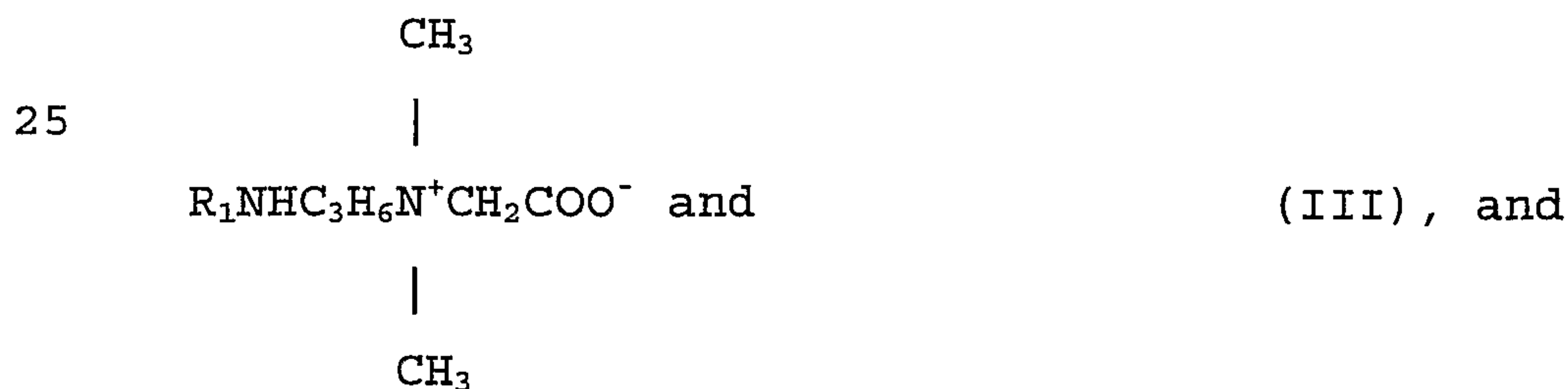
where R_2 is an acyl group with 18-22 carbon atoms, and R_3 , R_4 and R_5 have the meanings mentioned above, and

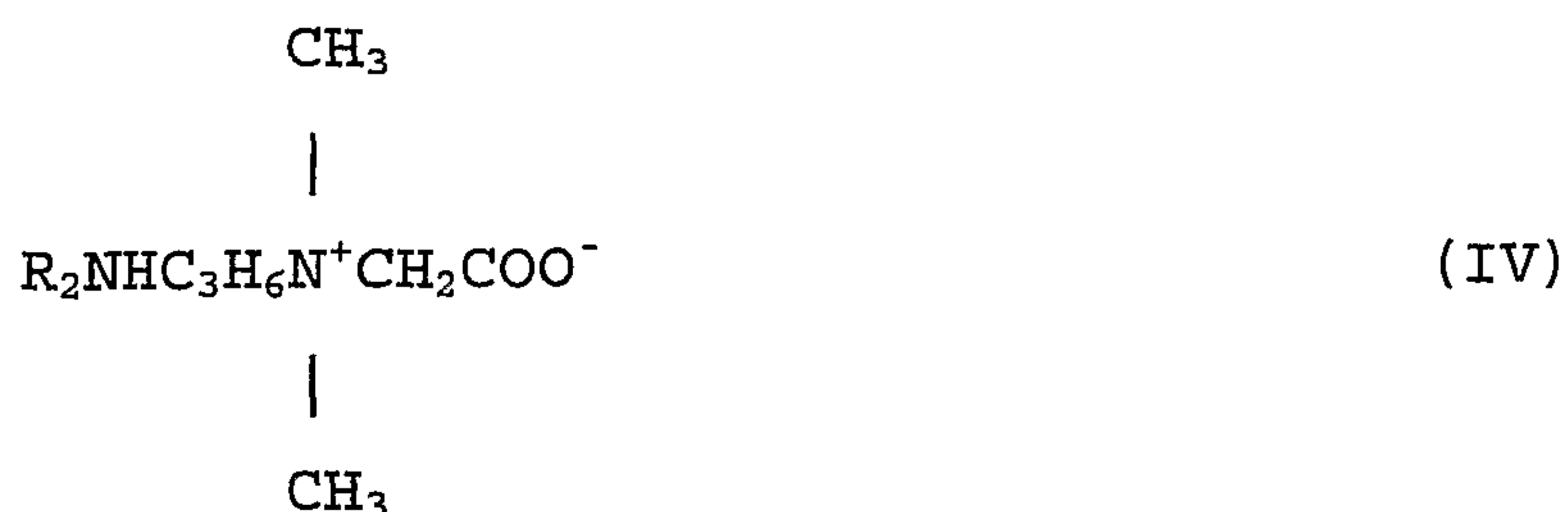
10 c) an anionic surfactant of the formulae



