



(11) **EP 2 688 977 B9**

(12) **CORRECTED EUROPEAN PATENT SPECIFICATION**

(15) Correction information:
Corrected version no 1 (W1 B1)
Corrections, see
Claims EN 14, 15

(51) Int Cl.:
C09K 8/584 ^(2006.01) **C07C 303/24** ^(2006.01)
C07C 303/42 ^(2006.01) **C11D 1/29** ^(2006.01)
C07C 305/02 ^(2006.01)

(48) Corrigendum issued on:
07.03.2018 Bulletin 2018/10

(86) International application number:
PCT/EP2012/001275

(45) Date of publication and mention
of the grant of the patent:
01.11.2017 Bulletin 2017/44

(87) International publication number:
WO 2012/126630 (27.09.2012 Gazette 2012/39)

(21) Application number: **12711345.4**

(22) Date of filing: **23.03.2012**

(54) **HIGHLY-CONCENTRATED FLOWABLE SALTS OF ALKYL POLYALKOXY SULPHATES**

HOCHKONZENTRIERTE FLIESSFÄHIGE SALZE VON ALKYL POLYALKOXY SULFATEN

SELS DE SULFATES D'ALKYL POLYALCOXY TRÈS CONCENTRÉS DOUÉS D'ÉCOULEMENT

(84) Designated Contracting States:
**AL AT BE BG CH CY CZ DE DK EE ES FI FR GB
GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO
PL PT RO RS SE SI SK SM TR**

(30) Priority: **24.03.2011 DE 102011015046**

(43) Date of publication of application:
29.01.2014 Bulletin 2014/05

(73) Proprietor: **SASOL Germany GmbH
20537 Hamburg (DE)**

(72) Inventors:
• **JAKOBS-SAUTER, Britta
40764 Langenfeld (DE)**

• **KALTWASSER, Uwe
45770 Marl (DE)**

(74) Representative: **Müller Schupfner & Partner
Patent- und Rechtsanwaltspartnerschaft mbB
Schellerdamm 19
21079 Hamburg (DE)**

(56) References cited:
EP-A2- 0 167 337 DE-A1- 19 714 043
GB-A- 2 168 095 US-A- 3 893 955
US-A- 3 931 271 US-A- 4 886 120

Remarks:

The file contains technical information submitted after
the application was filed and not included in this
specification

Note: Within nine months of the publication of the mention of the grant of the European patent in the European Patent Bulletin, any person may give notice to the European Patent Office of opposition to that patent, in accordance with the Implementing Regulations. Notice of opposition shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 2 688 977 B9

Description

[0001] The present invention relates to highly-concentrated compositions of salts of alkyl polyalkoxy sulphates, wherein in total at least 2/3 of all alkoxy units of the salts of alkyl polyalkoxy sulphates are propoxy units, a method of producing the composition and their use in oil and gas field applications.

[0002] Alkyl polyalkoxy sulphates often also called alkyl polyether sulphates, (fatty) alcohol polyglycol ether sulphates or (fatty) alcohol polyether sulphates, commonly known and referenced hereunder in short as ether sulphates or alkyl ether sulphate salts, are used as surfactants or emulsifiers in numerous consumer products such as cleaning agents, shampoos and cosmetics. Structurally they have a lipophilic alkyl group and a hydrophilic area composed of the polar ether groups and the chemically bonded sulphate anion. These physical properties make these compounds surfactants and allow them to emulsify fats and oils. They are not very sensitive to hard water and are generally easily biodegradable. Fatty alcohols are understood hereunder to reference C8- to C18- branched and/or unbranched aliphatic mono-alkanols.

[0003] Alkyl ether sulphates can be produced from fatty alcohols in that fatty alcohols are initially converted with alkylene oxide, usually ethylene oxide. EO references ethylene oxide or an ethylene oxide group ($-\text{CH}_2\text{CH}_2\text{O}-$). The average number of ether groups is normally between 1 and 12. The hydroxyether is then converted to an ester with sulphur trioxide which results in a sulphuric acid monoester or a sulphuric acid semiester. This acid is unstable and is converted into a salt with the use of alkali hydroxide or ammonia. Common commercial forms in the case of sodium ether sulphates with 2 or 3 EOs are aqueous paste-like compositions with a concentration of approximately 70% by weight or aqueous liquid compositions comprising up to 28% by weight anionic active substances (in each case measured as anionic active substance in accordance with DIN ISO 2271). Concentration ranges between approximately 30% by weight and below approximately 70% by weight active content (anionic active substance) result in non-flowable and non-pumpable compositions, as liquid crystalline structures in the form of hexagonal or cubic phases with a very high viscosity are formed. These often constitute a problem when diluting 70% ether sulphate pastes, which have a lamellar liquid crystalline structure, to the desired usage concentration.

