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(21) International Application Number: PCT/GB00/00841 (22) International Filing Date: 13 March 2000 (13.03.00) (30) Priority Data: 9905668.1 12 March 1999 (12.03.99) GB (71) Applicant (for all designated States except US): THE COURT OF NAPIER UNIVERSITY [GB/GB]; Merchiston Tower, 10 Colinton Road, Edinburgh EH10 5DT (GB). (72) Inventor; and (75) Inventor/Applicant (for US only): OLDFIELD, Christopher [GB/GB]; 82 Gateside Avenue, Haddington, East Lothian EH41 38D (GB). (74) Agent: MURGITROYD & COMPANY; 373 Scotland Street, Glasgow G5 8QA (GB).		(81) Designated States: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CR, CU, CZ, DE, DK, DM, 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, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, TZ, UA, UG, US, UZ, VN, YU, ZA, ZW, ARIPO patent (GH, GM, KE, LS, MW, SD, SL, SZ, TZ, UG, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Published <i>Without international search report and to be republished upon receipt of that report.</i>
(54) Title: A METHOD FOR THE EXTRACTION OF OIL BY MICROEMULSIFICATION (57) Abstract The invention provides a method for the removal of oil from oil-contaminated solid wastes such as drilling muds, of fractions thereof, by mixing the preparation with an aqueous surfactant preparation such that the oil is extracted as an oil-in-water (O/W) microemulsion. The microemulsion and solids phases can be separated by a suitable technique such as centrifugation; residual O/W microemulsion can be removed by an aqueous rinse. The oil can be recovered from the O/W micro emulsion by suitable techniques including, but not limited to, temperature-induced phase-separation.		

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1 **A METHOD FOR THE EXTRACTION OF OIL BY**
2 **MICROEMULSIFICATION**

3
4 This invention relates to a method for the extraction
5 of oil by microemulsification and in particular to a
6 method for the extraction of contaminating oil from
7 solids such as waste drilling muds.

8
9 Drilling muds are used as lubricants and stabilisers in
10 the drilling of wells as part of the oil winning
11 operation. There are a large number of different
12 formulations, but they can be subdivided into just two
13 groups, those based on water and those based on oil.
14 Water based muds use water with a potassium chloride
15 KCl) content of 75% weight (wt) and various silicates
16 comprising 25%. Ethylene glycol is often added,
17 together with other viscosifiers, to 3-5% wt. These
18 closely resemble oil-based muds in terms of their
19 measurable characteristics but in the field they are
20 distinctly lacking in performance when compared to oil

1 based muds. In particularly difficult drilling
2 situations, e.g. horizontal (as opposed to vertical)
3 drilling as practised in the North Sea, water based
4 muds cannot be used.

5

6 Oil-based muds are superior to water-based muds and are
7 used where drilling is difficult. For example, oil-
8 based muds are used exclusively in North sea oil-
9 winning operations, as a consequence of the practice of
10 horizontal drilling.

11

12 Oil-based muds consist of an oil, which may be of
13 mineral or synthetic origin, plus a detergent plus
14 variable amounts of colloidal clay (e.g. bentonite).
15 During drilling mud is pumped continuously to the drill
16 head. The oil itself lubricates and cools the drilling
17 bit, whilst the colloidal clays act as wall-building
18 agents, acting to stabilise the walls of the well. Mud
19 returning to the surface carries with it the rock
20 cuttings, which can be shale, sandstone or limestone,
21 depending on the character of the rock formation being
22 drilled. At the surface, the used mud is separated
23 into mud- and cuttings- fractions either by
24 centrifugation or by passage through a shale-shaker (a
25 vibrating wire mesh screen) which retains particulates
26 of diameter >100 micrometers, approx. The mud fraction
27 is recycled. The cuttings fraction, which may contain
28 up to 25% weight oil, is disposed of.

29

1 In the United Kingdom, The Brown Book (Department of
2 Trade and Industry - DTI - energy report for oil and
3 gas resources in the UK) states that roughly 350 wells
4 are drilled in the North Sea every year and each
5 produces an average of 300 tonnes of waste drilling
6 mud. Accordingly, it can be estimated that 105,000
7 tonnes of waste drilling mud are produced each year and
8 around 20,000 tones of drill cuttings are brought
9 ashore per annum for treatment.

10

11 Disposal of cuttings fraction causes problems. For
12 example, historically, in the North Sea, the cuttings
13 fraction has been dumped overboard, where it has
14 accumulated in piles at the base on the drilling
15 platform. The UKOOA (UK Offshore Operators
16 Association) estimates that to date between 1 and 1.5
17 million tonnes of cuttings currently lie on the sea bed
18 in the central and northern UK Continental Shelf (UKCS)
19 containing almost 70,000 tonnes of oil. Although this
20 practice dates back to the beginnings of North Sea oil-
21 winning operations, recent research has shown that the
22 material has a severe destabilising effect on the
23 benthic ecosystem due to the slow leaching of
24 hydrocarbons from the piles into the ocean environment.
25 Contrary to prior expectation, biodegradation of the
26 hydrocarbon fraction within the piles does not occur,
27 and it is now clear that this is due to the anaerobic
28 nature of the piles; biodegradation of hydrocarbons is
29 a strictly oxygen-requiring (aerobic) process.

1 The UKOOA has categorised the effects on the benthic
2 environment into four zones as follows:

3

4 1 Within the pile, typically with a footprint up to
5 50m, the natural fauna is absent. Recent studies
6 have discovered unusual species, normally found
7 around hydrothermal vents and natural oil seeps,
8 which have colonised cutting piles.

9

10 2 Typically, within 500m of the installation there
11 is an area of impoverished and highly modified
12 biological communities, characterised by
13 "opportunistic" species which can exploit these
14 conditions.

15

16 3 A "transition zone" within which the biological
17 communities return to normal, usually within 2km
18 of the installation.

19

20 4 A wider area within which chemical contamination
21 can be detected, although biological communities
22 appear normal.

23

24 As a consequence new legislation, limiting the oil-
25 content of cuttings dumped overboard to a maximum of 1%
26 wt (OSPAR Commission - Paris Commission Decision 92/2)
27 was introduced in 1996. It was also decided that whole
28 oil based muds should not be dumped or discharged at
29 sea.

30

1 Until the present time, a convenient rig-based
2 technology to achieve this does not exist.
3 Current remediation practices involve shipping the
4 cuttings fraction for treatment on-shore. These
5 treatments can be summarised as follows:

6
7 Land-farming: Land-farming is practised in countries
8 such as Canada and Norway. Natural microbial action in
9 the aerobic terrestrial environment leads to the
10 oxidation of residual hydrocarbon to carbon dioxide
11 (and water). This is a slow, land-intensive process
12 and is not an option for densely-populated countries
13 such as the UK.

14
15 Incineration: The possibility of high-temperature
16 incineration has been investigated in the past.
17 Incineration requires maintenance of extremely high
18 temperatures (up to around 750°C) in order to ensure
19 complete combustion and is correspondingly power-
20 intensive. As a consequence incineration is not
21 regarded as economical.

22
23 Distillation: The cuttings are heated in an oven to
24 around 350°C removing oil to around 0.5% by weight.
25 This is currently the most viable technology with three
26 plants operating in the UK, together treating most of
27 the 20,000 tonnes brought ashore. The process is
28 nevertheless energy intensive.

29

1 Solvent-extraction: This process is a modification of
2 distillation involving mixing of the waste with an
3 hydrocarbon solvent followed by the removal of the
4 hydrocarbon mixture by distillation. The process is
5 energy intensive and utilises considerable volumes of
6 organic solvent.

7
8 Microwave Assisted Processes: Microwave-assisted
9 extraction is a modification of the solvent extraction
10 process. Solvents in contact with a solid sample are
11 exposed to microwave energy to partition compounds from
12 the sample matrix into the solvent. The technology is
13 a direct descendent of closed-vessel microwave acid
14 digestions and solvent extractions. The two concepts
15 have been united, with the kinetics driven by elevated
16 temperatures and enabling extractions with reduced
17 volumes of solvent. Again this system is power and
18 energy intensive and is not regarded as economical.

