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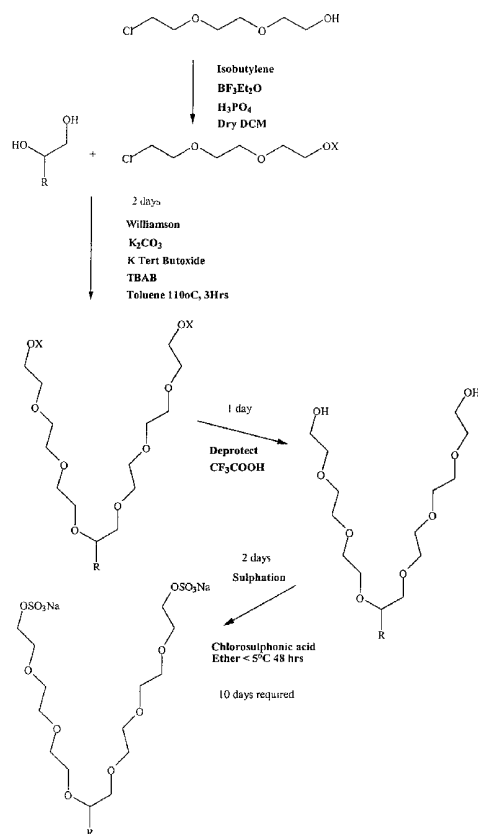
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[Continued on next page]

(54) Title: SURFACTANT



Suggested laboratory synthesis pathway
for manufacturing an O/W microemulsion forming
surfactant.

(57) Abstract: A compound having the general formula I wherein R comprises a hydrocarbon group including H, branched or linear alkyl chains, substituted alkyl, alkenyl, aryl, alkaryl or cyclic groups; R₁ is any of C, N, P, B, S, or SiO₄ or any subgroups thereof; R₂ is any of a covalent bond, O, CH₂, (CH₂)_n where n may be 1-10 carbons long; R₃ is any of a covalent bond, O, CH₂, (CH₂)_n where n may be 1-10 carbons long; R₂ and R₃ may be the same or different; R₄ is any of O, H, OH, CH₃, (CH₂)_nCH₃, (CH₂)_nOH, (CH₂)_nOX or any combinations thereof where n is from 1 to 10. OX is a water soluble group; chains a and b are in the range 1-10 carbons each; and the alkoxy chains c and d are in the range 1-20 units each.

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For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

1 **"Surfactant"**

2

3

4 This invention relates to surfactant compounds and
5 to the use of the compounds in the formation of oil-
6 in-water microemulsions.

7

8 Surfactants are surface active chemical agents. A
9 surfactant molecule comprises a water soluble
10 (hydrophilic) group and an oil soluble (hydrophobic)
11 group. As such surface active molecules will align
12 themselves at an oil/water interface with the water
13 soluble group being solubilised into the water
14 (aqueous) phase and the oil soluble group being
15 solubilised into the oil (organic) phase
16 accordingly.

17

18 The addition of surfactants to a mixture of oil and
19 water either increases or decreases the extent to
20 which the two liquids solubilise each other.
21 Surfactants reduce the interfacial surface tension
22 between the two immiscible liquids, enabling them to
23 be dispersed within each other. Depending on the
24 proportions and the precise nature of the chemical

1 components either water-in-oil (W/O) or oil-in-water
2 (O/W) dispersions may be produced. These mixtures
3 are called emulsions. Most current commercially
4 available surfactants, surfactant formulations and
5 products used are emulsion formers or emulsion
6 systems.

7
8 Emulsions have an inefficient molecular packing
9 capability at the oil/water interface which in turn
10 results in some direct oil/water contact at the
11 interface. The uncoated surfaces at the interface
12 are therefore directly exposed to the continuous
13 phase. This is a thermodynamically unfavourable
14 situation. As a result the droplets aggregate by
15 coalescing at their exposed surfaces, increasing the
16 surface area : volume ratio and hence minimising
17 oil : water contact. Hence the outcome of extensive
18 droplet coalescence is bulk-phase separation. Also
19 as a result of the inefficient molecular packing at
20 the interface emulsions have inherent higher surface
21 tensions.

22
23 Emulsions are therefore turbid and may remain stable
24 for a considerable length of time before phase
25 separation occurs. Emulsions are multiple phase,
26 cloudy colloidal systems in nature and, importantly,
27 are likely to require an energy input in order to
28 form.

29
30 Microemulsion systems, on the other hand, are
31 defined as being thermodynamically stable (they form
32 spontaneously on simple mixing at ambient

1 temperatures and pressures). They are single-phase
2 and optically transparent (isotropic) liquid
3 mixtures of oil, water and amphiphile i.e.
4 surfactant. As with emulsions microemulsions may be
5 (O/W) or (W/O) systems.

6
7 In oil-in-water (O/W) microemulsion systems the
8 continuous phase is water and the dispersed phase
9 consists of a monodispersion of oil droplets, each
10 coated with (and therefore encapsulated by) a close-
11 packed monolayer of surfactant molecules. Water-in-
12 oil (W/O) microemulsion systems are the inverse of
13 this scenario where water is the dispersed phase and
14 oil forms the continuous phase. These encapsulated
15 droplet structures are referred to as micelles. In
16 effect within microemulsions one phase is
17 solubilised within the other.

18
19 Microemulsions are usually optically transparent,
20 since the individual droplets are so small that they
21 do not scatter visible light (having diameters in
22 the region of only 3 - 200 nanometers). In
23 comparison micelles in emulsion systems are
24 typically larger than 200 nanometers and hence
25 emulsions scatter visible light and appear turbid or
26 opaque.

27
28 The inherent thermodynamic stability of
29 microemulsion systems arises from the fact that, due
30 to the close and efficient packing of the surfactant
31 molecules at the monolayer interface, there is no
32 direct oil/water contact. One result of this

1 extremely efficient molecular packing is low or
2 "ultra low" interfacial surface tensions which may
3 be several orders of magnitude lower than those
4 found in emulsion systems.

5
6 Apart from the significant physical differences
7 described above, which can be determined by visual
8 examination, emulsions and microemulsion systems can
9 be distinguished further by measuring the surface
10 tension at the oil-water interface. The surface
11 tension at plain oil-water interfaces is typically
12 of the order of 50 mNm^{-1} . Emulsions formed by mixing
13 oil, water and an "ordinary" (i.e. emulsion-
14 forming) surfactant are typically characterised by
15 surface tensions in the region of $0.1 - 1 \text{ mNm}^{-1}$,
16 whereas microemulsion systems are characterised by
17 far lower surface tensions in the region of $10^{-3} -$
18 10^{-6} mNm^{-1} . These latter values reflect the
19 efficiency of the molecular packing at the oil-water
20 interface and the complete absence of direct oil-
21 water contact.

22
23 The differences in physico-chemical behaviour
24 between emulsions and microemulsions described above
25 are the characteristics that provide microemulsion
26 systems with such unique and advantageous
27 characteristics.

28
29 The prior art has demonstrated that certain
30 chemicals eg. intermediate chain length alcohols can
31 dissolve and solubilise important quantities of oil
32 in water and it is thought that this is related to

1 the microheterogeneity of the water/alcohol
2 mixtures. The hydrocarbon fraction is preferentially
3 soluble in the alcohol microphases which enables an
4 increase in their formation. Many of these alcohols
5 for example are efficient at solubilising light oils
6 such as benzene or hexane in water.

7
8 However, prior research and development has shown
9 that these systems are not efficient at dissolving
10 heavier oils eg. decane, dodecane and tetradecane
11 due to the insolubility of the alcohol in the
12 heavier oils. Alcohols with longer chain lengths
13 must be used for these types of oil but in turn they
14 are not soluble in water. In order to modify these
15 systems such that O/W microemulsions may be formed
16 surfactants must be added to solubilise these
17 alcohols into water. The relationship is synergistic
18 as mutually the alcohols also increase the water
19 solubility of the surfactants.

20
21 Prior art in the field has therefore shown that by
22 combining surfactants or by combining surfactants
23 with co-surfactants in the correct proportions oil
24 dispersion capabilities in water are very
25 significantly improved. In fact as a rule these
26 combined "quaternary" surfactant/surfactant or
27 surfactant/co-surfactant types of system are
28 significantly more effective than the use of either
29 surfactant or alcohol for example separately.

30

1 However, currently no effective ternary system
2 adapted to form an O/W microemulsion is currently
3 available commercially.

4
5 Many quaternary surfactant/surfactant or surfactant/
6 co-surfactant systems are known in the prior art
7 which are capable of forming both O/W and W/O
8 microemulsions. The ability of surfactants to
9 stabilise W/O microemulsions without the need for a
10 co-surfactant is known in the art. For example
11 sodium bis 2-ethylhexyl sulphosuccinate (Aerosol-
12 OT), ammonium bis(ethylhexyl) hydrogen phosphate
13 (HN₄DEHP), and didodecyltrimethyl ammonium bromide
14 (DDAB) all preferentially form water-in-oil (W/O)
15 microemulsions without the need for a co-surfactant
16 or other chemical additive.

17
18 Many nonionic surfactants are known to be capable of
19 forming such true ternary O/W microemulsion systems
20 namely many of the Brij (Trade Mark)
21 (polyoxyethylene ethers), Span (sorbitan esters),
22 Tween (polyoxyethylene sorbitan esters), Myrj (Trade
23 Mark) and other such families of surfactant.

24
25 However, there are many disadvantages of using
26 microemulsions stabilised with known nonionic
27 surfactants in many applications. For example known
28 nonionic systems are known to be sensitive to very
29 small changes in environmental variables such as
30 temperature and salt concentration. As a result
31 these systems form very "unstable" (single phase)
32 microemulsions and exhibit very complex phase

1 behaviours. Although cost efficient to manufacture
2 microemulsions stabilised with known nonionic
3 surfactants are very unpredictable and may thus be
4 impractical to work with.

5

6 However, currently no effective ternary system
7 adapted to form an O/W microemulsion is currently
8 available commercially.

9

10 Accordingly, a need exists for "ternary" surfactant
11 systems which preferentially are capable of forming
12 oil-in-water (O/W) microemulsions without the need
13 for co-surfactants and/or other chemicals. In
14 particular, a need exists for anionic surfactants
15 adapted to form O/W microemulsions.

16

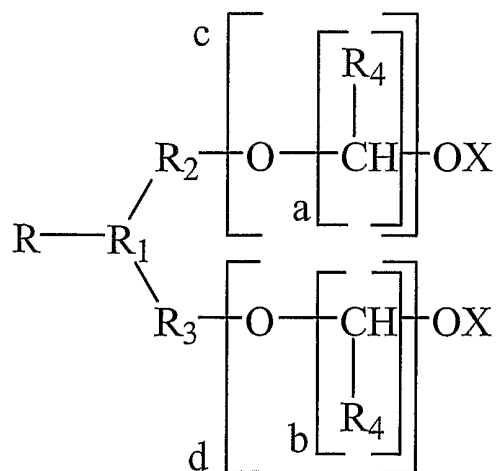
17 This invention therefore relates to the design and
18 synthesis of a range of specialist (oil-in-water)
19 microemulsion forming surfactants for use
20 (independently or as part of a chemical formulation)
21 for any number of suitable industrial, environmental
22 and domestic applications eg. the remediation of oil
23 contaminated aquifers.

24

25 According to the invention there is provided a
26 compound having the general formula I

27

28



wherein R comprises a hydrocarbon group including H, branched or linear alkyl chains, substituted alkyl, alkenyl, aryl, alkaryl or cyclic groups;

R₁ is any of C, N, P, B, S, or SiO₄ or any subgroups thereof;

R₂ is any of a covalent bond, O, CH₂, (CH₂)_n where n may be 1-10 carbons long;

R₃ is any of a covalent bond, O, CH₂, (CH₂)_n where n may be 1-10 carbons long;

R₂ and R₃ may be the same or different;

R₄ is any of O, H, OH, CH₃, (CH₂)_nCH₃, (CH₂)_nOH, (CH₂)_nOX or any combinations thereof where n is from 1 to 10.

OX is a water soluble group;

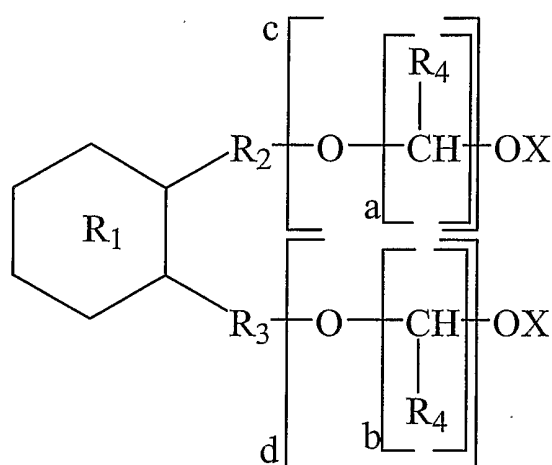
1 chains a and b are in the range 1 - 10 carbons each;
 2 and

3

4 the alkoxy chains c and d are in the range 1 - 20
 5 units each.