or a mixture thereof, where R_7 is an aliphatic group of 8-14, preferably 10-12, carbon atoms, A is an alkylene group having 2-4 carbon atoms, n is a number from 1 to 10, B is a sulphate group OSO_3M , E is a sulphate group OSO_3M or a sulphonate group $-SO_3M$ and M is a cationic, preferably monovalent group; the weight of a), b) and c) being 20-95% by weight, 0-70% by weight and 1-50% by weight, respectively, based on the total amount of a), b) and c).

20 In the zwitterionic surfactant of formulae I and II, R_3 and R_4 are independently of each other suitably methyl or hydroxyethyl, and R_5 is suitably methylene. Preferably the zwitterionic surfactants have the formula





where R_1 and R_2 have the meanings mentioned above.

The group R_1 is suitably a linear C-12 or C-14 acyl, but also branched acyl groups could advantageously be used. The acyl group R_2 can be either saturated or unsaturated but unsaturated acyl groups are preferred. Suitably the acyl group R_2 is derived from vegetable oils, such as soy oil, olive oil, rapeseed oil, linseed oil, safflower oil, sun flower oil, cottonseed oil and tall oil.

The anionic surfactants for use according to the invention are well-known products and so are also their production methods. Preferred anionic surfactants are those where R_7 contains 10-12 carbon atoms and for many formulations lauryl sulphate, a lauryl (oxyethylene)₁₋₃ sulphates, or lauryl sulphonate, or a mixture thereof, is preferred.

Preferably the drag-reducing agent comprises the component a) in an amount of 20-85% by weight, the component b) in an amount of 10-70% by weight, and the component c) in an amount of 4-35% by weight, calculated on the total weight of a), b) and c).

Ordinary sea-water or brackish water have normally a temperature in the range of 5-35°C, while process-water, sometime also called production water, derived at least partially from the water in the production stream of oil and water from the oil well after the removal of the oil phase, normally has a temperature of 30-65°C.

Fortunately, the temperature window, where the drag-reducing effect is substantial can be regulated by the size of the group R_1 . Thus R_1 preferably contains 12-14 carbon atoms, when the injection water is a seawater having a salt content of 2-6% and a temperature of 5-30°C, and 14-16 carbon atoms, suitably in combination with a zwitterionic surfactant of formula II, when the injection water is a production water based on a sea-water having a salt content of 2-6% and a temperature of 30-65°C.

Apart from the zwitterionic surfactant and anionic surfactants, the water-based system may contain a number of conventional components such as corrosion inhibitors and bactericides.

The present invention will now be further illustrated with the aid of the following examples.

Example 1

The drag-reducing properties of different drag-reducing additives were evaluated in a synthetic sea-water containing 568 mmols of chloride, 482 mmols of sodium, 54 mmols of magnesium, 28 mmols of sulphate, 10 mmols of calcium and 10 mmols of potassium per liter water. In the evaluation test, 40 ml of the synthetic sea-water containing the drag-reducing additives were stirred in a 50 ml glass beaker with a magnetic stirrer at a constant speed of 700 r.p.m. and at different temperatures. The inner diameter of the beaker was 40 mm and the stirrer bar was 6 x 20 mm. The absence of a vortex in the water surface or a vortex of maximum 2 mm indicated a considerable reduction of the drag. Without addition of a drag-reducing agent, the vortex was 30 mm.