19
20 Rig-based processing is desirable over land based
21 processing because it eliminates the costs associated
22 with transport to shore, since cleaned cuttings may be
23 disposed of. A viable rig-based technology for
24 cuttings remediation must reduce the residual
25 hydrocarbon (oil) content below 1% weight. The
26 infrastructure to support it must also conform to size,
27 weight- and power-requirements, and safety
28 considerations, commensurate with rig-operation. For
29 these reasons none of the process options listed above
30 are transferable to the rig environment.

1 The application of microemulsion systems for the
2 remediation of waste drilling muds is already known in
3 the art. PCT/GB098/02217 teaches that treatment of
4 waste drilling mud samples with a water-in-oil (w/o)
5 microemulsion preparation can reduce the residual oil
6 content to 3% wt.

7
8 The use of microemulsions is known in tertiary oil
9 recovery. In tertiary oil recovery, surfactant are
10 introduced to generate ultralow surface tensions to
11 displace oil from solid rock capillaries in nearly-
12 exhausted oil-wells. The surfactants are not employed
13 to remove contaminating oil from aggregate or solide
14 phases such as waste drilling muds. In tertiary oil
15 recovery, the oil is ultimately recovered as a water-
16 in-oil microemulsion. Similarly, microemulsions are
17 also employed in another subterranean application for
18 the extraction of tar sand.

19
20 An object of the invention is to overcome the problems
21 of the prior art.

22
23 A further object of the invention is to provide a
24 method for the extraction of contaminating oil from
25 solids such as waste drilling muds.

26
27 According to the invention there is provided a method
28 for the extraction of oil from a solid by
29 microemulsification comprising the steps of mixing an
30 oil-contaminated solid with a water-based solution of a

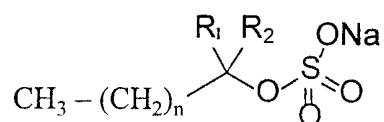
1 surfactant to form an oil-in-water (o/w) microemulsion
 2 and separating the o/w microemulsion and solid phases.

3

4 The invention also extends to a method for removing oil
 5 from drilling and mud wastes, or oil-contaminated
 6 fractions thereof, comprising the steps (1) of mixing
 7 the oil-contaminated material with a water-based
 8 solution of a surfactant which forms an oil-in-water
 9 (o/w) microemulsion; such that the oil is extracted as
 10 an o/w microemulsion; (2) of separating the o/w
 11 microemulsion and solids phases by an appropriate
 12 technique; and (3) of finally rinsing the solids with
 13 water or aqueous salts solution to remove residual o/w
 14 microemulsion.

15

16 The invention also provides a surfactant having the
 17 general formula:



18

19

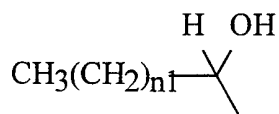
20 wherein

21

22 $\text{R}_1 = -\text{H}$ or $-\text{CH}_3$

23

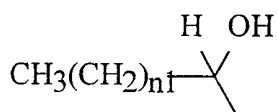
24 $\text{R}_2 =$



1 where $n1$ may take any value as long
 2 as, $n1 < n$

3

4 $R_1 = R_2 =$



5

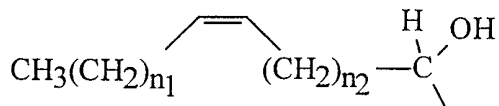
6 where $n1$ may take any value as long as
 7 $n1 < n$, or

8

9 $R_1 = -\text{H}$ or $-\text{CH}_3$

10

11 $R_2 =$



12

13 where $n1$ and $n2$ may take any value, as
 14 long as $(n1 + n2) < n$, or

15

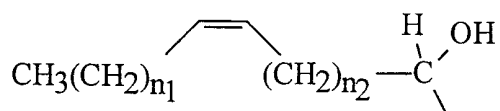
16

17

18

19

20 $R_1 = R_2 =$



21

1 where n_1 and n_2 may take any value, as
2 long as $(n_1 + n_2) < n$

3
4 Surprisingly, the applicants have found that the oil-
5 in-water microemulsion phase in a microemulsion
6 facilitates the highly effective extraction of oil from
7 oil contaminated solids. Extraction can be achieved
8 to levels below 1% which provides a significantly
9 greater efficacy than that which could be achieved with
10 water-in-oil microemulsions or by continuous rounds.
11 Similarly, such levels of efficiency cannot be achieved
12 with conventional emulsions.

13 The use of the oil-in-water phase within oil/water
14 systems facilitates the encapsulation of oil within the
15 system by the surfactant to eliminate contact between
16 the solid surface of the solid phase and the oil to
17 facilitate extractions of the oil. Accordingly,
18 although the applicants do not wish to be bound by a
19 theorem, it is believed that encapsulation of the oil
20 as opposed to mere reduction in surface tension
21 facilitates highly efficient extractions in accordance
22 with the method of the present invention.

23
24 The method of the present invention therefore
25 facilitates efficient extraction of oil employing oil-
26 in-water microemulsions by ensuring that extraction is
27 effected in the oil-in-water microemulsion phases of
28 the oil/water system.

29

1 For example, the applicants have found that where
2 extractions are attempted in the bicontinuous realm of
3 the system, oil within the system is re-exposed to
4 solids thereby preventing extraction.

5
6 As will be appreciated by those skilled in the art, the
7 oil-in-water microemulsion extraction is controllable
8 by adjusting the ratios of water: oil: surfactant and,
9 if necessary, co-surfactant and flocculant as required.
10 The ratios can be determined by assessing the oil
11 content of the material to be extracted and adjusting
12 the relative proportions of the components of the oil-
13 in-water system to ensure that extraction is effected
14 in oil-in-water microemulsion phase.

15
16 This invention therefore provides a method for the
17 remediation of waste drilling muds generated during
18 oil-winning operations. The process of the invention
19 relates to the removal of the oil from the particulate
20 solid fraction. The residual oil content of the
21 solids can be reduced to less than 1% by weight.
22 Accordingly, the solids treated according to the method
23 of the invention can be rendered harmless and can be
24 disposed of by dumping at sea or land-filling. As
25 described further below, solids such as waste muds
26 treated in accordance with the method of the invention
27 are treated with an aqueous surfactant solution such
28 that the oil is extracted as an oil-in-water (o/w)
29 microemulsion.

30

1 The invention provides a method for the removal of the
2 oil-component from cuttings which can be adapted for
3 use in the rig environment, and hence permit direct
4 overboard dumping of the cuttings. The process of the
5 invention can be adapted for the on or offshore
6 treatment of cuttings recovered from the sea bed.

7
8 Herein is described a process for the extraction of
9 oils from oil-contaminated solids, including waste
10 drill mud cuttings. The method involves washing the
11 cuttings at ambient temperature with an aqueous
12 solution of a surfactant solution, the surfactant being
13 one of the set of so-called microemulsion-forming
14 surfactants. Specifically, the detergent preparations
15 used in this process are capable of spontaneously
16 absorbing oils, forming so called oil-in-water (o/w)
17 microemulsions.

18 An oil-in-water microemulsion is defined as a
19 thermodynamically stable, single-phase mixture of oil,
20 water and surfactant, such that the continuous phase is
21 water (which may contain dissolved salts) and the
22 dispersed phase consists of a monodispersion of oil
23 droplets, each coated with a close-packed monolayer of
24 surfactant molecules. The inherent thermodynamic
25 stability arises from the fact that, due to the
26 presence of the surfactant monolayer, there is no
27 direct oil-water contact. Oil-in-water microemulsions
28 are often optically transparent.

29

1 The formation of an oil-in-water microemulsion is
2 critical to the present invention. A fundamental
3 distinction exists between microemulsions and ordinary
4 emulsions. Emulsions and microemulsions are similar
5 only in the superficial sense that they can be
6 described as mixtures of oil, water and an amphipathic
7 substance, usually called a surfactant.

8

9 Microemulsions by definition are thermodynamically
10 stable, that is, for a particular composition (type and
11 amount of each component), and a particular
12 temperature, the microemulsion regimen is preferred
13 over a system of separate phases of oil, water and
14 surfactant. The corollary of this argument is that
15 microemulsions form spontaneously when their
16 constituents are mixed together. Once formed,
17 microemulsions remain so (characterised macroscopically
18 as transparent single phases), unless some property is
19 changed. For example, increasing or decreasing the
20 temperature beyond certain limits, leads to phase
21 separation.