6

7 In an alternative embodiment the invention also
 8 provides a compound having the general formula II



9

10

11

12

13 wherein R_1 is any cyclic hydrocarbon which may or
 14 may not include non hydrocarbon elements;

15

16 R_2 is any of a covalent bond, O, CH_2 , $(\text{CH}_2)_n$ where n
 17 may be 1-10 carbons long;

18

19 R_3 is any of a covalent bond, O, CH_2 , $(\text{CH}_2)_n$ where n
 20 may be 1-10 carbons long;

21

22 R_2 and R_3 may be the same or different;

23

10

1 R_4 is any of O, H, OH, CH_3 , $(\text{CH}_2)_n\text{CH}_3$, $(\text{CH}_2)_n\text{OH}$,
 2 $(\text{CH}_2)_n\text{OX}$ where n is from 1 to 10 or any combination
 3 thereof;

4

5 OX is a water soluble group;

6

7 chains a and b are in the range 1 - 10 carbons each;
 8 and

9

10 the alkoxy chains c and d are in the range 1 - 20
 11 units each.

12

13 The invention also extends to a compound having the
 14 general structure III

15

16

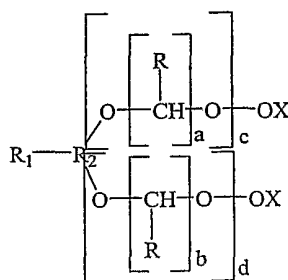
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18

19

20

21



22 where R_1 is a hydrocarbon group including H,
 23 branched or linear alkyl chains, substituted alkyl,
 24 alkenyl, aryl, alkaryl or cyclic groups;

25

26 R_2 is any of C, N, P, B, S, or SiO_4 or any subgroups
 27 thereof;

28

29 R is O, H, OH, CH_3 , $(\text{CH}_2)_n\text{CH}_3$, CH_2OH , $(\text{CH}_2)_n\text{OX}$ or any
 30 combinations thereof where n is from 1 to 10;

31

1 X is H, sulphate, sulphonate, carboxylate, a pH
 2 sensitive group, a mono- di- or oligio-saccharide or
 3 any combination thereof;

4

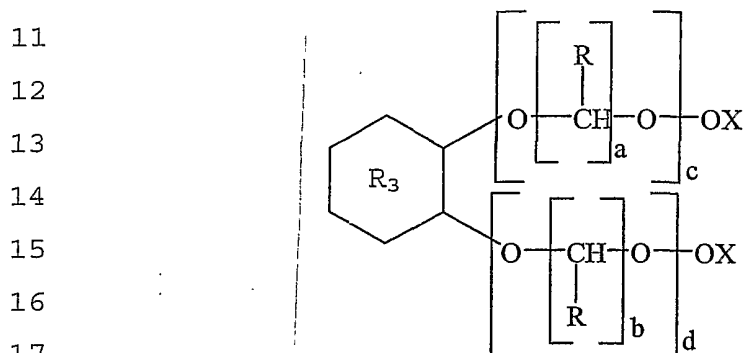
5 a and b in the range 1 - 10 each;

6

7 c and d are in the range 1 - 7 each;

8

9 In a further embodiment, the invention also extends
 10 to a compound having the general formula IV



18 where R₃ - any cyclic hydrocarbon;

19

20 R is O, H, OH, CH₃, (CH₂)_nCH₃, CH₂OH, (CH₂)_nOX or any
 21 combinations thereof where n is from 1 to 10

22

23 X is H, sulphate, sulphonate, carobxylate, a pH
 24 sensitive group, a mono- di- or oligio-saccharide or
 25 any combination thereof;

26

27 a and b are in the range 1 - 10;

28

29 c and d are in the range 1 - 7;

30 and

31 the R₃ cyclic hydrocarbon is a C1 to C24 hydrocarbon.

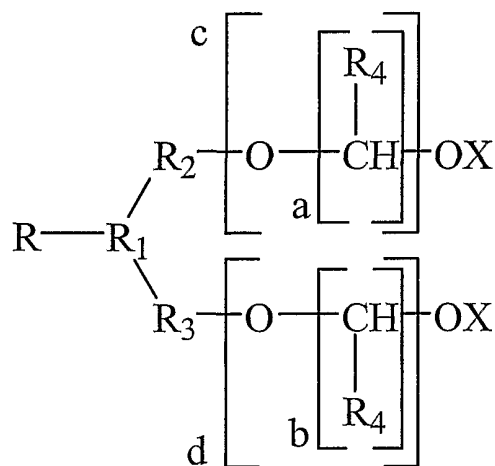
32

1 The invention also extends to a surfactant
 2 comprising a compound as defined above, to a method
 3 of forming an oil-in-water microemulsion and to the
 4 use of a compound as defined above in the formation
 5 of an oil-in-water microemulsion.

6

7 As indicated above, the compounds of the invention
 8 have the general formula:

9



I

10

11

12 where R is a hydrocarbon group including H, branched
 13 or linear alkyl chains, substituted alkyl, alkenyl,
 14 aryl, alkaryl or cyclic groups. This may optionally
 15 include non-hydrocarbon elements eg. ethers or
 16 esters. The chain length of the group should be C1
 17 to C30, preferably in the range C3 to C24, and most
 18 preferably C6 to C20;

19

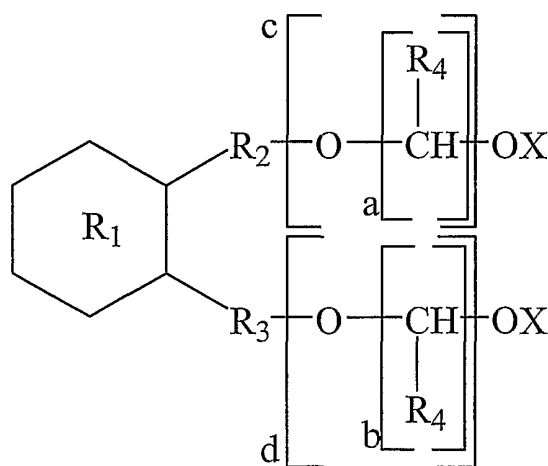
20 R₁ is any of C, N, P, B, S, or SiO₄ or any subgroups
 21 thereof and preferably Carbon;

22

1 R_2 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
2 may be of 1-10 carbons long and preferably 1-6
3 carbons long. The chain may be branched or un-
4 branched;
5
6 R_3 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
7 may be 1-10 carbons long and preferably 1-6 carbons
8 long. The chain may be branched or un-branched;
9
10 R_2 and R_3 can be the same or different and may or may
11 not be equal;
12
13 R_4 is any of O, H, OH, CH_3 , $(CH_2)_nCH_3$, $(CH_2)_nOH$,
14 $(CH_2)_nOX$ where n may be 1-10 and preferably is from 1
15 to 6 or any combinations thereof. R_4 groups on
16 different chains can be the same or different and
17 may or may not be equal;
18
19 OX is a water soluble group including but not
20 limited to OH, sulphate, sulphonate, carboxylate,
21 borate or borate based group, pH sensitive group eg.
22 lactone, or any mono- di- or oligo-saccharide eg.
23 galactose, fructose, sucrose, or maltose or any
24 combination thereof. Di-anionic surfactants are
25 preferred, most especially disulphate. The oxygen
26 atom may or may not be present depending on the
27 nature of the head group attached;
28
29 chains a and b are in the range 1 - 10 carbons each
30 and are preferably 1 - 8 carbons and most preferably
31 1 - 4 ie. are alkoxy moieties preferably ethoxy,

1 propoxy, butoxy or combinations thereof. The
 2 moieties may or may not be the same in each chain;
 3
 4 the alkoxy chains c and d are in the range 1 - 20
 5 units each and are most preferably 2 - 10 units long
 6 or any combinations thereof. Chains c and d may
 7 differ in value;
 8
 9 non-hydrocarbon groups may or may not be included in
 10 the 2 to 5 head group chains. If the head group
 11 chains do not contain non-hydrocarbon groups then
 12 the chains are preferably at least 4 carbons in
 13 length. The same R₄ groups would apply as above.

14
 15 In a second embodiment, the invention also extends
 16 to a compound having the general formula:



II

18
 19
 20 where R₁ = any cyclic hydrocarbon which may or may
 21 not include non hydrocarbon elements. The cyclic
 22 hydrocarbon may be C1 to C24 in composition,
 23 preferably C4 to C20 and most preferably C4 - C12.
 24 The ring may or may not contain any number of double

1 bonds. The ring may also contain up to 4 other
2 groups originating at any location. These adjoining
3 groups may include branched or linear alkyl chains
4 (branched or linear), substituted alkyl, alkenyl,
5 aryl, alkaryl or further cyclic groups and any
6 combinations thereof;
7
8 R_2 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
9 may be 1-10 carbons long and preferably 1-6 carbons
10 long. The chain may be branched or un-branched;
11
12 R_3 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
13 may be of 1-10 carbons long and preferably 1-6
14 carbons long. The chain may be branched or un-
15 branched;
16
17 R_2 and R_3 may or may not be equal;
18
19 R_4 is any of O, H, OH, CH_3 , $(CH_2)_nCH_3$, $(CH_2)_nOH$,
20 $(CH_2)_nOX$ where n may be 1 to 10 and is preferably 1
21 to 6 or any combinations thereof. R_4 groups on
22 different chains can be the same or different and
23 may or may not be equal;
24
25 OX is a water soluble group including but not
26 limited to OH, sulphate, sulphonate, carboxylate,
27 borate or borate based group, pH sensitive group eg.
28 lactone, or any mono- di- or oligo-saccharide eg.
29 galactose, fructose, sucrose, or maltose or any
30 combination thereof. Di-anionic surfactants are
31 preferred, most especially disulphate. The oxygen

1 atom may or may not be present depending on the
2 nature of the head group attached;

3

4 chains a and b are in the range 1 - 10 carbons each
5 and are preferably 1 - 8 carbons and most preferably
6 1 - 4 ie. are alkoxy moieties preferably ethoxy,
7 propoxy, butoxy or combinations thereof. The
8 moieties may or may not be the same in each chain;

9

10 The alkoxy chains c and d are in the range 1 - 20
11 units each and are most preferably 2 - 10 units long
12 or any combinations thereof. Chains c and d may
13 differ in value.

14

15 Non-hydrocarbon groups may or may not be included in
16 the 2 to 5 head group chains. If the head group
17 chains do not contain non-hydrocarbon groups then
18 the chains are preferably at least 4 carbons in
19 length. The same R₄ groups would apply as above.
20 Groups may originate from any position on the cyclic
21 group but preferably 2 chains should originate from
22 the 1,2 or 1,3 locations.

23

24 As described above the microemulsion fractions can
25 potentially be treated to recover the oil-phase,
26 preferably by adjusting the temperature, salinity,
27 or pH. For ionic surfactants this results in, for
28 example, a temperature induced phase separation,
29 which yields an upper phase containing the oil and
30 virtually no surfactant, and a lower phase of
31 aqueous surfactant. The oil phase can be separated

1 from the aqueous surfactant phase and both fractions
2 can be recycled.

3
4 A microemulsion or microemulsion forming formulation
5 including a surfactant of the invention is typically
6 made up of a suitable aqueous or organic solvent.
7 Typically the solvent can comprise from 1 to 99%wt
8 of the formulation. A suitable formulation may also
9 include other surfactant(s) which may be non-ionic,
10 anionic, cationic, zwitterionic, or amphoteric in
11 nature and which may be used in appropriate
12 proportions to enhance the capabilities of the
13 microemulsion or microemulsion forming system of the
14 invention.

15
16 If desired a microemulsion or microemulsion forming
17 surfactant formulation of the invention can comprise
18 one or more co-surfactant(s) which may be used in
19 appropriate proportions to enhance the capabilities
20 of the microemulsion or microemulsion forming
21 system.

22
23 One or more organic co-solvents may also be employed
24 if desired in order to enhance the capabilities of
25 the microemulsion or microemulsion forming system.

26
27 One or more chemical building agents may also be
28 included in order to enhance the capabilities of the
29 microemulsion or microemulsion forming system.
30 Similarly, chemical complexing or sequestering
31 agents can be included in formulations of the

1 invention in order to enhance the capabilities of
2 the microemulsion or microemulsion forming system.

3

4 If desired, one or more chemical components which
5 act as flocculating or coagulating agents can also
6 be used in order to allow the flocculation of fines
7 and hence prevent the build-up of fines in the
8 formulated system.

9

10 The invention also extends to a compound having the
11 general structure:

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22 III

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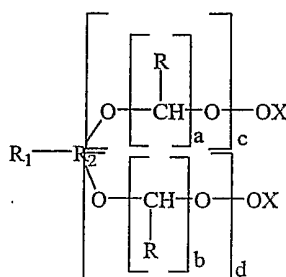
24 where R_1 is a hydrocarbon group including H,
25 branched or linear alkyl chains, substituted alkyl,
26 alkenyl, aryl, alkaryl or cyclic groups;

27

28 R_2 is any of C, N, P, B, S, or SiO_4 or any subgroups
29 thereof and preferably carbon;

30

31 R is O, H, OH, CH_3 , $(CH_2)_nCH_3$, CH_2OH , $(CH_2)_nOX$ or any
32 combinations thereof where n is from 1 to 10;



1
2 X is H, sulphate, sulphonate, carboxylate, a pH
3 sensitive group e.g. lactone, or any mono- di- or
4 oligio-saccharide e.g. galactose, fructose, sucrose,
5 or maltose or any combination thereof;
6
7 a and b are in the range 1 - 10 each and are
8 preferably 1 - 8 carbons long and most preferably
9 1 - 4;
10
11 c and d are in the range 1 - 7 each and are
12 preferably 1 - 5 units long or any combinations
13 thereof;
14
15 R1 may optionally include non-hydrocarbon elements
16 e.g. ethers or esters.
17
18 The chain length of the group should be C1 to C28,
19 preferably in the range C3 to C24, and most
20 preferably C8 to C20.
21
22 Di-anionic surfactants are preferred, and more
23 preferably is a disulphate.
24
25 Advantageously, a and b are in the range 1 to 4 such
26 that they are alkoxy moieties preferably ethoxy,
27 propoxy, butoxy or combinations thereof. Most
28 preferably the moieties are the same in each chain.
29
30 c and d may differ in value but preferably c and d
31 are equal in number.
32

1 Non-hydrocarbon groups may or may not be included in
 2 the 2 to 5 head group chains. If the head chains do
 3 not contain non-hydrocarbon groups then the chains
 4 are preferably at least 4 carbons in length. The
 5 same R groups apply as above.