The following surfactants were used in the tests. C12APB is a compound of formula I, where R_1 is a C_{12} acyl, R_3 and R_4 are methyl and R_5 is methylene;

C14APB is a compound of formula I, where R_1 is a C_{14} acyl, R_3 and R_4 are methyl and R_5 is methylene;

C16APB is a compound of formula I, where R_1 is a C_{16} acyl, R_3 and R_4 are methyl and R_5 is methylene;

5 C18APB is a compound of formula II, where R_1 is a C_{18} acyl derived from oleic acid, R_3 and R_4 are methyl and R_5 is a methylene;

10 LinAPB is a compound of formula II, where R_2 is an acyl derived from linseed oil, R_3 and R_4 are methyl and R_5 is methylene;

SoyAPB is a compound of formula II, where R_2 is an acyl derived from soy oil, R_3 and R_4 are methyl and R_5 is methylene;

15 CanAPB is a compound of formula II, where R_2 is an acyl derived from a rapeseed oil with a low content of erucic acid, R_3 and R_4 are methyl and R_5 is methylene;

C14D is an alkyl betaine of the formula C_{14} -alkyl $N^+(CH_3)_2CH_2COO^-$;

C16D is an alkyl betaine of the formula C_{16} -alkyl $N^+(CH_3)_2CHCOO^-$;

C10S is a decyl sulphate

20 C12S is lauryl sulphate

C12EOS is lauryl di(oxyethylene) sulphate, and

C12S03 is a lauryl sulphonate.

25 In Table 1 below the combinations of zwitterionic surfactants and anionic surfactants, the amounts of the individual surfactants used and the temperature range where the vortex was 2 mm or less.

Table 1 Combinations of zwitterionic and anionic surfactants and their temperature range with a considerable drag-reduction

Test	Zwitterionic compound		Zwitterionic compound		Anionic compound		Temp. range °C
	Type	Ppm	Type	ppm	Type	ppm	
1	C12APB	200	-	-	C12S	27	4-35
2	C14APB	200	-	-	C12S	30	16-46
3	C14APB	100	-	-	C12S	15	16-50
4	C14APB	200	-	-	C12EOS	45	12-45
5	C14APB	100	-	-	C12EOS	23	14-52
6	C16APB	200	-	-	C12S	25	30-66
7	C16APB	100	-	-	C12S	13	34-65
8	C14APB	100	C18APB	100	C12S	20	14-60
9	C16APB	100	C18APB	100	C12EOS	18	25-65
10	C12APB	50	C14APB	50	C12EOS	20	11-44
11	C14APB	50	C18APB	50	C12S	10	19-60
12	C16APB	50	C18APB	50	C12EOS	9	25-65
13	C14APB	100	LinAPB	100	C12S	32	4-49
14	C14APB	100	LinAPB	100	C12EOS	33	4-44
15	C14APB	100	SoyAPB	100	C12S	29	5-41
16	C14APB	100	SoyAPB	100	C12EOS	44	5-40
17	C14APB	50	LinAPB	50	C12EOS	16	7-42
18	C16APB	50	LinAPB	50	C12S	21	36-60
19	C14APB	58	CanAPB	18	C12S	14	6-50
20	C14APB	38	CanAPB	19	C12S	9	7-45
21	C14APB	100	CanAPB	100	C10S	39	< 4-44
22	C14APB	50	CanAPB	50	C10S	25	< 4-44
23	C14APB	140	CanAPB	60	C12S03	35	4-48
24	C14APB	70	CanAPB	30	C12S03	18	4-47

A	C18APB	200	-	-	C12S	20	27-49
B	C18APB	200	-	-	C12EOS	20	29-50
C	C18APB	100	-	-	C12EOS	10	40-51
D	LinAPB	100	-	-	C12S	15	20-30
E	SoyAPB	100	-	-	C12S	13	No effect
F	C14B	200	-	-	C12EOS	0-200	No effect
G	C14B	100	LinAPB	100	C12EOS	0-200	No effect
H	C16B	100	LinAPB	100	C12S	0-200	No effect
I	C16B	100	LinAPB	100	C12EOS	0-200	No effect

From the results obtained it is evident that an agent according to the invention has an excellent drag-reducing effect at dosages below 250 ppm.