22

23 Emulsions, by contrast, are not thermodynamically
24 stable. Emulsions form only by input of mechanical
25 energy (e.g. by shaking or sonication), and the
26 emulsion regimen can only be maintained by continuous
27 input of energy; when energy input is withdrawn the
28 emulsion phase separates, yielding distinct oil- and
29 water phases (the surfactant is distributed between the
30 two phases, or sometimes exists as a third phase).

1 There is no temperature at which such systems form
2 microemulsions.

3

4 Microemulsions form because the surfactants form a
5 close-packed monolayer at the oil-water interface,
6 which effectively excludes direct oil-water contact.
7 The corollary of this argument is that surfactants may
8 not stabilise microemulsions if they cannot saturate an
9 oil-water interface. Typically, these surfactants only
10 partially coat the interface, leaving uncoated areas
11 exposed to bulk continuous phase solvent.

12

13 For example, water-continuous emulsions typically
14 consist of oil droplets only partially covered with
15 surfactant; the uncoated surfaces are therefore
16 directly exposed to the continuous aqueous phase. This
17 is thermodynamically unfavourable; droplets aggregate
18 by coalescing at their exposed surfaces, increasing the
19 surface area : volume ratio and hence minimising oil :
20 water contact. The outcome of extensive droplet
21 coalescence is bulk-phase separation.

22 In microemulsions there are no uncoated surfaces;
23 therefore there is no driving force for phase-
24 separation.

25

26 The rate of phase separation of an emulsion can
27 actually be relatively slow; emulsions can be created
28 which only completely phase separate after several
29 weeks. Nevertheless the fundamental distinction between
30 emulsions and microemulsions remains. Indeed, the

1 interesting properties of microemulsions, both in
2 general and in the context of the specific application
3 described here, arises from the thermodynamic
4 properties arising from total oil:water exclusion
5 arising from interfacial close-packing of surfactants.

6
7 Apparent from gross physical differences, which can be
8 determined by visual examination (microemulsions show
9 no tendency to phase separate and are usually
10 transparent, whereas emulsions are opalescent or turbid
11 and inevitably phase-separate), the two can be
12 distinguished by measuring the surface tension and the
13 oil-water interface. The surface tension at plain oil-
14 water interfaces is typically of the order of 50 mNm⁻¹.
15 Emulsions formed by mixing oil water and an
16 'ordinary' (i.e. non-microemulsion-forming)
17 surfactant are typically characterised by surface
18 tensions of the order of 0.1 - 1 mNm⁻¹, whereas
19 microemulsions are characterised by far lower surface
20 tensions - of the order of 10⁻³ - 10⁻⁶ mNm⁻¹. These
21 latter values reflecting the absence of direct oil-
22 water contact.

23
24 The present invention exploits microemulsions. In
25 particular, the invention exploits the feature whereby
26 as an aqueous solution of an o/w microemulsion-forming
27 surfactant can absorb oil from a bulk oil phase,
28 forming an o/w microemulsion, so can the same solution
29 absorb oil from an oil-coated solid surface with the
30 same result. Furthermore, in the oil-in-water

1 microemulsion environment, the oil is effectively
2 encapsulated within the surfactant shell, and no longer
3 in direct contact with the original solid. The o/w
4 microemulsion can separated from the cleaned, oil-free
5 solids by straightforward physical means (filtration,
6 centrifugation).

7
8 Various embodiments of the invention will now be
9 described by way of example only, having regard to the
10 following drawings and non-limiting examples in which:

11
12 Figure 1 (a) is a pseudoternary phase diagram of
13 (SDS + B ratio, 1:1 by weight) 0.5M NaCl and
14 Novatec Base Fluid at 25° Celsius;

15
16 Figure 1 (b) is a pseudoternary phase diagram (SDS
17 + B, ratio, 1:1 by weight) 0.5M NaCl and Novatec
18 Base Fluid at 5° Celsius;

19
20 Figure 1 (c) is a pseudoternary phase diagram (SDS
21 + B, ratio 1:2 by weight) 0.5M NaCl and Novatec
22 Base Fluid at 25° Celsius;

23
24 Figure 1 (d) is a pseudoternary phase diagram (SDS
25 + B, ratio 1:2 by weight) 0.5M NaCl Base Fluid at
26 5° Celsius;

27
28 Figure 2 is a diagram of conductivity of the
29 system versus water : oil ratio for the
30 (SDS/B)/water/Novatec Base Oil System at 25°

1 Celsius with the (SDS + B): water ratio held at
2 1:1 (weight);

3

4 Figure 3 is a schematic diagram of the treatment
5 pathways for two waste drill mud samples, and

6

7 Figure 4 is a generic structure of alkyl sulphate
8 surfactants with oil/water microemulsion forming
9 potential with representative identities for R_1 and
10 R_2 .

11

12 As shown in the drawings, surfactant behaviour can be
13 quantified in terms of a triangular phase diagram. The
14 phase diagram for the system water/(SDS+B)/oil is shown
15 in Figure 1(a). Here, (SDS+B) is a mixture of the
16 surfactant sodium dodecyl sulphate (SDS) and butan 1-
17 ol(B). B acts as a cosurfactant, enhancing the O/W
18 microemulsion-forming properties of SDS. As long as
19 the SDS and B are held at constant ratio, they can be
20 treated as a single component for the purpose of
21 constructing the phase diagram. The phase diagrams in
22 Figures 1(a)-1(d) were constructed with the SDS: B
23 ratios held at 1:1 and 1:2 by weight at 25 and 5°C
24 respectively. The oil employed was Novatec B C14-C16
25 LAO Base Fluid (Trade Mark) (M-I Drilling Fluids UK
26 Ltd), a typical base fluid used in the preparation of
27 oil based drilling muds.

28

29 The apexes of the phase triangle each correspond to one
30 of the components in pure form-oil, water, or SDS+B at

1 the stated ratio. Any point on one of the vertices
2 corresponds to a mixture of two of those components in
3 defined ratio (given in percent weight; %wt).

4

5 Thus point A on the water-surfactant axis in Figure
6 1(a) corresponded to a system containing water and
7 (SDS+B) in 40:60 wt% ratio. Any point within the
8 triangle corresponded to a mixture of the three
9 components in defined ratio.

10

11 The physical state of the mixture at equilibrium was
12 mapped on to the phase diagram. The phase triangle in
13 Figure 1(a) was characterised by the prominent single
14 phase microemulsion region, IV, which extends from the
15 SDS+B/water axis towards the SDS+B/oil axis. Most
16 notably, for this system, region IV extended deep into
17 the water-corner of the diagram. This property was
18 extremely useful for the application described here.
19 Adjacent to IV is the large region II, which
20 corresponds to an equilibrium two-phase region, where
21 one phase was oil-continuous (w/o) microemulsion and
22 the other phase was water.

23

24 Within the Winsor IV realm, in moving leftwards from
25 the SDS+B/water axis to the oil corner, there was a
26 continuous evolution of microemulsion structure: oil-
27 in-water→bicontinuous→water-in-oil on addition with
28 oil. This cannot be seen by visual observation (all
29 compositions are optically transparent), but is
30 revealed by physical measurements, e.g. conductivity.

1 The plot of conductivity vs water: oil ratio at fixed
2 40:60% wt SDS+B (corresponding to the line A-A') in
3 Figure 1(a), is shown in Figure 2. It should be noted
4 that oil-in water microemulsions are highly conducting;
5 water-in-oil microemulsions are poor conductors and
6 bicontinuous systems display intermediate conductivity.

7
8 It can be seen from Figure 2 that oil in water (O/W)
9 microemulsion type extended well into the centre of
10 region IV in the phase diagram (point C in Figure 1(a)
11 and Figure 2).

12
13 The method of the invention exploits the ability of
14 water/(SDS+B) mixtures to spontaneously absorb oil from
15 the drill cuttings preparations to form an o/w
16 microemulsions. In accordance with the invention, the
17 capacity of a given preparation for oil roughly
18 corresponds to that corresponding to a final
19 composition on the edge of the oil-in-water realm - the
20 point C in Figures 1(a) and 2.