6
 7 The invention also provides compounds having the
 8 general formula

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20 IV

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22 where R_3 = any cyclic hydrocarbon which may or may
 23 not include non-hydrocarbon elements.

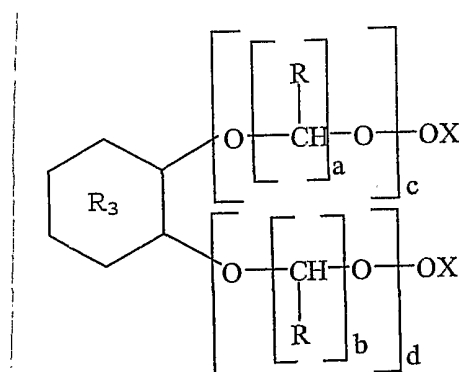
24

25 R is O, H, OH, CH_3 , $(CH_2)_nCH_3$, CH_2OH , $(CH_2)_nOX$ or any
 26 combinations thereof where n is from 1 to 10;

27

28 X is H, sulphate, sulphonate, carboxylate, a pH
 29 sensitive group e.g. lactone, or any mono- di- or
 30 oligio-saccharide e.g. galactose, fructose, sucrose,
 31 or maltose or any combination thereof;

32



1 a and b are in the range 1 - 10 each and are
2 preferably 1 - 8 carbons long and most preferably 1
3 - 4;

4

5 c and d are in the range 1 - 7 each and are
6 preferably 1 - 5 units long or any combinations
7 thereof.

8

9 The R₃ cyclic hydrocarbon may be C1 to C24 in
10 composition, preferably C4 to C20 and most
11 preferably C6 - C12. The ring may or may not
12 contain any number of double bonds. The ring may
13 also contain up to 4 other hydrocarbon groups or
14 chains originating at any location. The ring may
15 also contain adjoining R groups including alkyl
16 groups (branched or linear) and further cyclic
17 groups and any combinations thereof.

18

19 Di-anionic surfactants are preferred, most
20 especially disulphate.

21

22 a and b are preferably in the range 1 to 4 to
23 provide alkoxy moieties preferably ethoxy, propoxy,
24 butoxy or combinations thereof. Most preferably the
25 moieties are the same in each chain.

26

27 c and d may differ in value but preferably c and d
28 are equal in number.

29

30 Non-hydrocarbon groups may or may not be included in
31 the 2 to 5 head group chains. If the head chains do
32 not contain non-hydrocarbon groups then the chains

1 are preferably at least 4 carbons in length.
2 Chains may originate from any position on the cyclic
3 group but preferably 2 chains should originate from
4 the 1,2 or 1,3 locations.

5
6 The invention therefore provides microemulsion
7 forming surfactants developed for practical and cost
8 efficient applications. These surfactants permit
9 the use of O/W microemulsion and microemulsion
10 forming systems in particular in suitable
11 applications to replace more traditional emulsions
12 and emulsion forming systems.

13
14 The surfactants of the invention are designed to be
15 both easily biodegradable in the environment and
16 non-toxic in nature.

17
18 For example, in a preferred embodiment, the
19 surfactants of the invention have just two head
20 chains and as such the biodegradability and thus
21 the toxicity of the molecules is reduced as there is
22 less branching in their structure. The compounds of
23 the invention do not incorporate subgroups which may
24 be released as toxic secondary breakdown products.
25 This is a well known problem which has come to light
26 with some of the more traditional surfactant types
27 eg. those that contain benzene rings producing
28 phenol groups as breakdown products (sodium
29 dodecylbenzene sulphonate). Surfactant formulations
30 employing the compounds of the invention therefore
31 should not be dangerous, toxic, corrosive, flammable
32 or explosive.

1
2 Because the compounds of the invention are
3 microemulsion formers in their own right (forming
4 true ternary systems) the previously necessary and
5 costly development work and indeed use of complex
6 surfactant formulations for many applications may be
7 avoided. Accordingly, costs are reduced and
8 environmental benefits are enhanced. The compounds
9 of the invention may therefore be employed to
10 produce simpler and more efficient surfactant based
11 systems.

12
13 The advantages of the surfactant molecules and
14 microemulsion systems containing the molecules are
15 many depending on their application.

16
17 Because significant amounts of one phase may be
18 efficiently solubilised in the other and because
19 phase separation does not readily occur there may be
20 aesthetic reasons for their application in many
21 products.

22
23 Furthermore these molecules may be applied within
24 extremely efficient cleaning systems across the
25 board when compared to using emulsion forming
26 surfactants and emulsion type formulation systems.
27 This is due to both the inherent lower interfacial
28 surface tensions achieved by microemulsions and the
29 highly efficient solubilising capacity of
30 microemulsions described above compared to emulsion
31 systems.

32

1 Di-anionic surfactants are also known to have
2 extremely strong detergency properties when compared
3 to other types of surfactant eg. cationic
4 surfactants. Using molecules which are known to have
5 a very efficient level of detergency power has
6 obvious advantages over other surfactants for
7 general cleaning applications.

8
9 One advantage of the more advanced and specialised
10 molecular designs of the invention is that they may
11 be di- or even tri-anionic in nature (for example
12 have twin sulphate or sulphonate head groups). Di-
13 anionic surfactants are known to be less susceptible
14 to some environmental variables such as changes in
15 temperature or salt concentrations than are other
16 types of surfactant - including some singularly
17 anionic surfactants. Non-ionic surfactants in
18 particular are known to be greatly affected by such
19 variables. The same may be true for many quaternary
20 systems - especially those which have a considerable
21 nonionic constituent. Using the more robust
22 surfactants of the invention may be highly
23 advantageous when using these molecules in
24 industrial or domestic applications where the
25 environmental variables may be expected to change or
26 be highly variable. On the whole di-anionic systems
27 are therefore robust in nature.

28
29 Anionic surfactants are also known for their cost
30 advantages in general as being some of the cheaper
31 types of surfactant to manufacture on an industrial
32 scale.

1
2 As indicated above, a considerable advantage of
3 microemulsion systems is that the two different
4 phases can be cleanly separated from each other.
5 This is a very major advantage when considering
6 industrial applications where emulsion formation is
7 a problem causing difficult separation of the
8 organic and aqueous phases. In addition normal
9 emulsion forming surfactants have a tendency to
10 contaminate the organic phase rendering the recycled
11 organic product unusable for further applications.

12
13 Phase separation can be effected by several means
14 depending on the design of the surfactant system.
15 One method is by way of a thermally induced phase
16 separation. For example, an O/W microemulsion may be
17 warmed causing the surfactant to become more
18 hydrophilic in nature (more soluble in the aqueous
19 phase). The surfactant thus becomes preferably
20 soluble in the aqueous phase and migrates into this
21 phase from the micellar oil/water interface
22 releasing the oil to the surface which phase
23 separates out and rises to the surface as a less
24 dense layer. Such mixtures may be separated using
25 centrifugation techniques for example and the oil is
26 tapped off leaving an aqueous surfactant (or a
27 dilute O/W microemulsion containing only small
28 amounts of oil depending on recycling efficiency)
29 for recycling.

30
31 Alternatively if more concentrated surfactant
32 solutions are formed and utilised at higher

1 temperatures the O/W microemulsion may be cooled re-
2 crystallising the surfactant as the temperature
3 drops below the Critical Micellar Temperature (CMT)
4 which again releases the oil to the surface.

5
6 In addition if the surfactant is designed such that
7 the molecules contain a pH sensitive group eg. an
8 amine or a lactone group the surfactant may be
9 precipitated out of solution or the molecular
10 solubility characteristics changed by adjusting the
11 pH accordingly, via addition of chemicals or the
12 application of an electrical current, changing the
13 physico-chemical behaviour of the surfactant and
14 releasing the oil to the surface for separation. On
15 readjusting the pH the surfactant may be converted
16 back into its original form releasing it back into a
17 solution for recycling.

18
19 Another technique that may be used is to adjust the
20 salt concentration which, under suitable
21 circumstances for certain surfactants, inflicts a
22 change in the Winsor type system which can result in
23 the release of oil. Ultra-filtration, ultra-
24 centrifugation, and coalescing techniques/chemicals
25 may all be utilised to facilitate the recovery of
26 non-polar substances from the O/W microemulsion.

27
28 Yet another technique is to precipitate the
29 surfactant out of solution by chemical reaction
30 which would allow phase separation to occur
31 releasing surfactant free oil. This step may or may

1 not be reversible depending on the chemistry
2 involved.

3
4 Indeed phase separation using microemulsion systems
5 may not even need to be inflicted depending on the
6 type of microemulsion system utilised. For example
7 if a Winsor I type system is used (an O/W
8 microemulsion in the presence of an excess oil
9 phase) a significant amount of the oil is naturally
10 recycled to the surface of the system. Furthermore
11 the oil recovered again remains essentially
12 surfactant free and may be applied in turn to
13 further uses.

14
15 Another advantage in increasing the anionic nature
16 of these surfactants for environmental uses is that
17 they naturally repel fine colloidal clay
18 particulates which have a like negative charge.
19 Fines and colloidal clays are a common problem with
20 aqueous systems and using this type of molecule
21 ensures that the fines is separate out more easily
22 and less surfactant lost to the environment adhering
23 to the surface of the solids.

24
25 Readily available flocculating agents may also be
26 utilised effectively within water continuous O/W
27 microemulsion systems. This has not been the case
28 when emulsion systems are used as oil contact with
29 the flocculating / coagulating agents has occurred
30 disrupting the system and the action of the chemical
31 agents added. (Since O/W microemulsions are water
32 continuous and there is no direct contact with the

1 oil no interference occurs).

2

3 Various embodiments of the invention will now be
4 described, by way of example only, having regard to
5 the accompanying drawings in which:

6

7 Figure 1 is a pseudoternary phase diagram of
8 (SDS + B ratio, 1:1 by weight) in 0.58M NaCl and
9 Novatec (Trade Mark) Base Fluid at 25° Celsius;

10

11 Figure 2 is a ternary phase diagram of Nonionic
12 Union Carbide surfactant Triton RW-50 (Trade Mark) in
13 0.58M NaCl and Novatec B (Trade Mark) Base Fluid at
14 25°C.

15

16 Figure 3 is a ternary phase diagram of AOT
17 (Trade Mark) in 0.025M NaCl and Heptane at 25°C.

18

19 Figure 4 is a quaternary phase diagram of AOT
20 (Trade Mark) (at 1:2 weight ratio), water and Novatec
21 (Trade Mark) Base Fluid at 25°C).

22

23 Figure 5 is a shows molecular structure of
24 known W/O microemulsion forming surfactants - AOT
25 (Trade Mark) and NH₄DEHP respectively.

26

27 Figure 6 is a schematic representation of the
28 theory behind the surfactant / co-surfactant
29 monolayer structure in the SDS/B O/W microemulsion
30 system.

31

32 Figure 7 is a schematic representation of the

1 first step to O/W microemulsion forming surfactant
2 design;

3

4 Figure 8 is a schematic representation of the
5 second step to O/W microemulsion forming surfactant
6 design;

7

8 Figure 9 is a schematic representation of the
9 final step in O/W microemulsion forming surfactant
10 design;

11

12 Figure 10 is a photograph of MiFoS $Y_1 C_{12}$
13 aqueous colourless transparent solutions at 5%wt
14 @25°C and 10%wt @25°C in 0.58M NaCl

15

16 Figure 11 is a photograph of a crude oil
17 contaminated sample treated with 10%wt MiFoS $Y_1 C_{12}$
18 in 0.58M NaCl @25°C in which formation of the oil-
19 in-water (O/W) microemulsion and complete removal of
20 surfactant free oil is apparent;

21

22 Figure 12 is a synthesis pathway for the
23 sulphated Triton RW-50 reaction (non-ionic to di-
24 anionic tertiary amine oil-in-water O/W
25 microemulsion forming surfactant) (Y-shaped
26 surfactant);

27

28 Figure 13 is a synthesis pathway for
29 manufacturing an O/W microemulsion forming
30 surfactant (V-shaped surfactant); and

31

1 Figure 14 is an alternative synthesis pathway
2 for manufacturing an alternative O/W microemulsion
3 forming surfactant.

4
5 It has been shown that chemicals such as alcohols
6 have the potential to produce strong hydrogen bonds
7 with water. The alcohol co-surfactants also have a
8 significant effect in altering the Hydrophile-
9 Lipophile-Balance (HLB) of the aqueous system which
10 must be compatible with the required HLB of the oil
11 to be solubilised if oil solubilisation and
12 microemulsion formation is to occur. In addition it
13 has been shown that quarternary systems have a large
14 degree of flexibility in the molecular composition
15 of the interface. This allows for a fluid and
16 continuous change in the proportions of each
17 constituent as shown in Figure 8. The result is an
18 extremely adaptive system capable of instantaneous
19 alteration at the interface as required.

20
21 The surfactant components of the invention have
22 structural properties which stabilise O/W
23 microemulsions without the need for a co-surfactant
24 or other chemical additives.