[0004] Concentrations of slightly over 70% by weight and more are also no longer flowable or pumpable as crystallisation of the ether sulphate begins, whereas concentrations of around 70% by weight are often found to be flowable and pumpable.

[0005] Several solutions to prevent very high viscosities in ether sulphates have been described in the literature, such as the use of alkyl- or alkanol-amines as neutralizing agents or addition of organic solvents like alkylene glycols or short chain alcohols or polyalkylene sulphates or nonionic surfactants such as alcohol alkoxylates as viscosity reducers. Viscosity reducers need to be present in significant amounts, meaning more than the usual residual unsulphated matter under standard sulphation conditions. This can be achieved by either intentional incomplete sulphation reaction or by adding viscosity reducers in the neutralization step.

[0006] 1 EP 0 167 337 discloses concentrated aqueous liquid surfactant compositions based on alkoxylated ether sulfate surfactants. The compositions address the problem of remaining fluid at high surfactant concentrations, without the need to add additives or solvents. The problem is solved by using starting alcohols with medium-size carbon chain length combined with the use of oxypropylene units, where branched starting alcohols containing 4 to 11 carbon atoms can be used. The compositions remain fluid at concentrations up to 90% while they are readily diluted. The surfactant compositions are prepared by sulfation of alkoxylated alcohols, followed by neutralisation with a neutralisation agent having a concentration of 25-50%. GB 2 168 095 discloses a method for recovering oil from an oil-bearing formation at high salinity, using an ether sulfate surfactant comprising a C10-C20 alkyl group and oxypropylene units. Core flood experiments are conducted using iso-tridecyl propoxy sulfates.

[0007] Whereas the use of alcohol ether sulphates containing ethylene-oxy/ethylenoxide units as ether groups is well known in personal care, washing and cleaning formulations as well as in industrial applications, for example as emulsifiers for emulsion polymerisation, ether sulphates containing propylene-oxy units are less familiar on the market. To date, only up to 40% solutions of alkali fatty alcohol (poly)propoxy sulphates are available in a convenient, i.e. flowable and pumpable, viscosity range, and no supply forms which dissolve both in water and in oils are known.

[0008] For use in industrial applications such as textile and leather auxiliary agents, metal working and lubricants, oil and gas field chemicals or tertiary oil recovery, surfactants or emulsifiers are required which exhibit a high emulsifying effect for various oils with water. Products with a high active content are required in order to keep the amount used and raw material and transport costs associated therewith as low as possible. The products should also be available in the form of flowable and pumpable material which is as homogenous as possible, as this is the simplest form of transporting, storing and dispensing them for use. The products should be essentially free of organic solvents and/or other viscosity reducers, have a low salt content, mix well with water and oils and be easily dilutable to the desired usage concentration. In addition, as low a pour point as possible is desirable which allows it to be used at low temperatures.

[0009] The aim of the present invention is to find a highly-concentrated form of salts of alkylpolyalkoxysulphates, which is flowable at least at room temperature (25°C), more particularly in the range from 10°C to 35°C, and is essentially free of organic solvents or other viscosity modifying additives, dissolves easily in both water and oils, can be easily diluted

and has a pour point considerably below -5°C and more particularly even below -15°C .

[0010] This objective was achieved by the subject of the independent claims. Surprisingly it was found that highly-concentrated alkylpolyalkoxysulphate compositions containing

- a) more than 75 % by weight, preferably more than 80% by weight salts of alkyl polyalkoxy sulphates, wherein the alkyl polyalkoxy sulphates have in average 3 to 20 alkoxy groups, at least 2/3 of all alkoxy groups of the alkyl polyalkoxy sulphates are propoxy groups and the alkyl residue is a fatty alcohol residue with 12 to 18 carbon atoms and
- b) 1 to below 25 % by weight water, preferably 1 to below 20 % by weight water, satisfy the above requirements.