21
22 The method of extraction of oil can be controlled
23 simply by placing an upper limit on the cuttings:
24 surfactant solution (knowing the oil content of the
25 cuttings) so avoiding inadvertent entry into the w/o
26 microemulsion realm.

27
28 The microemulsion/cuttings mixture was easily separated
29 by centrifugation. The recovered cutting may contain
30 residual o/w microemulsion of composition C. This can

1 be extracted by water-washing. Here the deep
2 penetration of the Winsor IV realm into the water-
3 corner, was of significance since this meant that the
4 o/w microemulsion can be washed out simply by rinsing
5 with water or brine; this dilution does not lead to
6 phase separation of the residual o/w microemulsion.

7
8 To complete the extraction procedure, the cuttings
9 recovered by centrifugation, were washed with a volume
10 of water, so diluting the microemulsion to new
11 composition D in Figures 1(a) and 2. The cuttings
12 recovered by centrifugation following this washing step
13 were virtually oil-free.

14
15 In further experiments it was found that ``fines`` that
16 is, colloidal clays present either due to the presence
17 of such materials in the original drilling mud
18 preparation, or due to partial breakdown of the drill
19 cuttings, could be straightforwardly flocculated by the
20 addition of a commercially available flocculating agent
21 such as one of the Alcomer®, Magnafloc® or Zetag®
22 series, at concentrations of less than 1% wt.

23
24 In short, the invention relates to the extraction of
25 oils from waste drilling muds, or the cuttings fraction
26 thereof, by treatment with an aqueous surfactant
27 solution such that the oil is extracted as an o/w
28 microemulsion. The microemulsion phase is separated
29 from the cuttings by a suitable technique such as

1 centrifugation. The residual microemulsion is washed
2 out by an aqueous rinse.

3

4 The following examples are presented to demonstrate the
5 technology in operation. In the following examples,
6 waste muds or cuttings fractions were treated using the
7 following procedure.

8

9 1 A fixed weight of cuttings was slurried with a
10 fixed weight of a water + (SDS/B) mixture (e.g. of
11 composition A), leading to microemulsification of
12 the oil fraction. For maximum efficiency the
13 cuttings: surfactant solution ratio was such that
14 the final microemulsion composition corresponded
15 to a point within the oil-in-water microemulsion
16 realm (e.g. point C in Figure 1(a)).

17

18 2 The microemulsion and cuttings were separated by
19 centrifugation.

20

21 3 The residual o/w microemulsion in the cuttings was
22 removed by rinsing with water, followed by
23 centrifugation to separate the cuttings and the
24 'dilute' microemulsion phase. In terms of the
25 phase diagram, dilution corresponds to transfer
26 from point C to point D in Figure 1(a).

27

1 EXAMPLES

2

3 Sample 1: Shale cuttings returned from a North Sea
4 drilling rig. Cuttings comprised circa 3%
5 water, 7% oil, and 90% solids.

6 Extraction procedure: 60g (+/-0.5g) samples of oil
7 contaminated drill cuttings were weighed into clean dry
8 polycarbonate centrifuge bottles. 60g of aqueous
9 surfactant solution comprising 24g water, 18g SDS, and
10 18g B was added to each sample and the samples were
11 mixed in an orbital shaker at 300 rpm, for 5 minutes at
12 25°C. The samples were then centrifuged in an MSE
13 Coolspin swing out rotor centrifuge at 1000 rpm for a
14 period of 10 minutes. The O/W microemulsion was
15 decanted off and 100 mls of 0.5M NaCl was added to each
16 sample. Again the samples were shaken at 300 rpm for 5
17 minutes at 25°C followed by centrifugation at 1000 rpm
18 for 10 minutes. The "dilute" microemulsion was
19 decanted leaving cleaned samples. The rinsing process
20 was repeated.

21

22 Solids oil assay: Following treatment 50g (+/-0.5g) of
23 recovered samples were weighed into retort chambers and
24 the samples were retorted to 500°C for 45 minutes as
25 outlined in the international retort standard procedure
26 API Recommended Practice RP13B - Standard Procedure for
27 Field Testing Oil-Based Drilling Fluids (Guidelines for
28 sampling, analysis and calculation of oil on cuttings).
29 Results were expressed as grams of oil per kilogram of

1 dry retorted solids and were then calculated as % oil
2 content by weight dry cuttings.

3

4 The data are summarised in Table 1. The final oil
5 content of the cuttings was 0.54% by weight.

6

7

8 Table 1 Summary of Statistics for Sample 1 at each
9 treatment step

10

Steps	No	n	Mean Oil Cont (%)	Range	St Dev	% St Dev	95% L.C.L.	95% U.C.L.
Sample 1	0	12	6.12	4.66 - 7.34	0.74	12.09	5.66	6.59
first surfactant wash	1	4	14.26	12.13-19.50	3.52	24.68	8.67	19.86
first water rinse	2	6	1.15	0.63 -1.45	0.29	25.22	0.84	1.45
Second water rinse	3	4	0.54	0.16-0.89	0.3	55.56	0.06	1.02

11

12 In order to directly compare the effectiveness of the
13 oil extraction by o/w microemulsification vs.
14 straightforward surfactant washing, the above
15 experiment was repeated exactly, except that an aqueous
16 surfactant solution comprising 24g 0.5 mol per litre
17 aqueous sodium chloride solution, and 36g Triton®
18 R100, place of 18g SDS and 18g B. Triton® R101 is
19 commonly used as a cleaning agent in the oil- and
20 metallurgy industries; however, it is not a
21 microemulsion-forming surfactant.

22

23 The data show that this system was far less efficient
24 at oil-extraction compared with the microemulsion-
25 forming system of the invention.

26

1 Sample 2 Treatment of homogenised cuttings returned
 2 from a North Sea drilling rig. Sample
 3 comprised circa 10% water, 20% oil, and 70%
 4 solids by weight.

5
 6 Table 2

7

Steps	No	n	Mean Oil Cont (%)	Range	St Dev	% St Dev	95% L.C.L.	95% U.C.L.
Sample 1	0	12	6.12	4.66 - 7.34	0.74	12.09	5.66	6.59
first surfactant wash	1	6	6.86	5.11 - 8.00	1.27	18.51	5.53	8.19
first water rinse	2	6	3.68	3.14 - 4.22	0.45	12.23	3.21	4.16
Second water rinse	3	6	3.05	2.52 - 3.27	0.28	9.18	2.75	3.34

8
 9 Two cycles of treatment (one wash with surfactant
 10 solution 60g (60mls) of aqueous surfactant solution
 11 comprising 24g water, 18g SDS, and 18g B and two water
 12 rinses) were used to remediate this sample. Data are
 13 given in Table 3. The final oil content of the
 14 recovered solids was 0.90% wt.

15
 16 Table 3 Summary of Statistics for Sample 2 at each
 17 treatment step

18

Steps	No	n	Mean Oil Cont (%)	Range	St Dev	% St Dev	95% L.C.L.	95% U.C.L.
Sample 2	0	12	20.94	15.97-23.49	2.51	12.25	18.89	22.08
first surfactant wash	1	4	16.35	16.08 -16.74	0.31	1.9	15.87	16.84
first water rinse	2	4	3.59	2.60 - 4.70	0.9	25.07	2.15	5.03
Second water rinse	3	4	2.65	1.86 - 3.53	0.68	25.66	1.56	3.74
Second surfactant wash	4	4	11.61	8.91 - 12.53	1.8	15.5	8.75	14.48
first water rinse	5	4	1.46	0.6 - 2.05	0.61	41.78	0.48	2.43
Second water rinse	6	2	0.9	0.79 - 1.0	0.15	16.67	-0.44	2.23

19

1 The change in the oil content of the solids following
2 each step of the process is summarised in Figure 3.
3 The results prove that waste drilling muds, or cuttings
4 fractions thereof, may be remediated by use of this
5 technology to residual oil contents of less than 1% wt.
6 The apparent increases in oil content following the
7 aqueous surfactant wash was due to the presence of the
8 butan-1-ol component of residual o/w microemulsion, as
9 confirmed by gas chromatography.

10

11 It was necessary to treat Sample 2 twice because this
12 sample contained a high water and oil content (circa
13 10% wt and 21% wt respectively). Therefore the
14 surfactant solution was greatly diluted on addition,
15 resulting in a correspondingly reduced oil absorption
16 capacity.