25
26 As stated above anionic water-in-oil (W/O)
27 microemulsion forming surfactants such as Aerosol-OT
28 (Trade Mark) (AOT) for example and other surfactants
29 eg. ammonium bis(ethylhexyl) hydrogen phosphate
30 (NH_4DEHP) are well known and some are readily
31 available at industrial scales. The structures of
32 some of these types of molecule are shown in Figure

1 5. They are described as true ternary systems as
2 they do not require the use of other surfactants or
3 co-surfactants in order to form W/O microemulsion
4 systems. Their W/O microemulsion forming properties
5 are well understood and are well documented in the
6 literature. In turn these surfactants may be
7 combined with co-surfactant chemicals to enhance
8 their microemulsion forming capabilities and improve
9 the flexibility of the systems such that they may
10 also form quaternary O/W W/O microemulsions (for
11 example see the quaternary phase diagram in Figure 4
12 for AOT).

13

14 Surfactant molecules of this type are able to form
15 very large single phase (Winsor IV) regions within
16 their ternary phase diagrams (see AOT ternary phase
17 diagram Figure 3). In many cases very significant
18 amounts of water can be taken up into an oil
19 continuous W/O microemulsion using relatively small
20 quantities of surfactant.

21

22 Although the applicants do not wish to be bound by
23 any particular theorem it is thought that much of
24 the above capabilities are due to the fact that the
25 molecules are able to form a cone or V-shaped
26 structure at the oil-water interface. The molecules
27 possess a large degree of inherent flexibility in
28 their structure indicated by δ in Figure 5. In this
29 fashion the shape of the cone structure of the
30 molecules is highly variable. This capability also
31 allows the close packing efficiency of the molecules
32 at the interface. These characteristics provide

1 these systems with similar capabilities to
2 quaternary systems described above.

3

4 As a result of adjusting the angles of the cone
5 (unit shape) to effect the radius of curvature of
6 the interface the size and shape of the micelles
7 formed can vary accordingly depending on variables
8 such as the quantities of water taken up into the
9 system, the surfactant concentration, and other
10 environmental variables eg. the salt concentration
11 and temperature.

12

13 The Applicants have succeeded in replicating the
14 above phenomenon in O/W forming surfactants.

15

16 Surfactant behaviour can be quantitated in terms of
17 a triangular phase diagram. The phase diagram for
18 the quaternary O/W microemulsion system water /
19 (SDS+B) / oil is shown in Figure 1. Here, (SDS+B) is
20 a mixture of the surfactant sodium dodecyl sulphate
21 (SDS) and butan-1-ol (B). B acts as a co-surfactant
22 in the system, enhancing the O/W microemulsion-
23 forming properties of SDS. As long as the SDS and B
24 are held at constant ratio, they can be treated as a
25 single component for the purpose of constructing the
26 phase diagram.

27

28 The phase diagram in Figure 1 was constructed with
29 the SDS : B ratio held at 1 : 1 by weight at 25°C.
30 The oil used was a medium chain length oil (C14 -
31 C16) Novatec (Trade Mark) B Linear Alkyl Olefin
32 (LAO) Base Fluid supplied by M-I Drilling Fluids UK

1 Ltd. This oil was a typical base fluid used in the
2 preparation of oil based drilling muds for
3 industrial use in the oil and gas industry.

4
5 The apexes of the phase triangle each correspond to
6 one of the components in 100% pure form by weight
7 ie. oil, water, or (SDS+B) at the stated ratio. Any
8 point on one of the vertices between two of these
9 points corresponds to a mixture of those two
10 components in a defined ratio (given in percent
11 weight - %wt). Thus point A on the water-surfactant
12 axis in Figure 1 corresponds to a system containing
13 (SDS + B) and water in 40:60 %wt ratio respectively.
14 Any point within the triangle corresponds to a
15 unique combination of the three components in a
16 defined ratio. The physical state of the mixture at
17 equilibrium is mapped onto the phase diagram. The
18 phase triangle in Figure 1 is characterised by the
19 prominent single phase microemulsion region, known
20 as a Winsor IV system, which extends from the
21 SDS+B/water axis towards the SDS+B/oil axis.

22
23 (A similar phase diagram in Figure 2 shows the
24 Winsor IV region obtained for a known true ternary
25 nonionic microemulsion forming surfactant
26 manufactured by Union Carbide - Triton RW-50 (Trade
27 Mark).

28
29 An O/W microemulsion was therefore developed in
30 using the emulsion forming surfactant sodium dodecyl
31 sulphate (SDS). SDS requires a co-surfactant butanol
32 (B) to be added to the system in order that O/W

1 microemulsions can be formed with medium chain
2 length oils. As a result, the system used was termed
3 a pseudoternary or quaternary since the surface
4 active agent at the oil-water interface comprised
5 two separate constituents.

6
7 When using the SDS/B prototype system an excess of
8 butanol is added. Butanol is only partially soluble
9 in aqueous media (91mL^{-1} H_2O at 25°C) but is
10 completely miscible with ether and organic solvents.
11 The majority of the butanol in the microemulsion
12 prototype system therefore resides at the oil-water
13 interface of the micelles or within the oil phase
14 within the micellar structures themselves. As more
15 oil is taken up into the microemulsion system some
16 of the excess butanol within the micelles may
17 migrate to the interface in order to allow the
18 micelles to expand. The effect of this migration is
19 to increase the ratio of SDS:B at the interface and
20 thus to change the angle of the cone formed by the
21 SDS/B unit structures. This process allows more oil
22 to be taken up into the system and is shown
23 diagrammatically in Figure 6.

24
25 The SDS/B system was mimicked by combining the co-
26 surfactant and the surfactant molecules together in
27 a suitable ratio into one molecule in its own right
28 such that the above characteristics of the SDS/B
29 system could be duplicated in one molecular unit at
30 the interface. The most appropriate method of
31 achieving this was to attach the butanol molecules
32 at their base to the SDS molecule in such a fashion

1 that the hydroxyl groups were maintained at the
2 interface alongside the sulphate head group whilst
3 still maintaining the molecular inherent flexibility
4 such that it may adjust the angle of the unit cone
5 formed in the same way as in the SDS/B system. The
6 result was a molecule as shown in Figure 7 which is
7 generally Y shaped in structure.

8
9 This molecule was developed still further to
10 increase the inherent flexibility in the molecule to
11 form a more V shaped molecule as shown in Figure 8.
12 In all cases a similar number of hydrocarbon (water
13 insoluble / hydrophobic) and non-hydrocarbon (water
14 soluble / hydrophilic) groups of the molecule were
15 maintained in order to keep the same Hydrophile -
16 Lipophile Balance (HLB) of the system.

17
18 The Y and V shaped molecules were further modified
19 to more closely resemble a mirror image of AOT type
20 molecules i.e. instead of having a water soluble
21 tail group and oil soluble head groups the molecule
22 was designed to have an oil soluble tail group and
23 water soluble head groups as shown in Figure 9.

24
25 The ratios of hydrocarbon (water insoluble /
26 hydrophobic) and non hydrocarbon (water soluble /
27 hydrophilic) groups of the molecule may be adjusted
28 in order to change the Hydrophile - Lipophile
29 Balance (HLB) of the molecules depending on the
30 required HLB of the oil to be solubilised into the
31 O/W microemulsion.

32

1 The microemulsion forming surfactants outlined
2 herein are preferably anionic or nonionic Y (and V
3 shaped) surfactant molecules with microemulsion
4 forming capabilities whose generic designs are
5 outlined by the parameters laid out below. Anionic
6 molecules may have an alkali or alkaline earth metal
7 counter-ion eg. Na, Mg, Ca, K, or a substituted or
8 un-substituted ammonium ion etc.

9

10

11 This invention will now also be described having
12 regard to the following non-limiting examples:

13

1 **Examples**

2

3 In the examples the amounts of oil taken up into di-
4 anionic O/W microemulsion systems were studied using
5 a cloud point titration method. A pure oil was
6 slowly titrated into a weighed amount of the
7 transparent aqueous surfactant solution comprising a
8 known surfactant concentration by weight. The
9 systems were left to equilibrate overnight after
10 each addition of oil. The titration with oil was
11 continued until the surfactant solution reached the
12 cloud point and the system ceased to solubilise the
13 oil and thus became opaque. From this point phase
14 separation occurred releasing the excess un-
15 solubilised pure oil to the surface (Winsor I
16 system). The percentage weight (%wt) of oil that can
17 be solubilised into each transparent and stable
18 aqueous O/W microemulsion (ie. does not phase
19 separate) could then be calculated.

20

21 All studies were carried out at ambient temperature
22 (25°C) and at atmospheric pressure.

23

24 **Example 1**

25

26 The nonionic Union Carbide amine based surfactant
27 (Triton RW-50) (Trade Mark) was sulphonated using
28 known industrial chemical methods in the laboratory
29 shown in Figure 12. This produced a di-anionic
30 surfactant product which was found to be readily
31 soluble in distilled water at neutral pH.

32

1 100g of a 50%wt surfactant solution in distilled
2 water was prepared. This was titrated with toluene
3 (SD=0.865) until the cloud point was reached. The
4 system took up 30mls of toluene into an optically
5 transparent O/W microemulsion. This equated to
6 25.95g and a system containing 20.6%wt oil before
7 the aqueous O/W microemulsion system became opaque.

8

9 **Example 2**

10

11 As in Example 1, 100g of a 30%wt aqueous surfactant
12 solution using the above di-anionic surfactant
13 product was prepared in distilled water. This system
14 was titrated with heptane (SD=0.684). The system
15 took up 62.5mls of heptane into a transparent O/W
16 microemulsion before the cloud point was reached.
17 This equated to 42.8g or 29.94%wt oil solubilised.

18

19 **Example 3**

20

21 A synthesised di-anionic carbon based ethoxylated
22 surfactant as outlined in Figure 13 with a carbon
23 tail chain length of C₁₂ was employed. The
24 surfactant was readily soluble in water at low
25 temperatures. A 40%wt aqueous surfactant solution
26 was prepared using an OECD standard sea water
27 (brine) which contained 34g +/- 0.5g NaCl L⁻¹ in
28 water (0.58M NaCl). This surfactant system was
29 titrated with heptane (SD=0.684). The system took up
30 81.6mls heptane before the cloud point was reached.
31 This was equivalent to 55.84g or 35.84%wt oil.

32

1 **Example 4**

2

3 A synthesised carbon based ethoxylated di-anionic
4 surfactant as outlined in Figure 13 with a carbon
5 tail chain length of C_{14} was employed. Again the
6 surfactant was readily soluble in water at
7 temperatures below 60°C . A 30%wt aqueous surfactant
8 solution was prepared again using an OECD standard
9 sea water (brine) containing $34\text{g} \pm 0.5\text{g NaCl L}^{-1}$ in
10 water (0.58M NaCl). This surfactant system was
11 titrated with a medium chain length (C_{14} - C_{16}) Linear
12 Alkyl Olefin (LAO) synthetic base oil (Novatec Base
13 Fluid) (Trade Mark) supplied by MI Drilling Fluids
14 UK Ltd (SD=0.771). The system was capable of taking
15 up 10mls of this oil into an O/W microemulsion
16 before the cloud point was reached. This was
17 equivalent to 7.71g or 7.16%wt oil.

18

19 **Example 5**

20

21 Figures 11 and 12 should be referred to. In this
22 example a long chain oil contaminated sample has
23 been shaken for a period of 2 minutes with a 10%wt
24 surfactant solution in brine as was used and
25 demonstrated in Example 3 above. It can be clearly
26 seen that a Winsor I system was formed. The
27 contaminated sample has been thoroughly cleaned of
28 the crude oil which is released to the surface as a
29 pure oil phase (free of surfactant) and a
30 transparent O/W microemulsion has been formed in the
31 aqueous surfactant phase.

32

1 Surfactants of the invention are therefore capable
2 of forming true ternary O/W microemulsion systems.
3 This has been demonstrated when using both distilled
4 water and brine as the aqueous phase. In addition it
5 has been demonstrated that both light oils and
6 heavier oils can be solubilised into O/W
7 microemulsion systems using these molecular designs.
8 Furthermore the cleaning capabilities of these
9 surfactant systems and the recovery of surfactant
10 free oil from the contaminated sample has been
11 demonstrated. In all cases these results have been
12 achieved without the need for mixing or formulating
13 surfactants and indeed the requirement of co-
14 surfactant and/or co-solvent chemical additives has
15 not been necessary. These are thus true ternary O/W
16 microemulsion systems using di-anionic microemulsion
17 forming surfactants.

18

19 Accordingly, the invention provides novel and
20 inventive molecules with surface active properties
21 providing the surfactant molecules with suitable
22 microemulsion forming capabilities. These
23 microemulsion forming surfactants have been
24 facilitated for the practical and cost efficient use
25 of the technology for a variety of industrial,
26 environmental and domestic applications. The designs
27 outlined herein may enable and permit the use of, in
28 particular, di-anionic O/W microemulsion (forming)
29 surfactants and microemulsion surfactant based
30 formulations in such applications to replace more
31 traditional emulsion forming surfactants, emulsion
32 forming surfactant formulations, and emulsion

1 systems. Examples of applications of this technology.
2 and product formulations therefore include, but are
3 not limited, to the remediation of oils from
4 (ground) water and aquifers.

5

6 However, if desired, the molecular designs outlined
7 herein may be combined with other chemicals in
8 suitable proportions in order to increase the
9 microemulsion capabilities of these systems.