[0011] Particularly preferred as salts of alkyl polyalkoxy sulphates are those in which - if present - the various alkoxy units are present in one molecule chain (and not only as a mixture of homoalkoxylates) and more particularly alkyl polypropoxy sulphates (also known in simplified form as (fatty) alcohol propoxy sulphates).

[0012] In contrast, fatty alcohol ethoxy sulphate pastes or fatty alcohol propoxy sulphates with smaller active contents are no longer flowable or pumpable or not easy to dilute or have higher pour points or are insoluble in oil or exhibit a combination thereof.

[0013] Preferred forms of embodiment form the subject matter of the sub-claims or are described below.

[0014] Suitable for use as fatty alcohols or fatty alcohol residues are linear or branched primary alcohols with 12 to 18 carbon atoms, preferably with 12 to 17, more particularly with 12 to 15 carbon atoms, and preferably more particularly mixtures containing at least more than 25 mol% branched primary alcohols.

[0015] Particularly suitable are the above fatty alcohols or alcohol residues with more than 40 mol% branched portions and very particularly fatty alcohols with on average at least one branch per molecule, more particularly (greater than 50 %) on the C2, C3 or C4 carbon atom, more particularly on the C2 carbon atom. The branching preferably has 1, 2, 3 and/or 4 carbon atoms.

[0016] The alkoxylation takes place with an average of 3 to 20 alkoxy groups, preferably 3 to 16 in accordance with the methods known to a person skilled in the art, whereby the alkoxyates can exhibit a conventional or a narrow homolog distribution. Contents of ethylene oxide groups or higher alkylene oxide such as butylene oxide groups are possible, if at least 2/3 of all alkoxy groups are propylene oxide. Particularly preferably the alkoxyate exclusively has 3 to 13, more particularly 4 to 10, propoxy groups.

[0017] The sulphation of the alcohol propoxylates can take place in a known manner for fatty alcohol ether sulphates with the usual methods, whereby the use of falling film reactors is preferred. As sulphation agents oleum, chlorosulphonic acid, amidosulphonic acid (sulfamic acid) or more particularly sulphur trioxide, for example, can be considered, whereby the latter is used diluted with an inert gas. The resulting sulphuric acid semi-ester is not stable and must therefore immediately be transferred into a neutralisation cycle in which it is converted, under high shear, with as highly concentrated aqueous alkali hydroxide as possible, more particularly 50% sodium hydroxide solution. In the preferred forms of embodiment the temperature during neutralisation is kept at 45 to 65°C , more particularly 50 to 60°C , at a pH value (related to 1 % of the product in water) of pH 10 and higher, more particularly at least 11 and higher, in order to avoid viscosity peaks in the medium concentration ranges.

[0018] The thus obtained highly-concentrated alcohol ether sulphate (salt) contains smaller portions of alcohols, propylene glycols (also sulphated) and alcohol propoxylates. The proportion of unsulphated material in the end product is typically 0 to 10 % by weight, preferably 0 to less than 5 % by weight. The content of alkyl polyalkoxy sulphate salts in accordance with the invention in the compositions is more than 75 % by weight, more particularly more than 80 % by weight, preferably more than 82 % by weight and more particularly up to 95 % by weight.

[0019] The obtained product can, but does not have to be mixed with commercially available preservatives and/or buffers in order to increase the stability to chemical decomposition and/or the stability to microorganisms in possibly diluted form. In a preferred form of embodiment 0.05 to 5% by weight, more particularly 0.1 to 2% by weight of citric acid is added to the product.

[0020] The compounds are used as an oil-soluble lubricant, e.g. in metal working, but more particularly as a surface active substance (surfactant) for deployment in improved or tertiary crude oil recovery. Together with the entrapped crude oil, the aqueous surfactant solution, which can also contain other components such as polymers, solvents, co-surfactants, salts, alkalisation agents, preserving agents, forms a micro-emulsion which is characterised by an extremely low interfacial tension and can thereby solubilise and mobilise the oil.