17

18 The microemulsion fractions can be treated to recover
19 the oil-phase, preferably by increasing the
20 temperature. For ionic surfactants, this results in a
21 phase separation which yields an upper phase containing
22 the oil and virtually no surfactant, and a lower phase
23 of aqueous surfactant. The aqueous surfactant phase can
24 be recycled for another round of cuttings treatment;
25 the recovered oil phase is of a quality suitable for
26 re-use as drill mud fluid, or for any other desired
27 application.

28

29 The ability to flocculate fines using commercially
30 available flocculating agents already in use in the

1 oil-industry is particularly important for recycling,
2 since the addition of flocculating agents to the
3 aqueous surfactant solution will inhibit the
4 accumulation of fines which would otherwise limit the
5 number of recycles considerably.

6

7 In a preferred embodiment, the invention extends to the
8 cleaning of drill cuttings and other oil-contaminated
9 solid wastes use aqueous solutions containing a single
10 surfactant, rather than surfactant/cosurfactant
11 mixture.

12

13 The ability of surfactants to stabilise microemulsions
14 without the need for a co-surfactant is clear in the
15 art. Thus sodium bis 2-ethylhexyl sulphosuccinate
16 (Aerosol-OT) and didodecyltrimethyl ammonium bromide
17 (DDAB) both form water-in-oil (w/o) microemulsions
18 without the need for co-surfactant.

19

20 Surfactant molecules which in the absence of a
21 cosurfactant form o/w microemulsions are not available
22 commercially. Figure 4 describes a generic group of
23 surfactants which have structural properties which are
24 expected to stabilise o/w microemulsions without the
25 need for a co-surfactant.

26

27 These surfactants are substituted alkyl sulphates where
28 R_1 and R_2 are straight- or branched- chain hydrocarbons
29 or substituted hydrocarbons. R_1 and R_2 are not
30 necessarily identical. The number of carbon units, n ,

1 in each chain is variable. The examples in Figure 4
2 are presented to illustrate the range of structures
3 claimed as surfactants with o/w microemulsion forming
4 properties. The total range of structures is not
5 limited to these.

6
7 The process of the invention represents a significant
8 improvement over the prior art since it teaches that
9 the oil content can be reduced to less than 1% wt.
10 Furthermore this invention uses an oil-in-water
11 microemulsion (that is a water-continuous microemulsion
12 preparation) rather than a water-in-oil microemulsion
13 (that is an oil continuous microemulsion preparation).
14 In attaining residual oil contents of less than 1% wt,
15 this invention represents a significant advance in oil
16 extraction technology.

17
18 In summary the invention provides a method whereby oil
19 can be recovered from waste drilling muds, or fractions
20 thereof derived by prior separation processes, by
21 extraction as an oil-in-water microemulsion.

22
23 The surfactant formulation employed in the method of
24 the invention can includes any o/w microemulsion-
25 forming surfactant, or mixture of surfactants,
26 including, but not limited to, those described herein.
27 The surfactant may be cationic, non-ionic or anionic in
28 nature; anionic surfactants are not limited to the
29 class of alkylsulphates described herein.
30

1 The surfactant formulation may include a component
2 which behaves as a co-surfactant, that is enhancing, or
3 otherwise modulating, the o/w microemulsion-forming
4 properties of the surfactant. The surfactant
5 formulation may also contain any substance or
6 substances which would cause solids in colloidal
7 suspension to flocculate (flocculating agents). In
8 another embodiment, the surfactant formulation can
9 contain dissolved salts of any description, at any
10 concentration.

11

12 The invention therefore provides:

13

- 14 - a process technology whereby the invention is
15 applied with physical separation of the o/w
16 microemulsion phase and cleaned solids by
17 centrifugation, filtration or any other suitable
18 process.
- 19
- 20 - a process technology which is used for the
21 recycling of waste drilling muds, or fractions
22 thereof, including cuttings fractions derived from
23 waste muds.
- 24
- 25 - a process technology which is used for the
26 recycling of waste drilling muds or fractions
27 thereof, where the original mud composition is of
28 any formulation, and the oil is of mineral or
29 synthetic origin, and may be hydrocarbon or non-
30 hydrocarbon in nature.

- 1 - a process technology which can be applied for the
2 remediation of waste drilling muds or fractions
3 thereof in an on- or off-shore environment.
4
- 5 - a process technology which utilises any suitable
6 method for recovering the oil from the o/w
7 microemulsion phase, including but not limited to,
8 a temperature-induced phase separation.
9
- 10 - a process technology which can be applied to the
11 extraction of any kind of hydrocarbon or other
12 petrochemical from any oil-contaminated material
13 including, but not limited to, sand, soils and
14 swarf contaminated with oil-based cutting fluids,
15 generated in metal fabrication.
16
- 17 The present invention has many advantages which
18 include:
19
- 20 - The process technology does not require
21 sophisticated plant or other equipment. The
22 initial microemulsification step can be achieved
23 by slurring the surfactant preparation with
24 drilling mud, or cuttings fractions at ambient
25 temperature, followed by centrifugal separation.
26 Centrifugation is a commonly used technique within
27 the oil industry in both the on- and off-shore
28 environment. The rinsing step and final
29 separation can be achieved similarly. The
30 recovery of the oil from the o/w microemulsion can

1 similarly be achieved by straightforward means. A
2 feature of the invention is that phase separation
3 leading to recovery and recycling of aqueous
4 surfactant and oil phases can be achieved through
5 a modest increase in temperature.

6
7 - The invention requires commodity inexpensive
8 materials. Apart from water and possibly salt,
9 the only addition required is surfactant and
10 possibly co-surfactant and possibly flocculant.
11 Accordingly, the surfactant can be recycled with
12 minimal losses per cycle.

13
14 - This invention, which teaches that oil can be
15 extracted from waste drilling muds, or fractions
16 thereof, into an o/w microemulsion, is
17 significantly more effective than that achieved by
18 washing with a water-in-oil w/o microemulsion.
19 Specifically, the extraction efficiency obtained
20 with O/W microemulsion is typically six- to ten-
21 times greater than that taught for the W/O
22 microemulsion-based separation.

23
24 - Furthermore, the o/w microemulsion-based
25 separation system has a unique advantage over the
26 W/O microemulsion-based separation in that
27 flocculants may be included in this water-based
28 formulation. Addition of flocculant to a W/O
29 microemulsion-based formulation cannot confer any

1 specific benefit since flocculants are inactive in
2 oil-based media.

1 **CLAIMS**

2

3 1. A method for the extraction of oil from a solid by
4 microemulsification comprising the steps of mixing an
5 oil-contaminated solid with a water-based solution of
6 a surfactant to form an oil-in-water (o/w)
7 microemulsion and separating the o/w microemulsion
8 and solid phases.

9

10 2. A method as claimed in Claim 1 further comprising
11 the step of rinsing the solids with an aqueous
12 solution.

13

14 3. A method as claimed in Claim 2 characterised in
15 that the aqueous solution comprises an aqueous salt
16 solution.

17

18 4. A method as claimed in any of Claims 1 to 3
19 characterised in that the o/w microemulsion and solid
20 phases are separated by centrifugation.

21

22 5. A method as claimed in any of claims 1 to 4
23 characterised in that the surfactant comprises an o/w
24 microemulsion-forming surfactant.

25

26 6. A method as claimed in any of claims 1 to 5
27 characterised in that the aqueous surfactant solution
28 comprises water and a salt.

29

1 7. A method as claimed in Claim 6 characterised in
2 that the salt comprises sodium chloride.

3

4 8. A method as claimed in any of claims 1 to 7
5 characterised in that the water-based solution of a
6 surfactant further comprises a co-surfactant.

7

8 9. A method as claimed in any of claims 1 to 8
9 characterised in that the water-based solution of a
10 surfactant further comprises a flocculating agent.

11

12 10. A method as claimed in any of claims 1 to 9
13 characterised in that the extraction steps are
14 carried out at ambient temperature or below.

15

16 11. A method as claimed in any of claims 1 to 10
17 characterised in that the oil is recovered from the
18 o/w microemulsion.

19

20 12. A method as claimed in claim 11 characterised in
21 that the oil is recovered by temperature-induced
22 phase separation.