5

Example 2

Drag-reducing agents containing C14APB and CanAPB in equal amounts and C12S in varying amounts were tested in injection waters containing different amounts of the synthetic salt described in Example 1. In one test,
10 production water from the North Sea was used. The tests were performed in the same manner as in Example 1. The following results were obtained.

15

Table 2 Efficacy of drag-reducing agents in injection waters of different salt contents

Test	C14APB+CanAPB ppm	C12S ppm	Salt content %	Temp. range °C
25	200	35	0.03	< 5-58
26	100	18	0.015	< 5-50
27	200	35	0.6	< 5-47
28	100	40	0.6	< 5-46
29	200	22	1.0	< 5-46
30	100	40	1.0	< 5-46
31	200	35	3.0	< 5-47
32	100	18	3.0	< 5-47
33	200	38	~ 3.0 ¹⁾	< 5-51
K	200	0-200	0.00	No effect

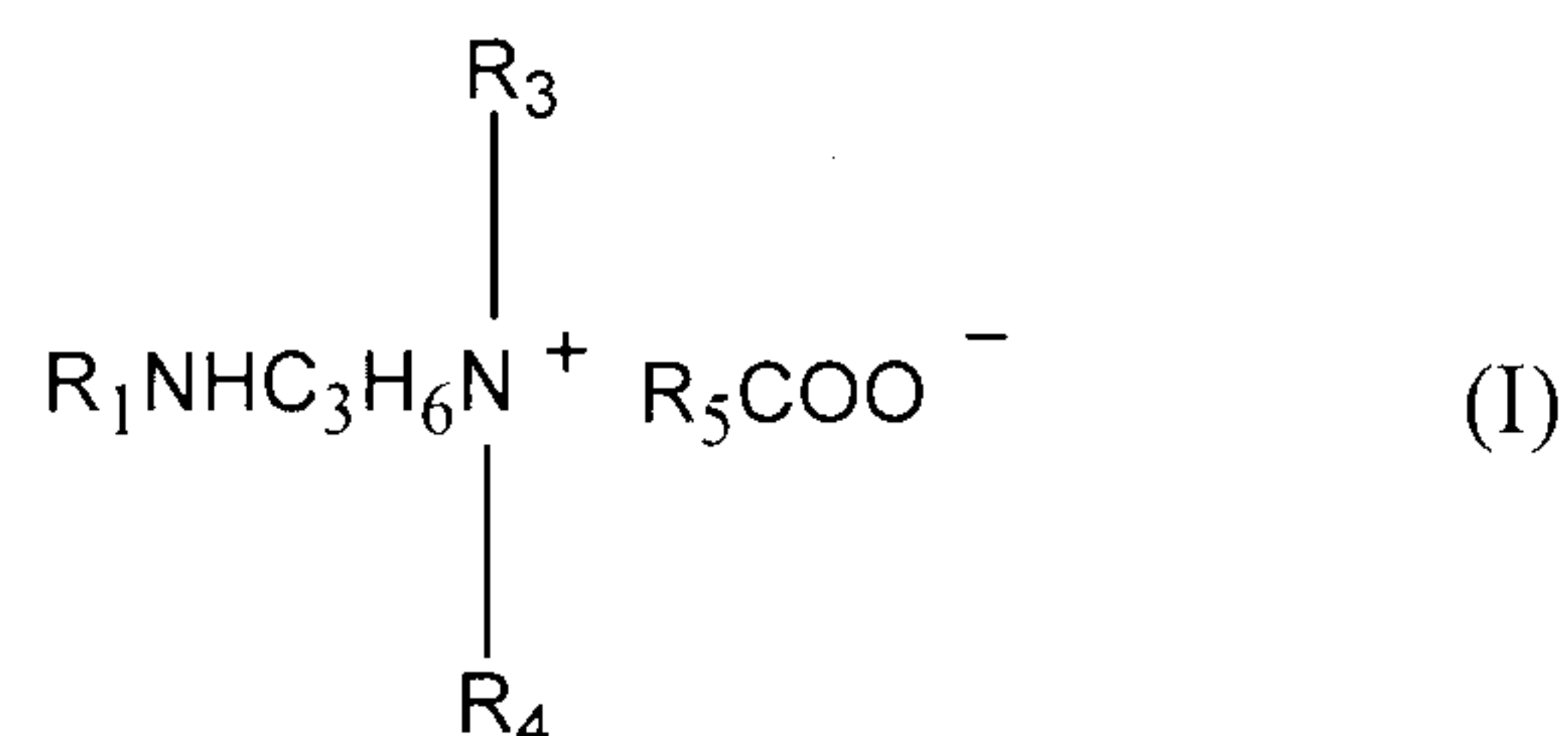
¹⁾ Production water from the North Sea containing less than
5 20 ppm of hydrocarbons