[0021] The flowability of a liquid phase depends on many external factors such as the temperature, the container, the pump and the viscosity. In connection with the invention flowable means that at a temperature of 25°C and a shear rate of $D=10\text{s}^{-1}$ the composition has a viscosity of less than 10000 mPas, preferably even less than 5000 mPas. The viscosity can be determined with the aid of commercially available measuring devices such as rotational viscometers or rheometers with cone/plate measuring geometry in accordance with DIN 53019.

[0022] The oil solubility of the compound in accordance with the invention is preferably at least 5 % by weight in paraffin

oil (e.g. Merkur® WOP 100 PB) or mineral oil (e.g. Shell Gravex® 915), whereby at 25°C gentle stirring results in a clear solution.

[0023] To determine the dilutability, at room temperature (25°C) the product is mixed with water at such a ratio that a 20% by weight solution (anionic active substance) is produced. If this can take place in a glass beaker through manual stirring with a spatula or glass rod without passing through highly viscous states which can no longer be stirred and therefore mixed by hand the product is by definition easily dilutable. If not, the product cannot be easily diluted in water.

[0024] In connection with this invention the pour point means that (in accordance with ASTM D97-09) the product is cooled in 3°C steps. If after 10 minutes at this temperature it does not flow within 5 seconds of tilting the container into the horizontal, the 3°C higher value is taken as the pour point.

Example 1

[0025] A branched primary C12/C13 alcohol (ISALCHEM® 123) with on average 8 propoxy groups was sulphated in a continuous sulphation apparatus.

[0026] Raw material: ISALCHEM® 123 + 8 PO (OH number: 83.2 mg KOH/g, water: 0.03%, molecular weight: 674.3 g/mol). At a V₂O₅ catalyst gaseous SO₂ was converted to SO₃ at high temperature. The gas was cooled and diluted with air (dew point -60°C). The proportion of SO₃ in the air was 7% by volume.

[0027] In a falling film reactor with distributors the propoxylated alcohol was made to react with the SO₃/air mixture. The reaction gas flows through the falling film reactor at high speed and generates high turbulences on contact with the propoxylated alcohol. This resulted in an intensive exchange of substances. Intensive cooling of the falling film reactor ensures the removal of the reaction heat. Gas/liquid separation was carried out at the outlet of the falling film reactor. The fluid phase is taken for neutralisation, the gaseous phase for exhaust gas treatment.

[0028] The product is pumped around in a neutralisation circuit with the appropriate neutralisation medium. A pH value regulator adds the appropriate quantity of alkaline components, in this case aqueous NaOH, 50% by weight. At the same time the product is homogenised in the circuit through a very highly shearing mixer tool. The finished product was removed continuously from the neutralisation circuit. 0.1% by weight citric acid was added to the finished product.

[0029] The conversion parameters were as follows:

Temperature in the converter:	450°C
SO ₃ concentration in the reaction gas:	7% by volume
Molar ratio propoxylate/SO ₃ :	SO ₃ in excess
Quantity used (propoxylate):	3.9 kg/hour
hydroxyl number material used:	83.2 mg KOH/g
Temperature at the lower outlet of the falling film reactor:	25 - 30°C
Theoretical acid number, sulphuric acid semi-ester:	74.4 mg KOH/g
Actual acid number, sulphuric acid semi-ester	94 mg KOH/g
Temperature neutralisation circuit:	55-60°C

[0030] A product with the following composition was obtained:

Anionic active substance	90 +/- 1 % by weight (DIN ISO 2271)
Unsulphated material (non-ionic substance):	< 1% by weight% (DIN EN 13273)
Na ₂ SO ₄ :	0.55% by weight
Free alkali:	0.01% by weight
Water:	around 10% by weight

with the following properties:

pH 1% in water:	9.3
Pour point:	-24 °C
5 % tel quel in paraffin oil:	clearly soluble
5 % t.q. in mineral oil:	clearly soluble
Viscosity (in mPas, at pH > 11.25 °C und 10 s ⁻¹):	1100

Other examples

[0031] In an analogue manner to example 1 a branched primary C14/C15 alcohol (ISALCHEM® 145) with on average 8 propoxy groups, a partially branched primary C14/C15 alcohol (LIAL® 145) with on average 3.8 PO (propoxy) groups, a partially branched primary C14/C15 alcohol (LIAL® 145) with on average 9.8 PO groups, a partially branched primary C12/C13 alcohol (SAFOL® 23) with on average 6.5 PO groups, a partially branched primary C12/C13 alcohol (SAFOL® 23) with on average 12.5 PO groups, a partially branched primary C16/C17 alcohol (LIAL® 167) with on average 4 PO groups, a linear C12 alcohol with on average 12.8 PO groups and a linear C12/C14 alcohol with on average 4 PO groups were converted to the corresponding alcohol propoxy sulphate salts. The obtained compounds and properties are out in table 1 below.