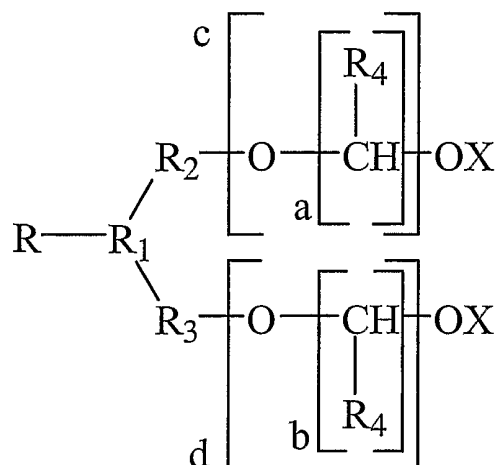
1 CLAIMS

2

3 1. A compound having the general formula I

4

5



6

7

8

9 wherein R comprises a hydrocarbon group including H,

10 branched or linear alkyl chains, substituted alkyl,

11 alkenyl, aryl, alkaryl or cyclic groups;

12

13 R₁ is any of C, N, P, B, S, or SiO₄ or any subgroups

14 thereof;

15

16 R₂ is any of a covalent bond, O, CH₂, (CH₂)_n where n

17 may be 1-10 carbons long;

18

19 R₃ is any of a covalent bond, O, CH₂, (CH₂)_n where n

20 may be 1-10 carbons long;

21

22 R₂ and R₃ may be the same or different;

23

1 R_4 is any of O, H, OH, CH_3 , $(CH_2)_nCH_3$, $(CH_2)_nOH$,
2 $(CH_2)_nOX$ or any combinations thereof where n is from
3 1 to 10.

4
5 OX is a water soluble group;

6
7 chains a and b are in the range 1 - 10 carbons each;
8 and

9
10 the alkoxy chains c and d are in the range 1 - 20
11 units each.

12
13 2. A compound as claimed in Claim 1 wherein R
14 further comprises a non-hydrocarbon element.

15
16 3. A compound as claimed in Claim 2 wherein the
17 non-hydrocarbon element comprises an ether or an
18 ester group.

19
20 4. A compound as claimed in any of Claims 1 to 3
21 wherein R has a chain length of C1 to C30.

22
23 5. A compound as claimed in any of Claims 1 to 4
24 wherein R has a chain length of C3 to C24.

25
26 6. A compound as claimed in any of Claims 1 to 5
27 wherein R has a chain length of C6 to C20.

28
29 7. A compound as claimed in any of Claims 1 to 6
30 wherein n in the $(CH_2)_n$ group of R_2 is from 1 to 6.

31
32 8. A compound as claimed in any of Claims 1 to 7
33 wherein n in the $(CH_2)_n$ group of R_3 is from 1 to 6.

1

2 9. A compound as claimed in any of Claims 1 to 8
3 wherein OX is selected from the group comprising OH,
4 sulphate, sulphonate, carboxylate, borate, a borate
5 based group or a pH sensitive group.

6

7 10. A compound as claimed in Claim 9 wherein the pH
8 sensitive group is selected from the group
9 comprising lactone, or a mono-, di- or oligo-
10 saccharide.

11

12 11. A compound as claimed in Claim 10 wherein the
13 saccharide comprises galactose, fructose, sucrose,
14 or maltose or any combination thereof.

15

16 12. A compound as claimed in any of Claims 1 to 11
17 wherein a and b range from 1 to 8 carbons.

18

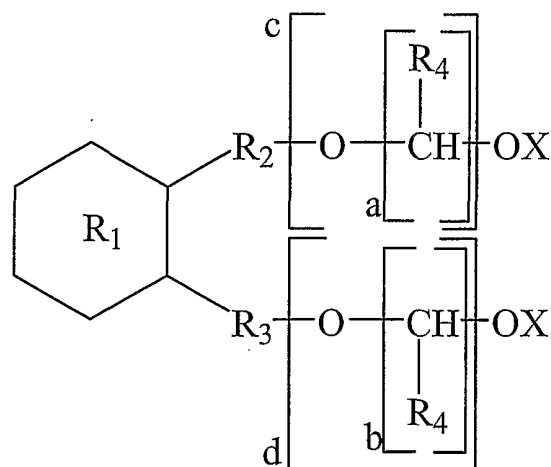
19 13. A compound as claimed in any of Claims 1 to 12
20 wherein a and b range from 1 to 4.

21

22 14. A compound as claimed in any of Claims 1 to 13
23 wherein the alkoxy chains c and d comprise from 2 to
24 10 units.

25

26 15. A compound having the general formula II



1

2

3

4

5 wherein R_1 is any cyclic hydrocarbon which may or
6 may not include non hydrocarbon elements;

7

8 R_2 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
9 may be 1-10 carbons long;

10

11 R_3 is any of a covalent bond, O, CH_2 , $(CH_2)_n$ where n
12 may be 1-10 carbons long;

13

14 R_2 and R_3 may be the same or different;

15

16 R_4 is any of O, H, OH, CH_3 , $(CH_2)_nCH_3$, $(CH_2)_nOH$,
17 $(CH_2)_nOX$ where n is from 1 to 10 or any combination
18 thereof;

19

20 OX is a water soluble group;

21

22 chains a and b are in the range 1 - 10 carbons each;
23 and

24

1 the alkoxy chains c and d are in the range 1 - 20
2 units each;

3

4 16. A compound as claimed in Claim 15 wherein the
5 cyclic hydrocarbon is a C1 to C24 cyclic
6 hydrocarbon.

7

8 17. A compound as claimed in Claim 15 or Claim 16
9 wherein the cyclic hydrocarbon is a C4 to C20
10 hydrocarbon.

11

12 18. A compound as claimed in any of Claims 15 to 17
13 wherein the cyclic hydrocarbon is a C4 to C12
14 hydrocarbon.

15

16 19. A compound as claimed in any of Claims 15 to 18
17 wherein the cyclic ring comprises at least one
18 double bond.

19

20 20. A compound as claimed in any of Claims 15 to 19
21 wherein the cyclic ring comprises up to 4 adjoining
22 groups.

23

24 21. A compound as claimed in Claim 20 wherein the
25 adjoining groups are selected from the group
26 comprising branched or linear alkyl chains,
27 substituted alkyl, alkenyl, aryl, alkaryl, a cyclic
28 group or a combination thereof.

29

30 22. A compound as claimed in any of Claims 15 to 21
31 wherein n in the $(CH_2)_n$ group of R_2 is from 1 to 6.

32

23. A compound as claimed in any of Claims 15 to 22 wherein OX is selected from the group comprising OH, sulphate, sulphonate, carboxylate, borate, a borate based group or a pH sensitive group.

24. A compound as claimed in Claim 23 wherein the pH sensitive group is selected from the group comprising lactone, or a mono-, di- or oligo-saccharide.

10

11 25. A compound as claimed in Claim 24 wherein the

12 saccharide is selected from the group comprising

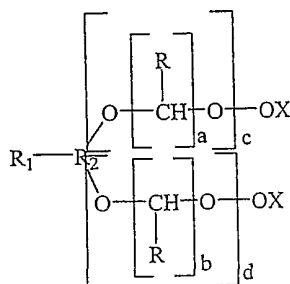
13 lactone, or a mono-, di- or oligio-saccharide.

15 26. A compound as claimed in any of Claims 15 to 25
16 wherein a and b range from 1 to 8 carbons.

18 27. A compound as claimed in any of Claims 15 to 26
19 wherein a and b range from 1 to 4.

21 28. A compound as claimed in any of Claims 15 to 27
22 wherein the alkoxy chains c and d comprise from 2 to
23 10 units.

25 29. A compound having the general structure III



1 where R_1 is a hydrocarbon group including H,
 2 branched or linear alkyl chains, substituted alkyl,
 3 alkenyl, aryl, alkaryl or cyclic groups;

4

5 R_2 is any of C, N, P, B, S, or SiO_4 or any subgroups
 6 thereof;

7

8 R is O, H, OH, CH_3 , $(\text{CH}_2)_n\text{CH}_3$, CH_2OH , $(\text{CH}_2)_n\text{OX}$ or any
 9 combinations thereof where n is from 1 to 10;

10

11 X is H, sulphate, sulphonate, carboxylate, a pH
 12 sensitive group, a mono- di- or oligio-saccharide or
 13 any combination thereof;

14

15 a and b in the range 1 - 10 each;

16

17 c and d are in the range 1 - 7 each;

18

19 30. A compound having the general formula IV

20

21

22

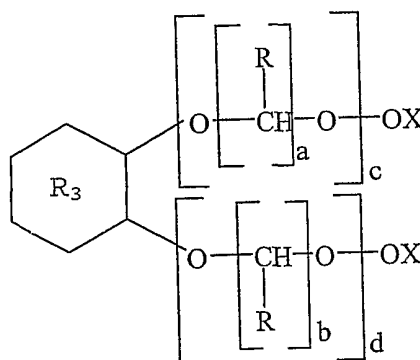
23

24

25

26

27



28 where R_3 - any cyclic hydrocarbon;

29

30 R is O, H, OH, CH_3 , $(\text{CH}_2)_n\text{CH}_3$, CH_2OH , $(\text{CH}_2)_n\text{OX}$ or any
 31 combinations thereof where n is from 1 to 10

32

1 X is H, sulphate, sulphonate, carboxylate, a pH
2 sensitive group, a mono- di- or oligio-saccharide or
3 any combination thereof;

4

5 a and b are in the range 1 - 10;

6

7 c and d are in the range 1 - 7;

8 and

9 the R₃ cyclic hydrocarbon is a C1 to C24 hydrocarbon;

10

11 31. A surfactant comprising a compound as claimed
12 in any of Claims 1 to 30.

13

14 32. A surfactant as claimed in Claim 31 wherein the
15 surfactant is an anionic surfactant.

16

17 33. A surfactant as claimed in Claim 32 wherein the
18 surfactant is a non-ionic surfactant.

19

20 34. A surfactant as claimed in Claim 32 further
21 comprising an alkali or alkaline earth metal
22 counter-ion.

23

24 35. A method of forming an oil in water
25 microemulsion comprising mixing a solution of a
26 compound as claimed in any of Claims 1 to 30 with an
27 oil to form the oil in water microemulsion.

28

29 36. Use of a compound as claimed in any of Claims 1
30 to 30 in the formation of an oil-in-water
31 microemulsion.

32

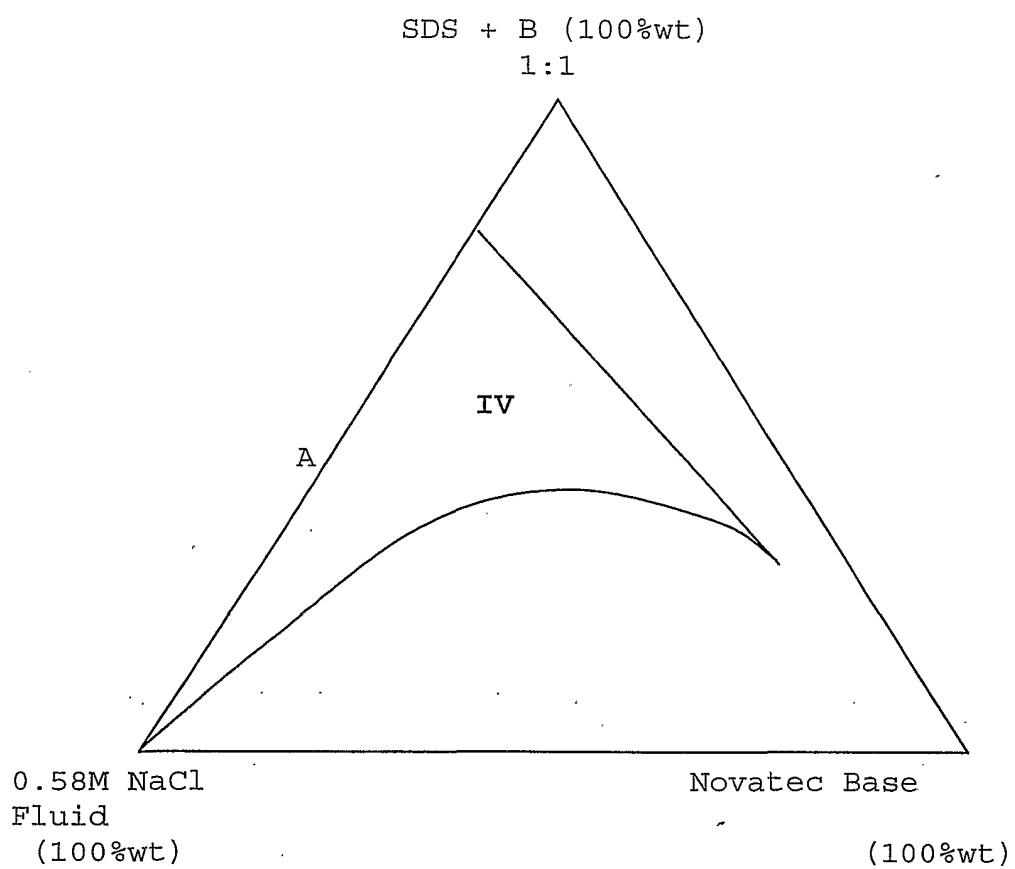


Figure 1. Pseudoternary phase diagram (SDS + B ratio, 1:1 by weight) 0.58M NaCl and Novatec Base Oil at 25°C.