The results clearly show that the drag-reducing agents of the present invention have an essential effect in injection waters with different contents of electrolyte.

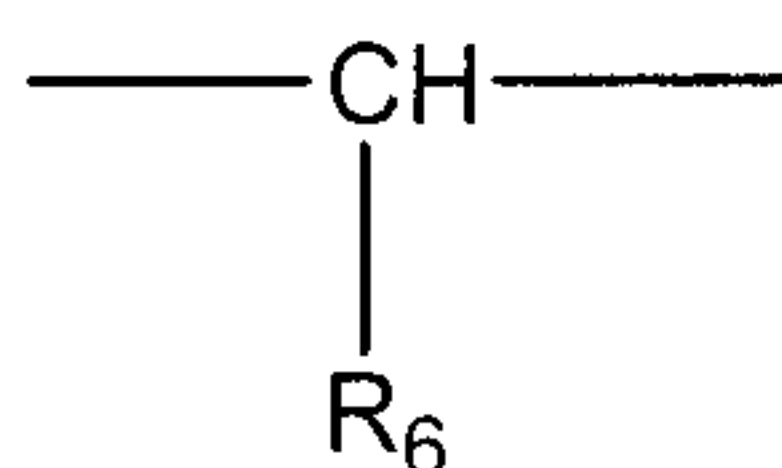
CLAIMS:

1. Use of a drag-reducing agent containing:

a) a zwitterionic surfactant of the formula:

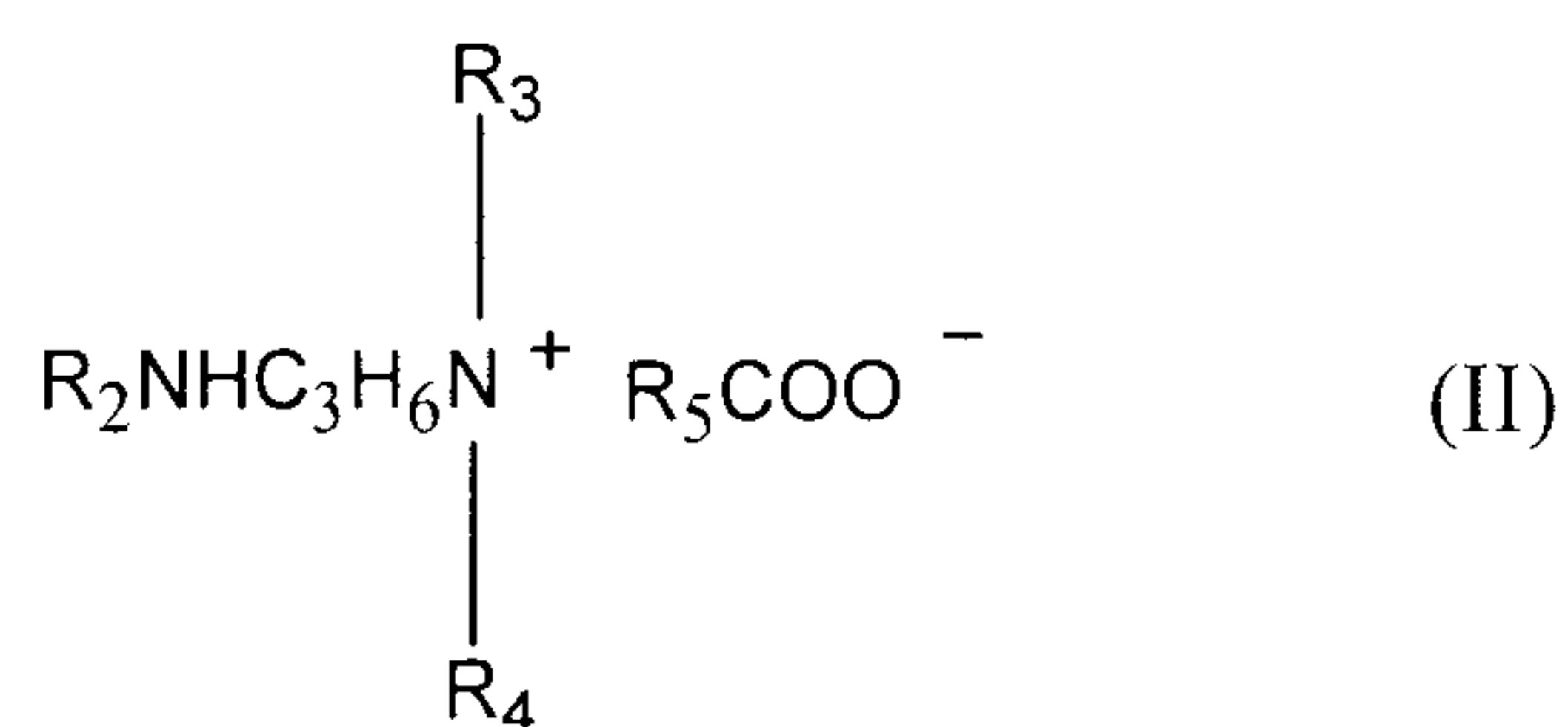


where R_1 is acyl group with 12-16 carbon atoms, R_3 and R_4 are independently of each other an alkyl group of 1-4 carbon atoms or an hydroxyalkyl group of 2-4 carbon atoms and R_5 is an alkylene group of 1-4 carbon atoms, or a group:



where R_6 is an alkyl group of 1-3 carbon atoms,

b) a zwitterionic surfactant of the formula:



where R_2 is an aryl group with 18-22 carbon atoms, and R_3 , R_4 and R_5 have the meanings mentioned above; and

c) an anionic surfactant of the formula:



or a mixture thereof, where R_7 is an aliphatic group of 8-14 carbon atoms, A is an alkylene group having 2-4 carbon atoms, n is a number from 1 to 10, B is a sulphate group OSO_3M , E is a sulphate group OSO_3M or a sulphonate group $-SO_3M$ and M is a cationic group;

the weight of a), b) and c) being 20-95% by weight, 0-70% by weight and 1-50% by weight, respectively, based on the total amount of a), b) and c);

in an amount of a), b) and c) of 50-400 ppm in water having an electrolyte content from 0.01-7% by weight.

2. Use according to claim 1, wherein R_5 is CH_2 .
3. Use according to claim 1 or 2, wherein said a cationic group M is a monovalent group.
4. Use according to any one of claims 1 to 3, wherein the component a) and b) are present in an amount of 20-85% by weight and 10-70% by weight, respectively.
5. Use according to any one of claims 1 to 4, wherein R_2 contains at least 50% by weight of unsaturated acyl groups.
6. Use according to claim 5, wherein R_2 contains at least 20% by weight of unsaturated acyl groups having two or more double bonds.
7. Use according to any one of claims 1 to 6, wherein c) is lauryl sulphate, a lauryl (oxyethylene)_n sulphate, where n is 1-3, or lauryl sulphonate.
8. Use according to any one of claims 1 to 7, characterized in that the water has an electrolyte content of 0.3-6% by weight.

9. A drag-reducing agent, characterized in that it contains the components a), b) and c) as defined in any one of claims 4 to 7.
10. Injection water for the treatment of oil reservoirs, characterized in that the water contains the components a), b) and c) as defined in any one of claims 1 to 7, in a total amount of 50-400 ppm and has an electrolyte content of 0.01-7% by weight.
11. Injection water according to claim 10, characterized in that it contains electrolytes in an amount of 0.3-6% by weight.
12. Injection water according to claim 10 or 11, characterized in that the water is sea-water or production water.