[0032] Comparative examples (not in accordance with the invention):

ISALCHEM™ 123+8PO SO₃Na anionic active 26.7% by weight, unsulphated material 2.6% (calculated on 100% by weight active): not clearly soluble in mineral oil and paraffin oil, pour point -6 °C.

ISALCHEM™ 145+8PO SO₃Na anionic active 33.3 % by weight, unsulphated material 9.4% (calculated on 100% by weight active): not clearly soluble in mineral oil and paraffin oil, pour point +3°C.

MARLINAT™ 242/70 (C12C14+2EO SO₃Na anionic active 70 % by weight): not clearly soluble in mineral oil and paraffin oil, not easily dilutable.

SAFOL™ 23 2EO SO₃Na anionic active 70 wt. %: not clearly soluble in mineral oil and paraffin oil, not easily dilutable.

ALFOL™ 1218 7EO (narrow range) SO₃Na high active (> 75 wt. % anionic active matter): viscosity at 25 °C /10s⁻¹ > 20000mPas, not easily dilutable

Table 1

	ISALCHEM 145+8 PO SO ₃ Na	LIAL 145+3.8 PO SO ₃ Na	LIAL 145+9.8 PO SO ₃ Na	SAFOL 23+6.5 PO SO ₃ Na	SAFOL 23+12.5 PO SO ₃ Na	Linear C12+12.8 PO SO ₃ Na	Linear C12C14+4 PO SO ₃ Na
Anionic active substance, a- WAS (% by weight)	89.2	89.3	83.0	89	83	89	80
Unsulphated material (% by weight)	2.1	2	9	1	3	7	<1
Na ₂ SO ₄ (% by weight)	0.6	0.4	0.6	0.3	0.3	0.5	0.3
Free alkali (% by weight)	0.04	0.04	0.7	0.1	0.1	0.1	1.6
Water (% by weight)	8.1	10.6	8	8	6	6	17
pH 1 % in water	9.5	9.5	11.1	10.1	9.9	9.1	11.6
Pour point (°C)	-21	-18	-21	< -24	< -24	< -24	n.d.
5 % t.q. in mineral oil	Clear	Clear	Clear	Clear	Clear	Clear	Clear
Viscosity(mPas, at pH >11,25 °C and 10 s ⁻¹)	1300	1600	1200	1000	1200	1050	9000
Easily dilutable	Yes	Yes	Yes	Yes	Yes	Yes	Yes

Claims

1. Highly-concentrated alkyl polyalkoxy sulphate composition, flowable at least at 25°C, containing

- 5 a) more than 75 % by weight salts of alkyl polyalkoxy sulphates, whereby the alkyl polyalkoxy sulphates have in average 3 to 20 alkoxy groups, at least 2/3 of all alkoxy groups of the alkyl polyalkoxy sulphates are propoxy groups and the alkyl residue is a fatty alcohol residue with 12 to 18 carbon atoms and
b) 1 to below 25 % by weight water,
wherein flowable means having a viscosity of below 10000 mPas measured in accordance with DIN 53019 at
10 25°C and with a shear rate of $D = 10s^{-1}$.

2. Composition in accordance with claim 1, whereby the fatty alcohol residue has 12 to 17 und more particularly 12 to 15 carbon atoms.

15 3. Composition in accordance with claim 1 or 2, wherein the fatty alcohol residue is present in the form of a mixture containing branched fatty alcohol residues, preferably more than 40 mol % branched fatty alcohol residues.