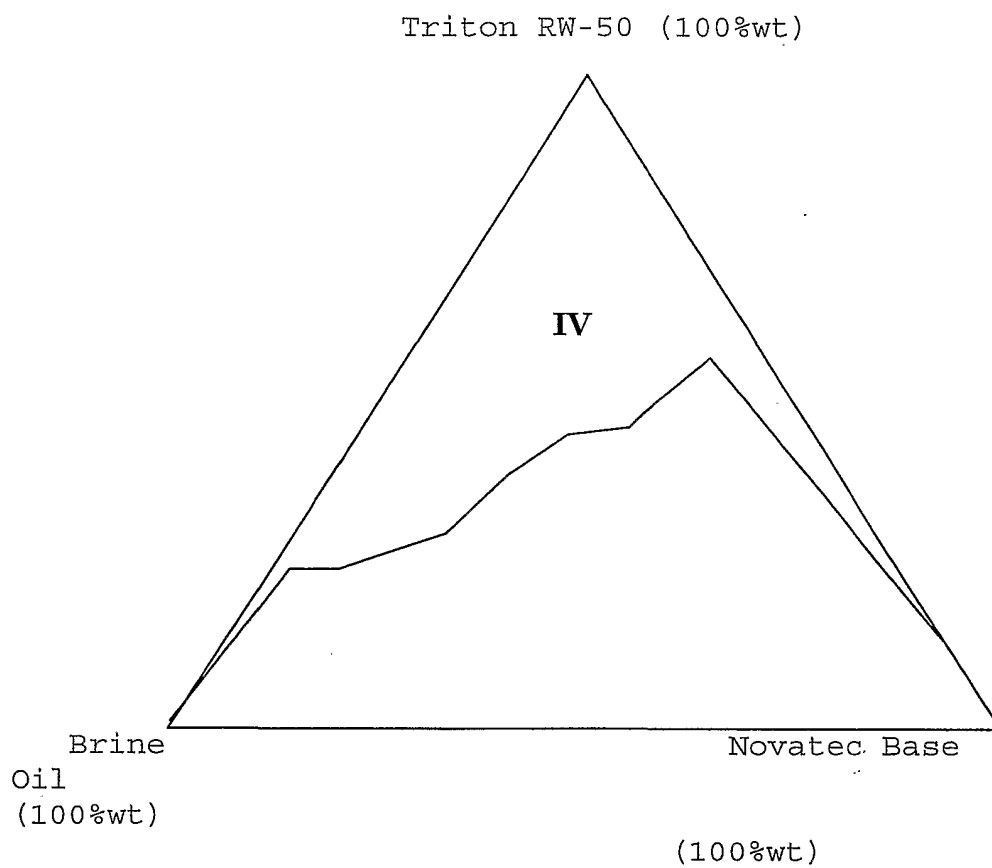


Figure 2. Ternary phase diagram (Nonionic Triton RW-50, 0.58M NaCl and Novatec B Base Fluid at 25°C).

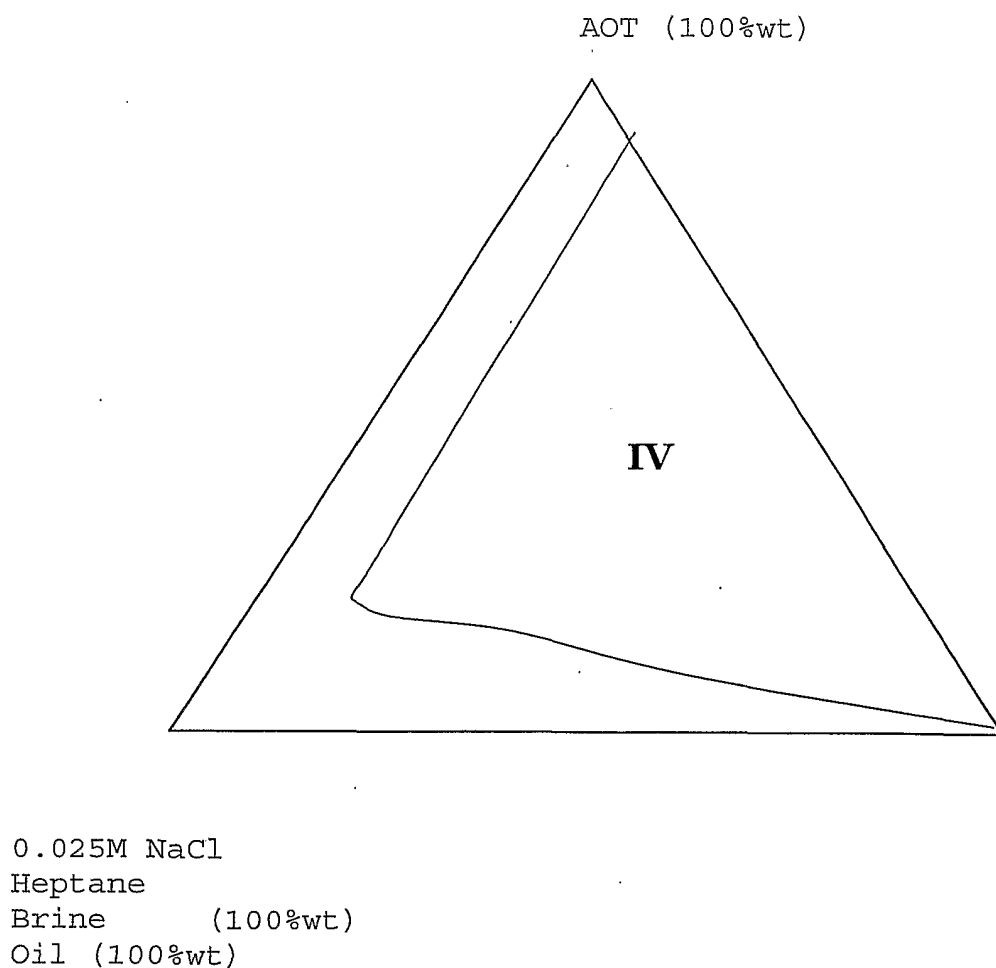


Figure 3. Ternary phase diagram (AOT, 0.025M NaCl and Heptane at 25°C).

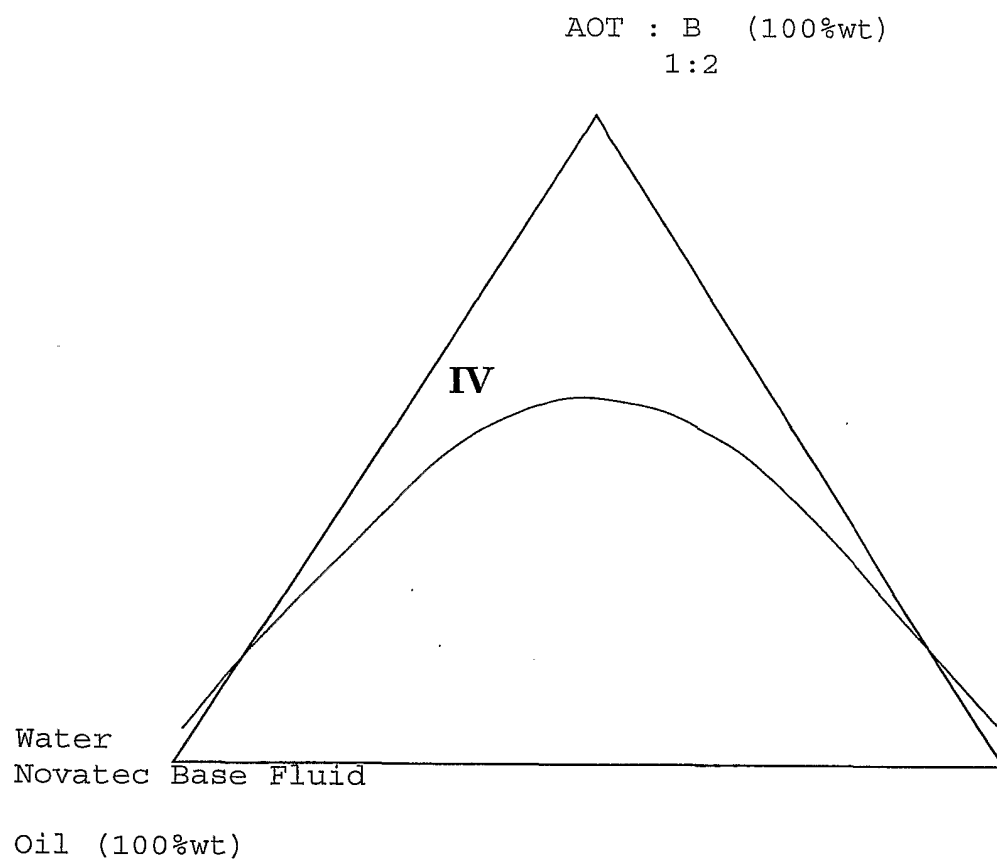


Figure 4. Ternary phase diagram (AOT:B at 1:2 weight ratio, water and Novatec Base Fluid at 25°C).

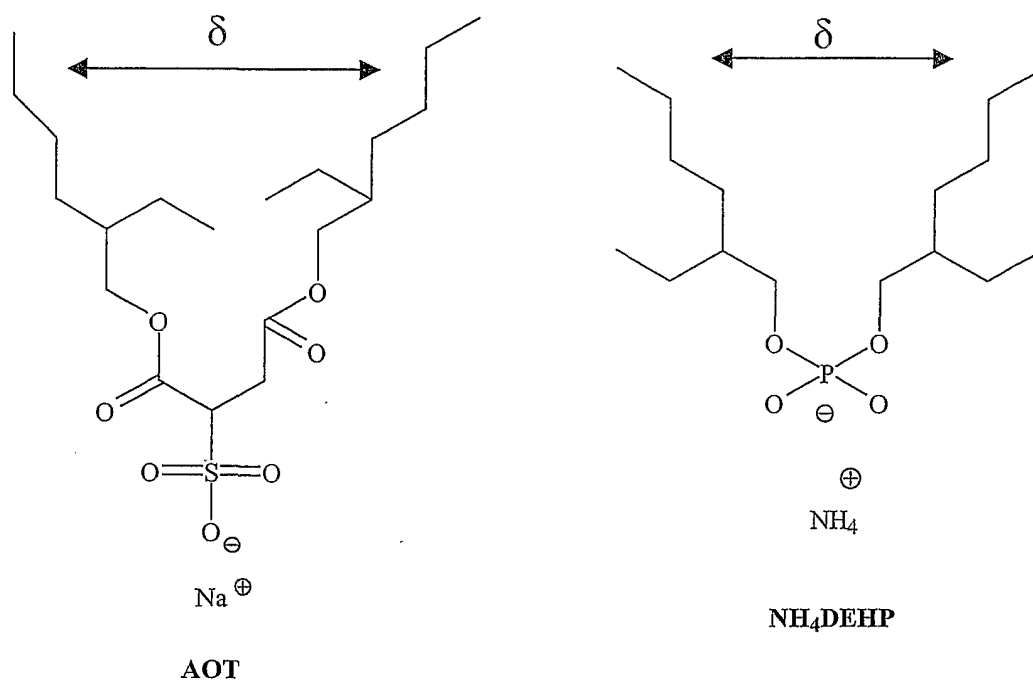
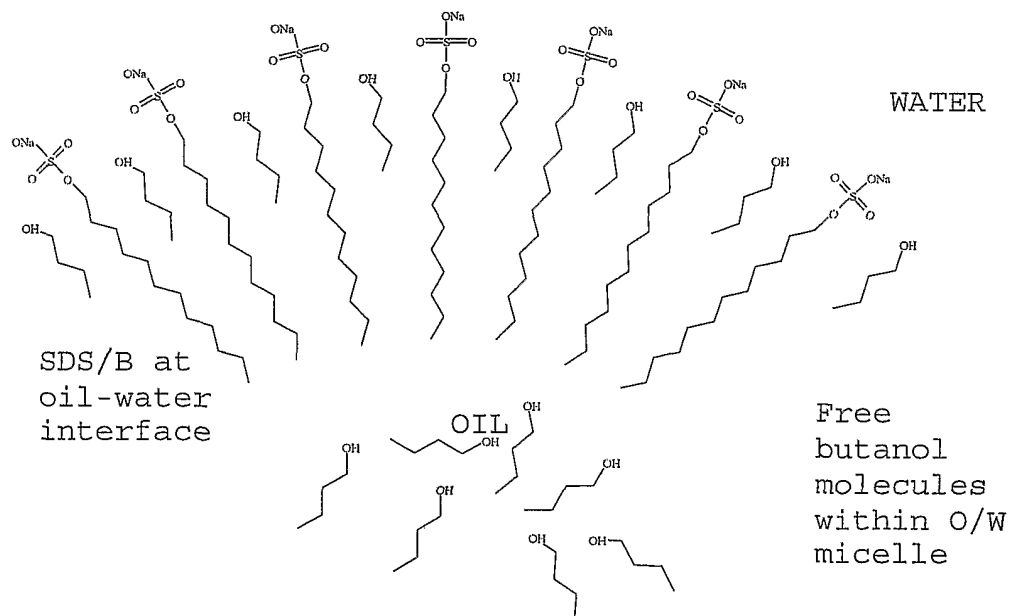
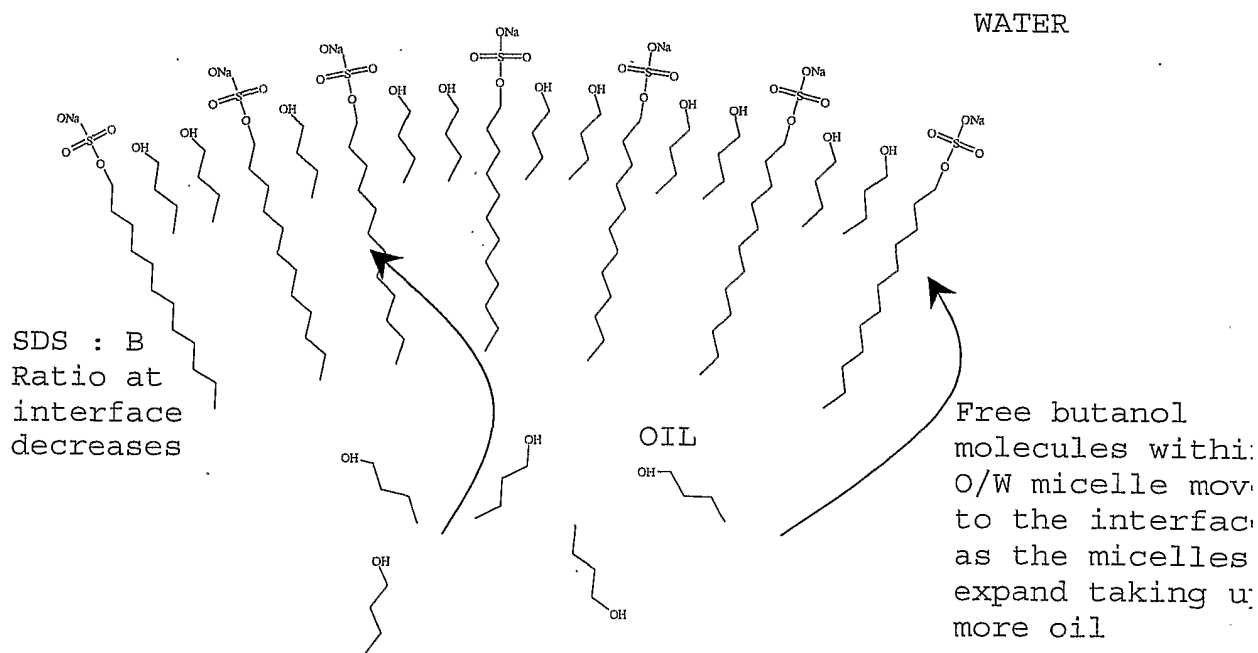