23

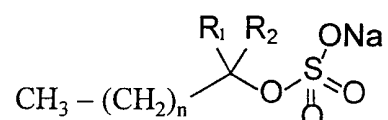
24 13. A method as claimed in any of claims 1 to 12
25 characterised in that the solid is selected from the
26 group comprising a drilling mud waste, sand, soils,
27 metal fabrication swarf, newly manufactured printed
28 circuit boards and fractions thereof.

29

1 14. A method as claimed in any of claims 1 to 13
2 characterised in that the solid comprises drilling
3 mud wastes or oil contaminated fractions thereof.
4

5 15. A method for removing oil from drilling and mud
6 wastes, or oil-contaminated fractions thereof,
7 comprising the steps (1) of mixing the oil-
8 contaminated material with a water-based solution of
9 a surfactant which forms an oil-in-water (o/w)
10 microemulsion; such that the oil is extracted as an
11 o/w microemulsion; (2) of separating the o/w
12 microemulsion and solids phases by an appropriate
13 technique; and (3) of finally rinsing the solids with
14 water or aqueous salts solution to remove residual
15 o/w microemulsion.
16

17 16. A surfactant having the general formula:



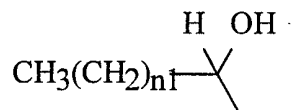
18

19 wherein

20

21 $\text{R}_1 = -\text{H}$ or $-\text{CH}_3$

1 $R_2 =$

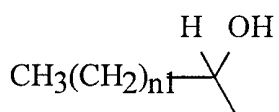


2 where $n1$ may take any value as long as

3 $n1 < n$,

4

5 $R_1 = R_2 =$



6

7 where $n1$ may take any value as long as

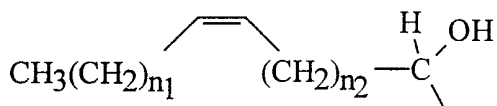
8 $n1 < n$, or

9

10 $R_1 = -\text{H}$ or $-\text{CH}_3$

11

12 $R_2 =$



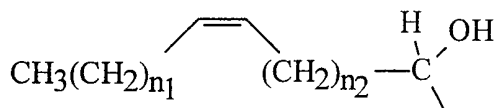
13

14 where $n1$ and $n2$ may take any value, as

15 long as $(n1 + n2) < n$, or

16

17 $R_1 = R_2 =$

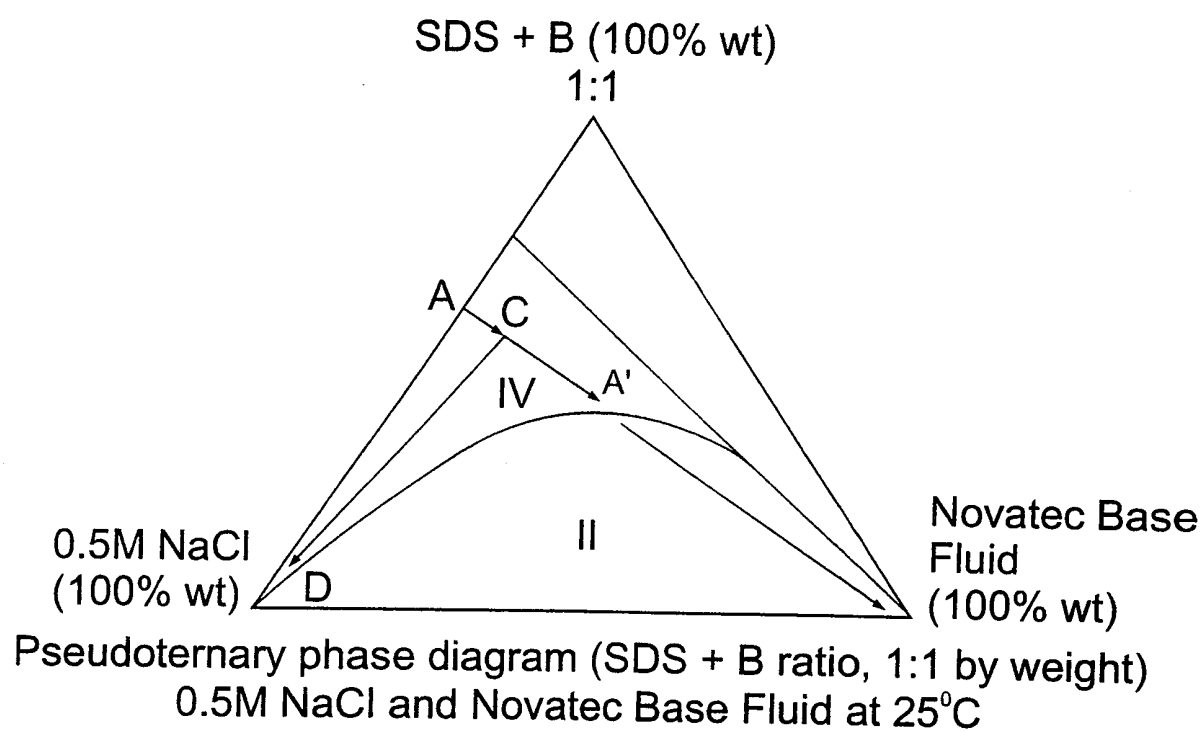
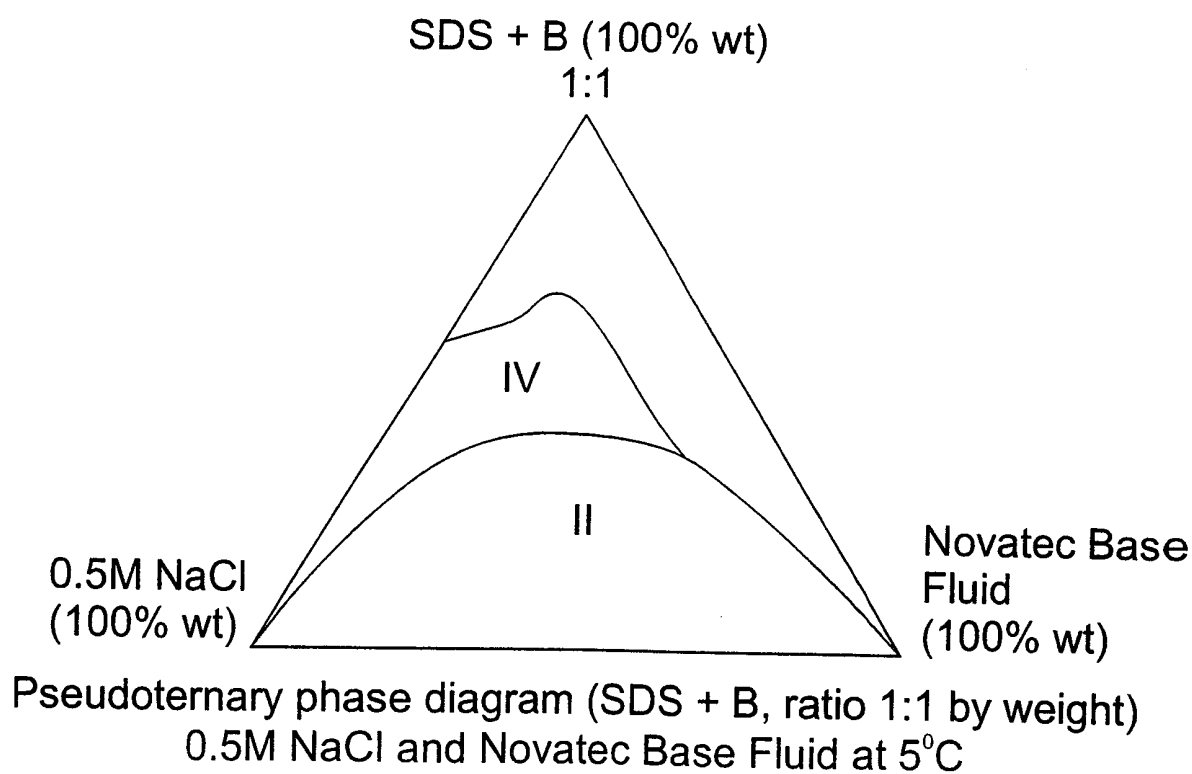