4. Composition in accordance with claim 3, wherein more than 50% of the branches are arranged on the C2 carbon atom.

20 5. Composition in accordance with at least one of the preceding claims, wherein the alkoxy groups of the alkyl polyalkoxy sulphate salts are exclusively propoxy groups, namely in average 3 to 13 propoxy groups, more particularly in average 4 to 10 propoxy groups.

25 6. Composition in accordance with at least one of the preceding claims, wherein the proportion of the salts of the alkyl polyalkoxy sulphates is greater than 80 to 95 % by weight.

7. Composition in accordance with at least one of the preceding claims, wherein the proportion of water is 5 to 18 % by weight.

30 8. Composition in accordance with at least one of the preceding claims, wherein the salts are sodium and/or potassium salts.

9. Composition in accordance with at least one of the preceding claims with a pour point of less than -5°C, preferably -15°C.

35 10. Composition in accordance with at least one of the preceding claims also containing 0.05 to 5 % by weight, in particular 0.1 to 2 % by weight, buffers.

40 11. Composition in accordance with at least one of the preceding claims containing

- a) 0 to 10 % by weight, more particularly 0 to less than 5 % by weight non-ionic substance in accordance with DIN EN 13273:2001 and/or.
b) less than 8 % by weight, more particularly less than 4 % by weight other ionic substances.

45 12. Composition in accordance with at least one of the preceding claims comprising less than 5 weight % of compounds not mentioned in any of claims 1 to 9.

50 13. Method of producing the composition in accordance with at least one of the preceding claims comprising at least the following steps:

- in a falling film reactor an alkoxyated fatty alcohol is reacted with SO_3 , wherein the alkoxyated fatty alcohol has in average 3 to 20 alkoxy groups, at least 2/3 of all alkoxy groups of the alkyl polyalkoxy sulphates are propoxy groups and the alkyl residue is a fatty alcohol residue with 12 to 18 carbon atoms, and
- gas/liquid separation takes place and the liquid phase is neutralised with an alkali hydroxide in aqueous solution
55 comprising more than 25 weight% alkali hydroxide.

14. Method in accordance with claim 13 comprising one or more of the following process steps:

- a) the conversion takes place with SO_3 at 20 to 60°C, more particularly at 25 to 40°C.
- b) the neutralisation takes place at 30 to 70°C, more particularly at 50 to 60°C, and preferably with alkali hydroxides with an aqueous proportion of less than 55 % by weight, more particularly sodium hydroxide or potassium hydroxide;
- c) on completion of the neutralisation a pH of greater than 10, preferably greater than or equal to 11 is set;
- d) an SO_3 /air mixture with 3 to 10 % by weight SO_3 is used;
- e) the alkoxylated fatty alcohol has exclusively proxy groups, namely in average 3 to 13 propoxy groups more particularly in average 4 to 10 propoxy groups.

15. Use of the composition in accordance with at least one of claims 1 to 12, optionally after dilution and further additions, in supporting crude oil extraction, in particular improved or tertiary crude oil recovery.

Patentansprüche

1. Hochkonzentrierte zumindest bei 25°C fließfähige Alkylpolyalkoxysulfat - Zusammensetzung enthaltend

a) größer 75 Gew.% Salze von Alkylpolyalkoxysulfaten, wobei die Alkylpolyalkoxysulfate im Mittel 3 bis 20 Alkoxygruppen aufweisen, zumindest 2/3 aller Alkoxygruppen der Alkylpolyalkoxysulfate Propoxy-Gruppen sind und der Alkylrest ein Fettalkoholrest mit 12 bis 18 Kohlenstoffatome ist und

b) 1 bis 25 Gew.% Wasser,
wobei fließfähig eine Viskosität von geringer als 10000 mPas bedeutet, gemessen gemäß DIN 53019 bei 25°C und mit einer Scherrate von $D = 10 \text{ s}^{-1}$.

2. Zusammensetzung gemäß Anspruch 1, wobei der Fettalkoholrest 12 bis 17 und insbesondere 12 bis 15 Kohlenstoffatome aufweist.

3. Zusammensetzung gemäß Anspruch 1 oder 2, wobei der Fettalkoholrest in Form einer Mischung enthaltend verzweigte Fettalkoholreste vorliegt, vorzugsweise größer 40 mol% verzweigte Fettalkoholreste.