Figure 5. Molecular structures of known W/O microemulsion forming surfactants - AOT and NH₄DEHP



Micelle has a high radius of curvature.



Micelle has a lower radius of curvature - more oil taken up into the system.

Figure 6. Theory behind surfactant / co-surfactant monolayer structure in the SDS/B O/W microemulsion system.

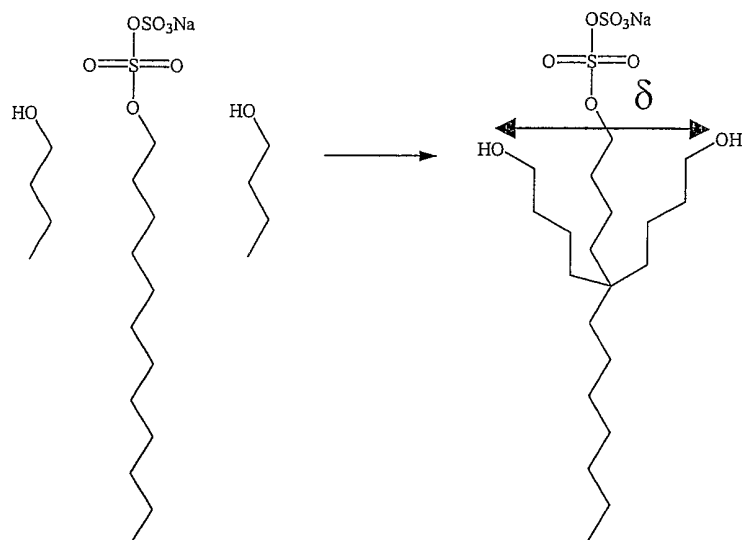


Figure 7. First step to O/W microemulsion forming surfactant design.

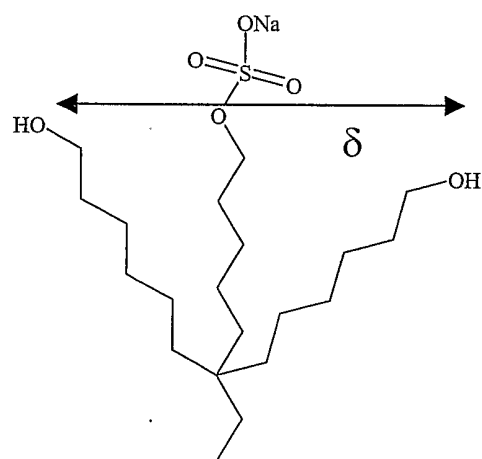


Figure 8. Second step to O/W microemulsion forming surfactant design.

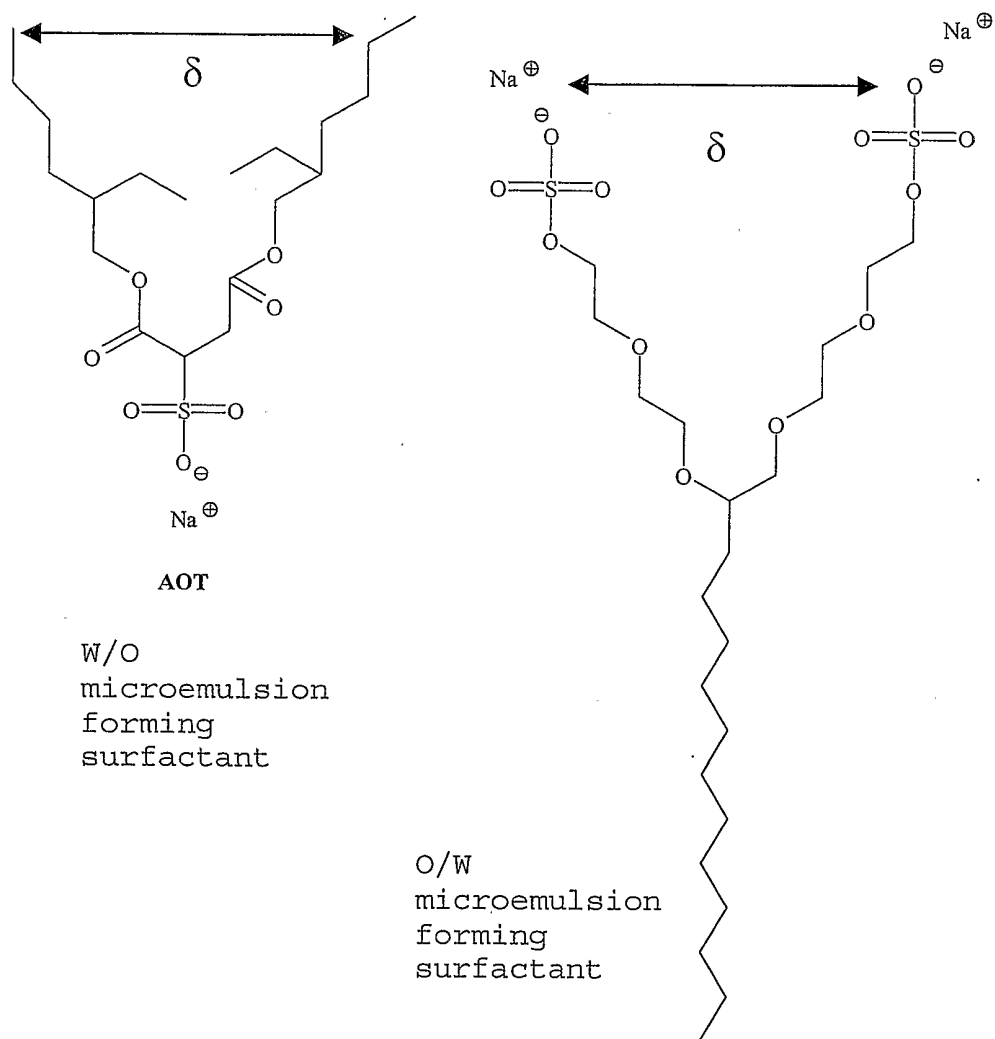


Figure 9. Final step in O/W microemulsion forming surfactant design.

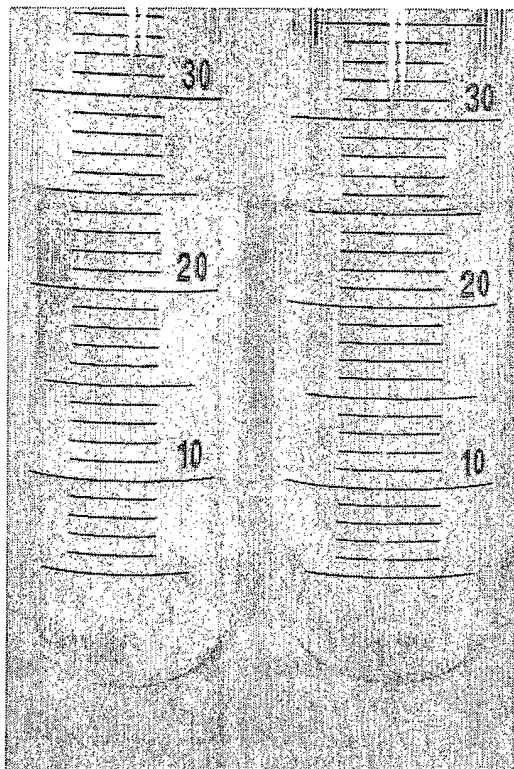


Figure 10. MiFoS $Y_1 C_{12}$ aqueous colourless transparent solutions at 5%wt @25°C and 10%wt @25°C in 0.58M NaCl

10/13

10/13

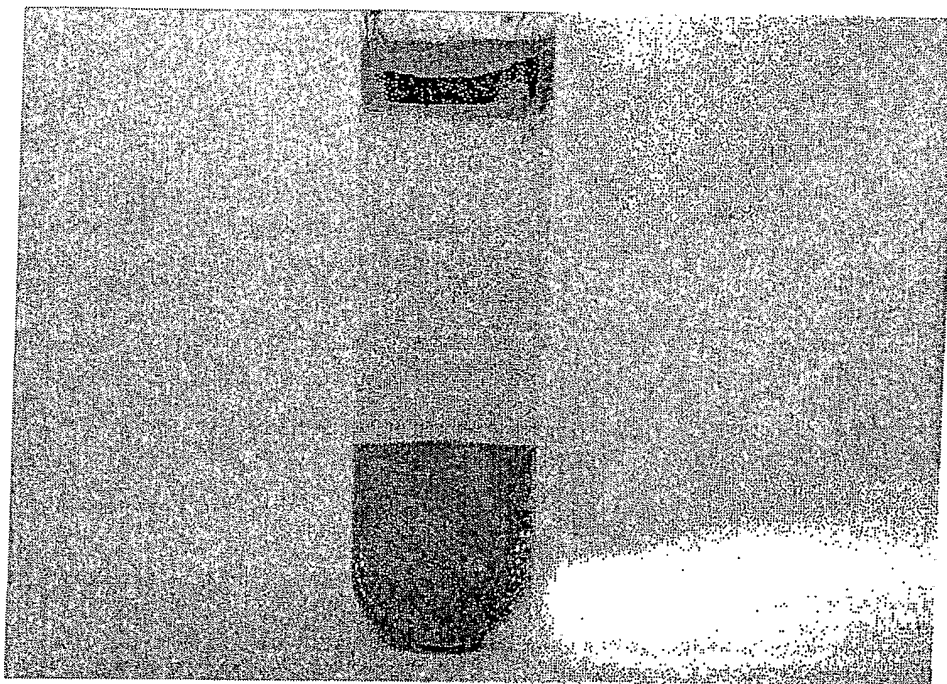


Figure 11. Crude Oil contaminated sample treated with 10%wt MiFoS $Y_1 C_{12}$ in 0.58M NaCl @25°C. Note formation of oil-in-water (O/W) microemulsion and complete removal of surfactant free oil.