18

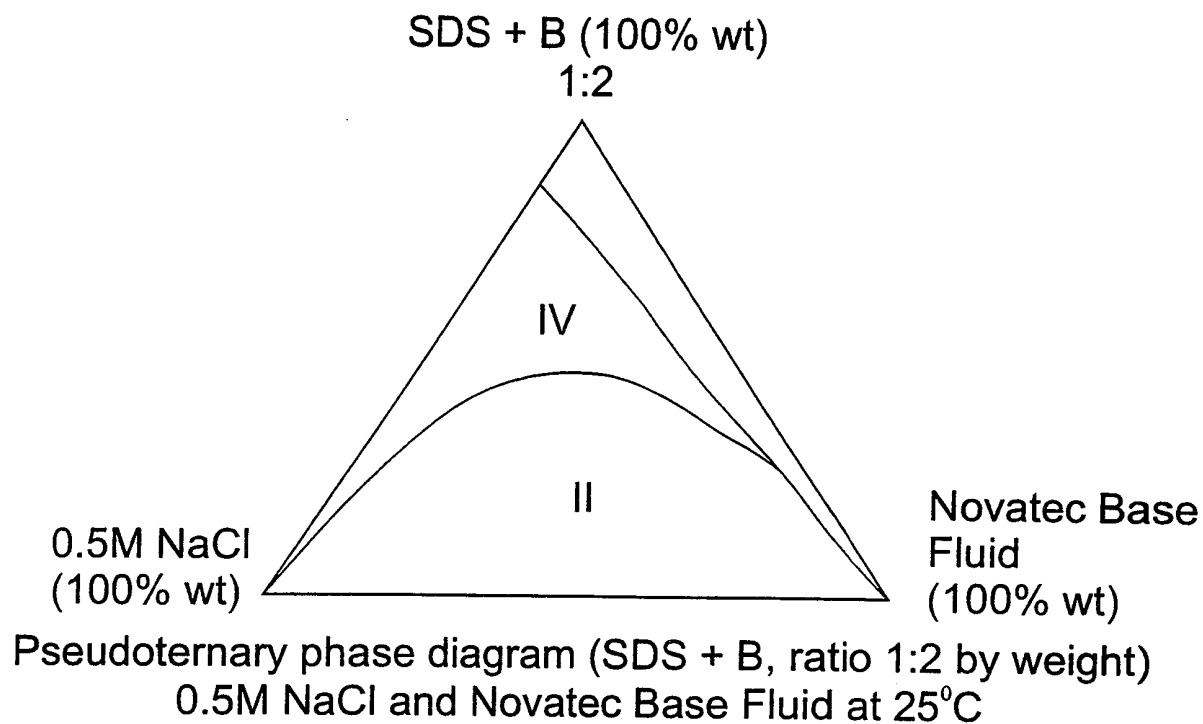
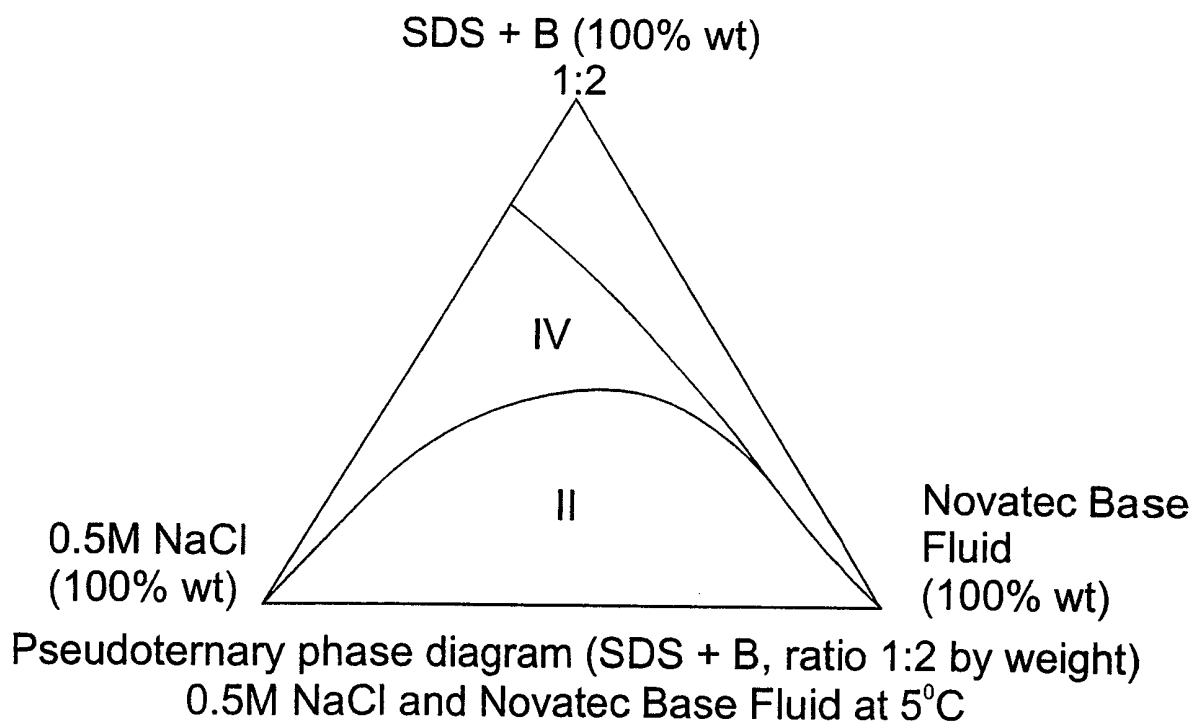
19 where $n1$ and $n2$ may take any value, as