4. Zusammensetzung gemäß Anspruch 3, wobei größer als 50% der Verzweigungen am C2- Kohlenstoff-Atom angeordnet sind.

5. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche, wobei die Alkoxygruppen der Salze von Alkylpolyalkoxysulfaten ausschließlich Propoxygruppen sind, nämlich im Mittel 3 bis 13 Propoxygruppen sind, insbesondere im Mittel 4 bis 10.

6. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche, wobei der Anteil der Salze der Alkylpolyalkoxysulfate größer als 80 bis 95 Gew.% beträgt.

7. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche, wobei der Anteil des Wassers 5 bis 18 Gew.% beträgt.

8. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche, wobei die Salze Natrium- und/oder Kaliumsalze sind.

9. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche mit einem Pourpoint kleiner -5°C, vorzugsweise -15°C.

10. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche enthaltend weiterhin 0,05 bis 5 Gew.%, insbesondere 0,1 bis 2 Gew.%, Puffer.

11. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche enthaltend

a) 0 bis 10 Gew.%, insbesondere 0 bis kleiner als 5 Gew.%, nicht-ionische Substanzen gemäß DIN EN 13273:2001 und/oder

b) weniger als 8 Gew.%, insbesondere weniger als 4 Gew.%, andere ionische Substanzen.

12. Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche enthaltend weniger als 5 Gew.% Verbindungen, die in einem der vorhergehenden Ansprüche 1 bis 9 nicht genannt sind.

13. Verfahren zur Herstellung der Zusammensetzung gemäß zumindest einem der vorhergehenden Ansprüche umfassend zumindest folgende Schritte:

- in einem Fallfilmreaktor wird ein alkoxylierter Fettalkohol mit SO_3 zur Reaktion gebracht, wobei der alkoxylierte Fettalkohol im Mittel 3 bis 20 Alkoxygruppen hat, mindestens 2/3 aller Alkoxygruppen des Alkylpolyalkoxysulfats Propoxygruppen sind und der Alkylrest ein Fettalkoholrest mit 12 bis 18 Kohlenstoffatomen ist, und
- eine Gas- / Flüssigkeitstrennung erfolgt und die flüssige Phase wird mit wässrigem größer 25 Gew.%igem Alkalihydroxid neutralisiert.

14. Verfahren gemäß Anspruch 13, umfassend einen oder mehrere der folgenden Prozessschritte:

- a) die Umsetzung erfolgt mit SO_3 bei 20 bis 60°C, insbesondere bei 25 bis 40°C;
- b) die Neutralisation erfolgt bei 30 bis 70°C, insbesondere bei 50 bis 60°C, und vorzugsweise mit Alkalihydroxiden mit einem Wasseranteil von kleiner 55 Gew.%, insbesondere Natriumhydroxid oder Kaliumhydroxid;
- c) mit Abschluss der Neutralisation wird ein pH von größer 10, vorzugsweise größer oder gleich 11, eingestellt;
- d) ein SO_3 /Luftgemisch mit 3 bis 10 Gew.% SO_3 wird eingesetzt;
- e) der alkoxylierte Fettalkohol hat ausschließlich Propoxygruppen, nämlich im Durchschnitt 3 bis 13 Propoxygruppen, insbesondere im Mittel 4 bis 10 Propoxygruppen.

15. Verwendung der Zusammensetzung gemäß zumindest einem der Ansprüche 1 bis 12, ggf. nach Verdünnung und weiterer Additivierung in der Unterstützung der Erdölförderung, insbesondere der verbesserten oder tertiären Erölförderung.

Revendications

1. Composition de sulfates d'alkylpolyalcoxy très concentrés, doués d'écoulement au moins à 25°C, contenant :

- a) plus de 75 % en poids de sels de sulfates d'alkylpolyalcoxy, moyennant quoi les sulfates d'alkylpolyalcoxy ont en moyenne 3 à 20 groupes alcoxy, au moins 2/3 de tous les groupes alcoxy des sulfates d'alkylpolyalcoxy sont des groupes propoxy et le résidu alkyle est un résidu d'alcool gras ayant 12 à 18 atomes de carbone et
 - b) 1 à moins de 25 % en poids d'eau,
- dans laquelle doué d'écoulement signifie avoir une viscosité inférieure à 10 000 mPas, mesurée conformément à la norme DIN 53019 à 25°C et à un taux de cisaillement de $D = 10 \text{ s}^{-1}$.