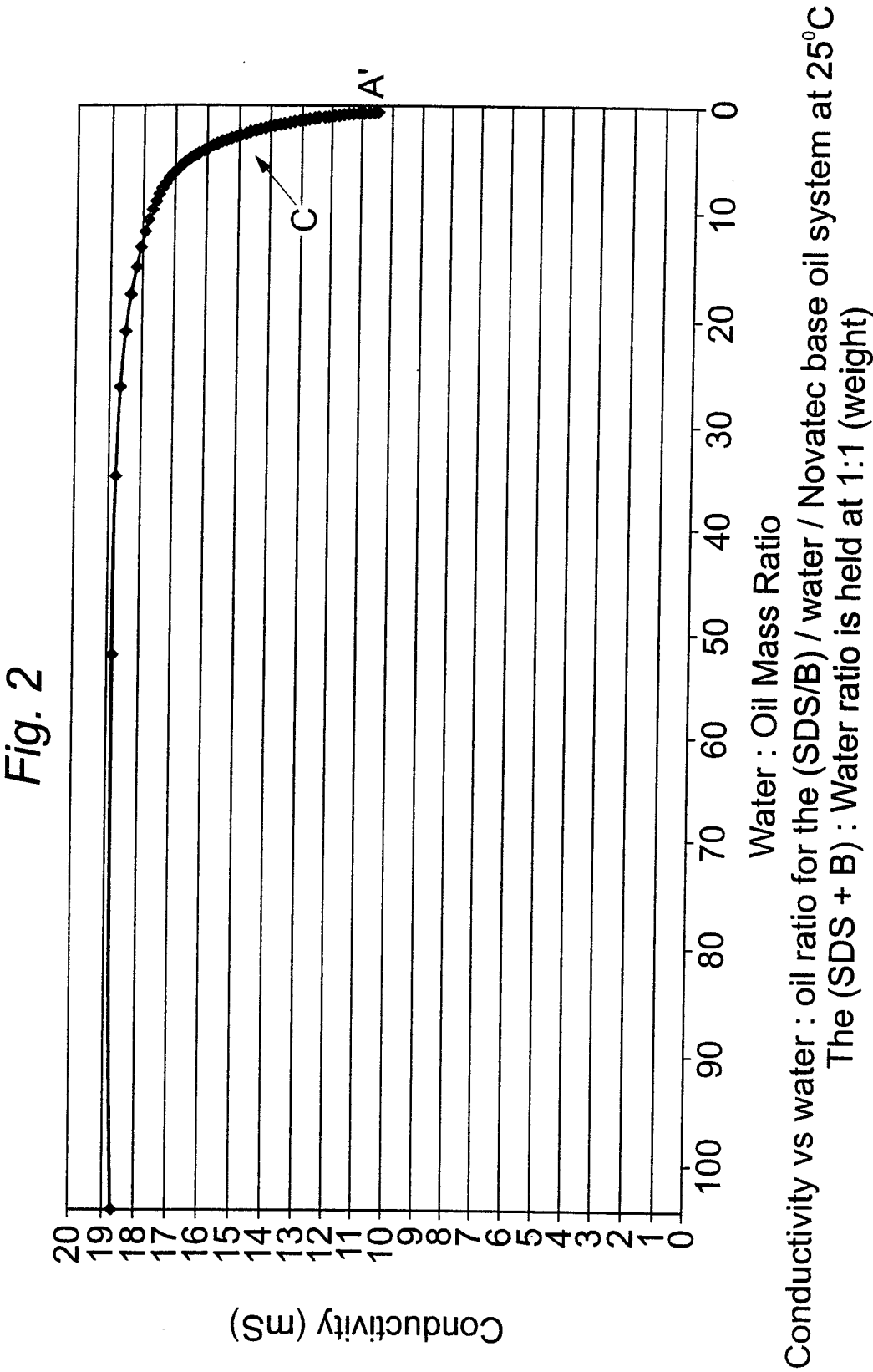
20 long as $(n1 + n2) < n$

1 / 6

*Fig. 1a**Fig. 1b*

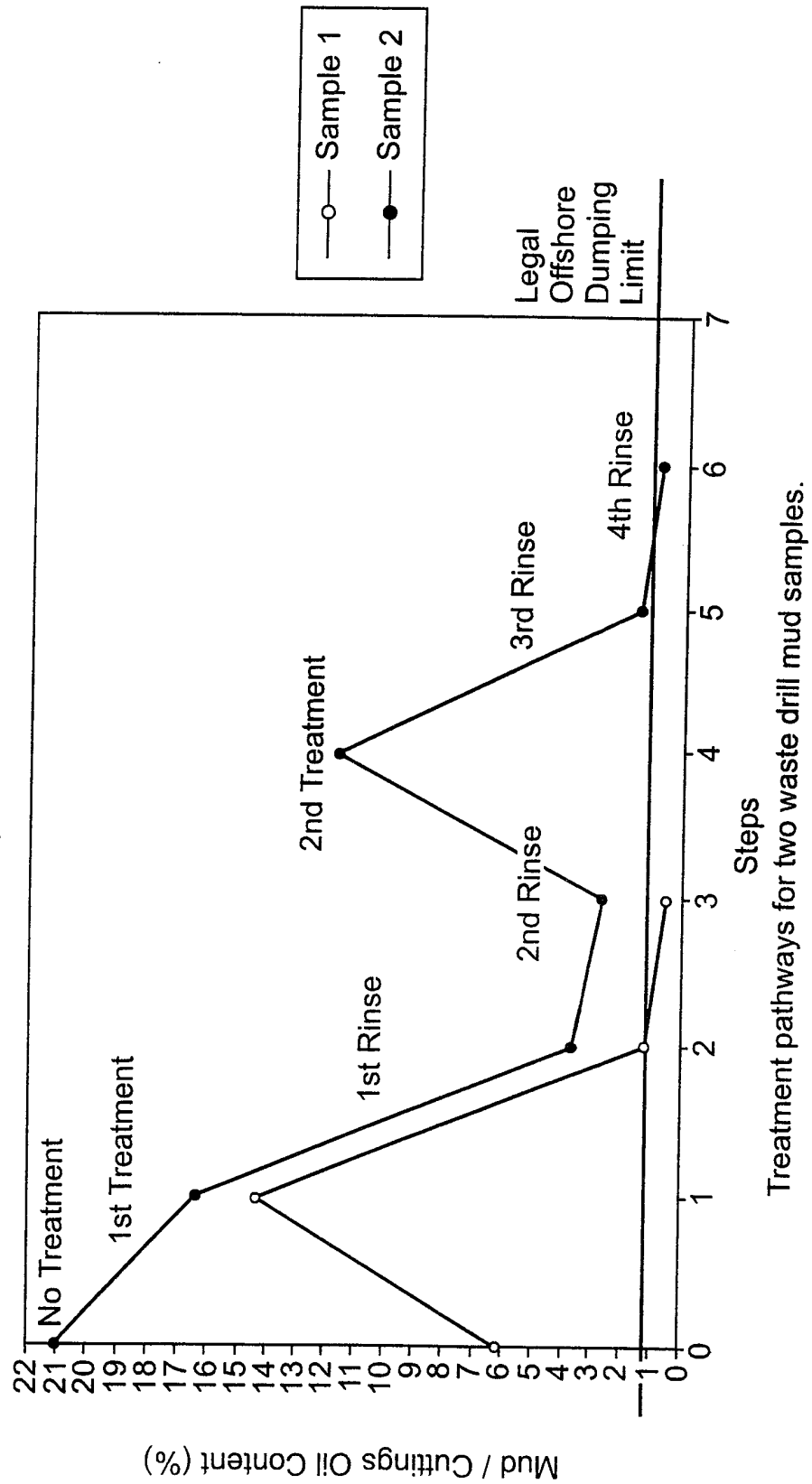
2 / 6

*Fig. 1c**Fig. 1d*

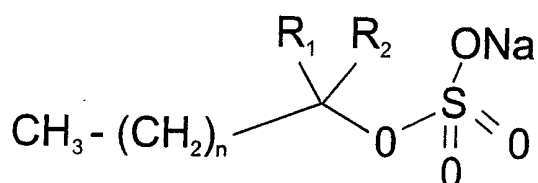


4 / 6

Fig. 3



5 / 6



Generic structure of alkyl sulphate surfactants with O/W microemulsion forming potential

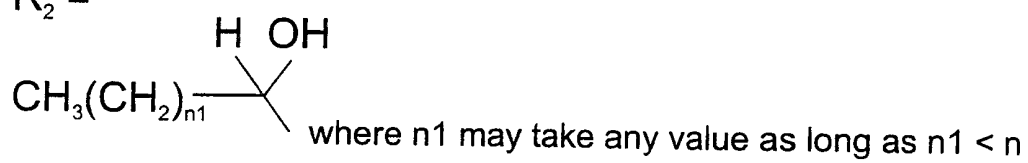
Fig.4

Different classes of surfactant may be defined according to the identities of R_1 and R_2 .
Examples given below. The range of surfactants based on this generic structure is not limited to those given in these examples

Class I

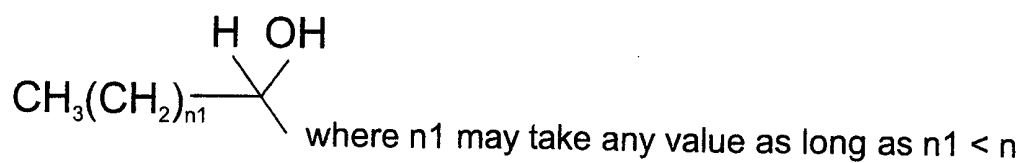
$\text{R}_1 = -\text{H}$ or $-\text{CH}_3$

$\text{R}_2 =$

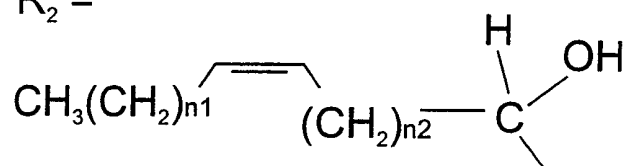
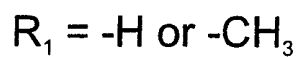


Class II

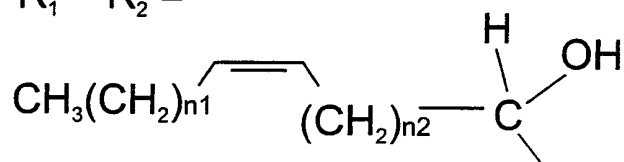
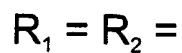
$\text{R}_1 = \text{R}_2 =$



6 / 6

Class III

where n_1 and n_2 may take any value, as long as $(n_1 + n_2) < n$

Class IV

where n_1 and n_2 may take any value, as long as $(n_1 + n_2) < n$