2. Composition selon la revendication 1, moyennant quoi le résidu d'alcool gras possède 12 à 17 et plus particulièrement 12 à 15 atomes de carbone.

3. Composition selon la revendication 1 ou 2, dans laquelle le résidu d'alcool gras est présent sous la forme d'un mélange contenant des résidus d'alcool gras ramifiés, de préférence plus de 40 % en moles de résidus d'alcool gras ramifiés.

4. Composition selon la revendication 3, dans laquelle plus de 50 % des ramifications sont disposées sur l'atome de carbone C2.

5. Composition selon au moins l'une des revendications précédentes, dans laquelle les groupes alcoxy des sels de sulfate d'alkylpolyalcoxy sont exclusivement des groupes propoxy, notamment en moyenne 3 à 13 groupes propoxy, plus particulièrement en moyenne 4 à 10 groupes propoxy.

6. Composition selon au moins l'une des revendications précédentes, dans laquelle la proportion de sels de sulfates d'alkylpolyalcoxy est supérieure à 80 à 95 % en poids.

7. Composition selon au moins l'une des revendications précédentes, dans laquelle la proportion d'eau est de 5 à 18 % en poids.

8. Composition selon au moins l'une des revendications précédentes, dans laquelle les sels sont des sels de sodium et/ou de potassium.

9. Composition selon au moins l'une des revendications précédentes ayant un point d'écoulement inférieur à -5°C, de préférence -15°C.

10. Composition selon au moins l'une des revendications précédentes, contenant aussi 0,05 à 5 % en poids, en particulier 0,1 à 2 % en poids de tampons.

11. Composition selon au moins l'une des revendications précédentes contenant

a) 0 à 10 % en poids, plus particulièrement 0 à moins de 5 % en poids d'une substance non ionique d'après la norme DIN EN 13273 :2001 et/ou

b) moins de 8 % en poids, plus particulièrement moins de 4 % en poids d'autres substances ioniques.

12. Composition selon au moins l'une des revendications précédentes comprenant moins de 5 % en poids de composés non mentionnés dans l'une quelconque des revendications 1 à 9.

13. Procédé de production de la composition selon au moins l'une des revendications précédentes, comprenant au moins les étapes suivantes :

- dans un réacteur à film tombant, un alcool gras alcoxylé est mis à réagir avec du SO₃, où l'alcool gras alcoxylé a en moyenne 3 à 20 groupes alcoxy, au moins 2/3 de tous les groupes alcoxy des sulfates d'alkylpolyalcoxy sont des groupes propoxy et le résidu alkyle est un résidu d'alcool gras ayant 12 à 18 atomes de carbone, et
- la séparation gaz/liquide a lieu et la phase liquide est neutralisée avec un hydroxyde alcalin en solution aqueuse comprenant plus de 25 % en poids d'hydroxyde alcalin.

14. Procédé selon la revendication 13, comprenant une ou plusieurs des étapes de procédé suivantes :

- a) la conversion a lieu avec du SO₃ à une température de 20 à 60°C, plus particulièrement 25 à 40°C,
- b) la neutralisation a lieu à une température de 30 à 70°C, plus particulier 50 à 60°C, et de préférence avec des hydroxydes alcalins ayant une proportion aqueuse inférieure à 55 % en poids, plus particulièrement de l'hydroxyde de sodium ou de l'hydroxyde de potassium ;
- c) à l'issue de la neutralisation, un pH supérieur à 10, de préférence supérieur ou égal à 11 est ajusté ;
- d) un mélange SO₃/air ayant 3 à 10 % en poids de SO₃ est utilisé ;
- e) l'alcool gras alcoxylé possède exclusivement des groupes propoxy, notamment en moyenne 3 à 13 groupes propoxy, plus particulièrement en moyenne 4 à 10 groupes propoxy.

15. Utilisation de la composition selon au moins l'une des revendications 1 à 12, éventuellement après dilution et autres additions, dans l'assistance à l'extraction du pétrole brut, en particulier la récupération améliorée ou tertiaire du pétrole brut.

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- EP 0167337 A [0006]
- GB 2168095 A [0006]