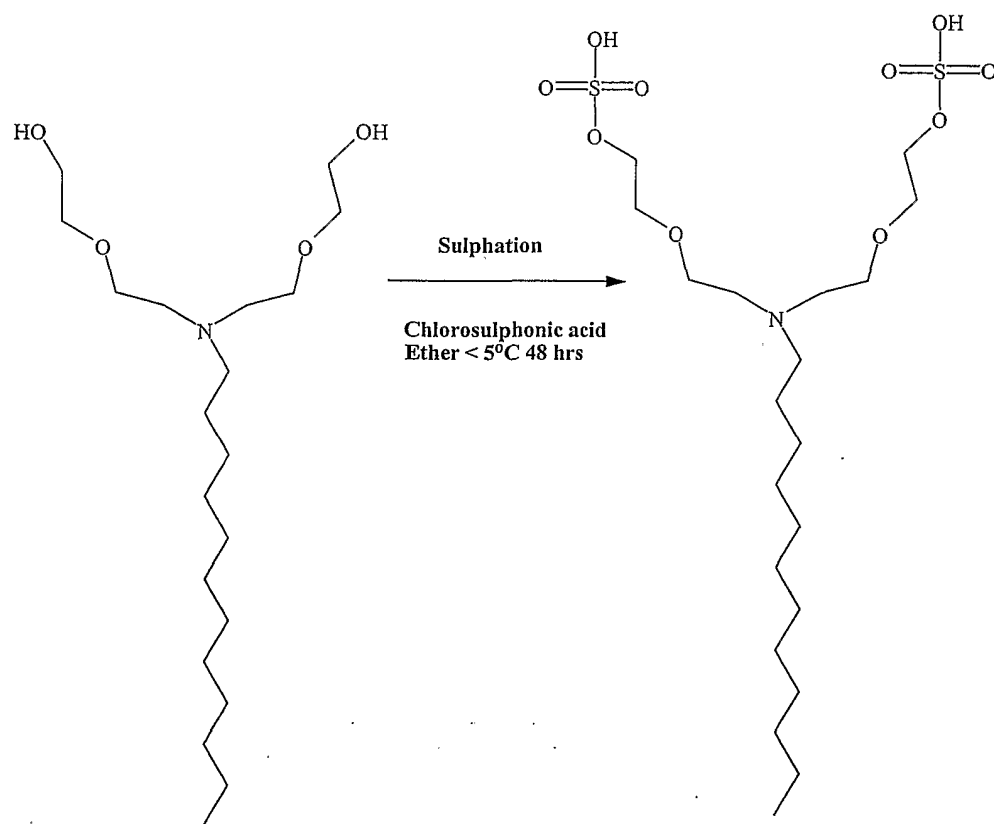


Figure 12. Sulphated Triton RW-50 reaction (non-ionic to di-anionic tertiary amine oil-in-water O/W microemulsion forming surfactant)

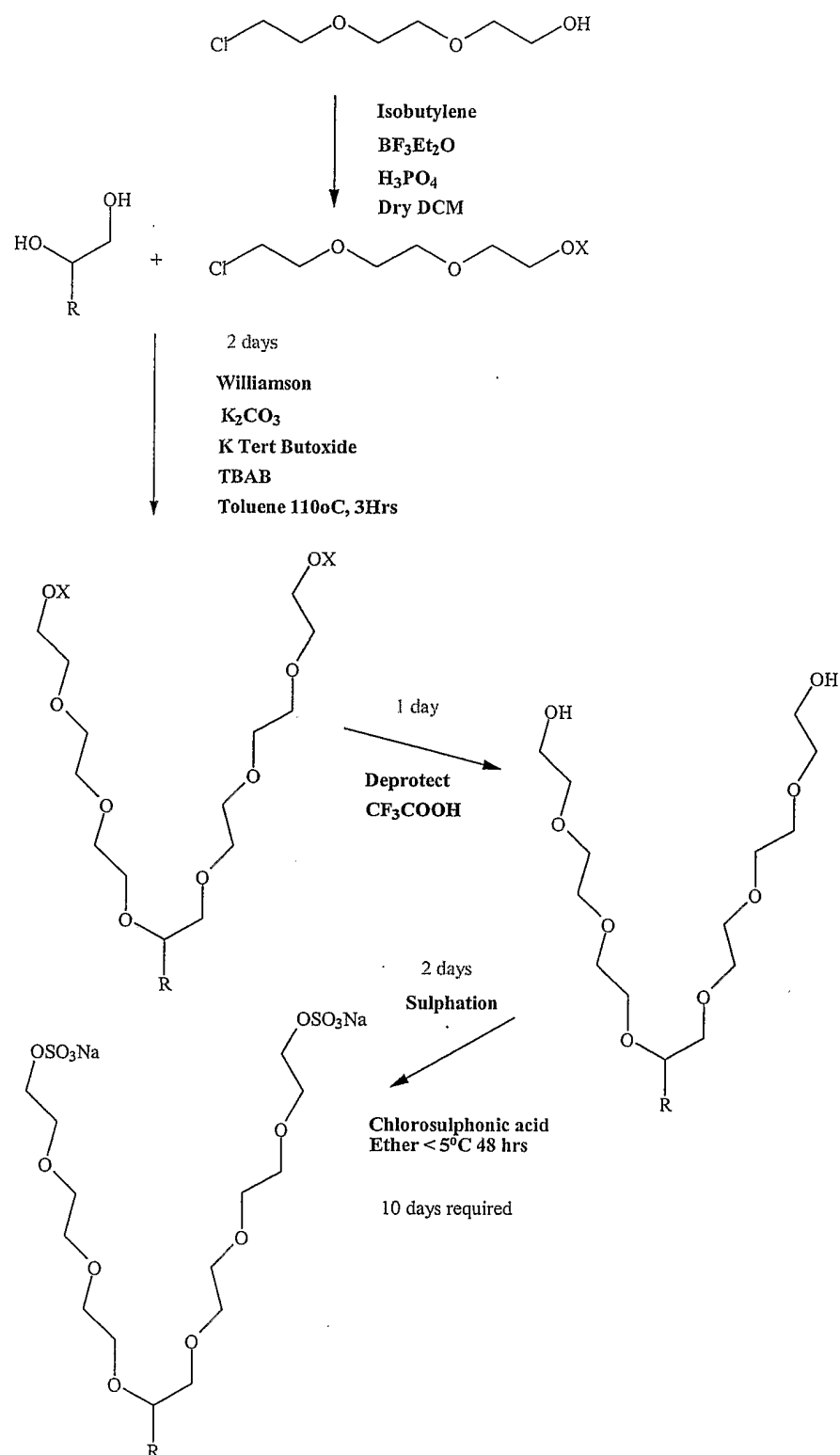


Figure 13. Suggested laboratory synthesis pathway for manufacturing an O/W microemulsion forming surfactant.

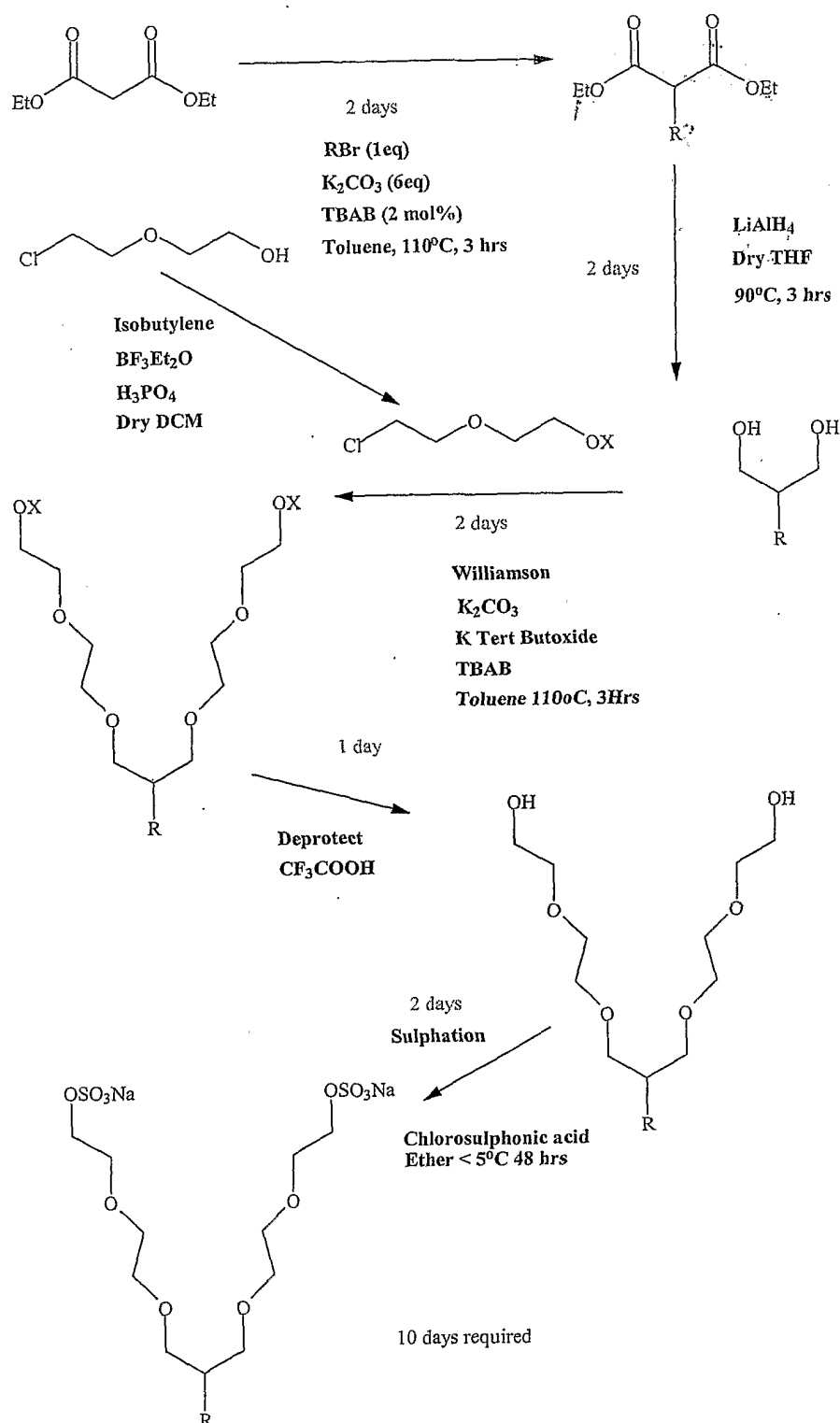


Figure 14. Suggested laboratory synthesis pathway for manufacturing an O/W microemulsion forming surfactant.

INTERNATIONAL SEARCH REPORT

International Application No
PCT/GB 01/03953

A. CLASSIFICATION OF SUBJECT MATTER
IPC 7 C07C305/10 C11D1/16 C11D1/29

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
IPC 7 C07C C11D

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

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

BEILSTEIN Data, WPI Data, EPO-Internal, PAJ, CHEM ABS Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 832 965 A (PROCTER & GAMBLE) 1 April 1998 (1998-04-01) page 11; claim 5 ---	1,4-9, 12-14, 31,32,34
X	WO 98 00498 A (PROCTER & GAMBLE) 8 January 1998 (1998-01-08) page 8 -page 9; claim 2 ---	1,4-9, 12-14, 31,32,34
X	US 3 832 408 A (R. ANDERSON) 27 August 1974 (1974-08-27) column 1, line 38 - line 68; examples 6,8 --- -/--	1,4-9, 12-14, 31,32,34

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
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- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- *&* document member of the same patent family

Date of the actual completion of the international search

11 December 2001

Date of mailing of the international search report

20/12/2001

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INTERNATIONAL SEARCH REPORT

In tional Application No

PCT/GB 01/03953

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category °	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	GB 1 563 089 A (ALBRIGHT & WILSON) 19 March 1980 (1980-03-19) the whole document ---	1,4-9, 12-14, 31,32,34
X	US 2 944 900 A (B.H. CARROLL, ET AL.) 12 July 1960 (1960-07-12) column 5, line 5 - line 32 ---	1,12-14
X	PATENT ABSTRACTS OF JAPAN vol. 001, no. 013 (C-005), 22 March 1977 (1977-03-22) -& JP 51 128912 A (RIKEN VITAMIN CO LTD), 10 November 1976 (1976-11-10) abstract ---	1-9, 12-14, 31,32,34
P,X	PATENT ABSTRACTS OF JAPAN vol. 2000, no. 12, 3 January 2001 (2001-01-03) -& JP 2000 256549 A (KAO CORP), 19 September 2000 (2000-09-19) abstract ---	1-9, 12-14, 31,32,34
A	FR 2 733 982 A (RHONE POULENC CHIMIE) 15 November 1996 (1996-11-15) the whole document -----	1,31

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Continuation of Box I.2

Claims Nos.: 1-28 (partially), 29, 30, 31-36 (partially)

Present claims 1-36 relate to an extremely large number of possible compounds and methods. In fact, the claims contain so many poorly defined terms and expressions that a lack of clarity within the meaning of Article 6 PCT arises to such an extent as to render a meaningful search of the claims impossible.

In particular, it is impossible to determine what is defined by the following phrases:

(1) "R comprises a hydrocarbon group including H, branched or linear alkyl chains, substituted alkyl, alkenyl, aryl, alkaryl or cyclic groups" (Claims 1, 29), "a non-hydrocarbon element" (Claim 2), "an ether group or an ester group" (Claim 3)

The use of the words "comprising" and "including" are not limiting and as a result no limitation has been put on the possible values which R can take. Furthermore, no limit has been put on the length of the alkyl and alkenyl chains nor the nature of the aryl, alkaryl and cyclic groups. Indeed aryl and alkaryl groups appear to be included in the definition "cyclic groups", leading to double definition. The expression "a non-hydrocarbon element" defines what this aspect of R is not, but gives no indication of what is included in the definition. The expression "an ether group or an ester group" provides little extra concrete structural information.

(2) "subgroups thereof" (Claims 1, 29)

No definition of what is meant by this expression appears anywhere in the claims or in the description.

(3) "water-soluble group" (Claims 1, 15), "a pH sensitive group" (Claims 9, 23, 29, 30)

The use of these expressions results in X being defined in terms of its properties and not its chemical structure. Consequently, it is not possible to determine which groups are meant by this expression.

(4) "a borate based group" (Claims 9, 23)

It is not possible to determine what structural group is meant by this expression.

(5) "any cyclic hydrocarbon group which may or may not include non hydrocarbon elements" (Claim 15), "any cyclic hydrocarbon" (Claims 16-18, 30), "the cyclic ring comprises up to 4 adjoining groups" (Claim 20), "the group comprising branched or linear alkyl chains, substituted alkyl, alkenyl, aryl, alkaryl, a cyclic group or a combination thereof" (Claim 21)

The first two expressions give no information as to exactly what chemical groups are meant. The third gives no information as to what the "four adjoining groups" are, and the last gives little extra structural information.

FURTHER INFORMATION CONTINUED FROM PCT/ISA/ 210

Consequently, the search has been carried out for those parts of the application which do appear to be clear, namely all compounds which contain two groups $(OCH_2CH_2)_n-OSO_3M$ (Claims 1, 15) or $(OCH_2CH_2O)_n-OSO_3M$ (peroxy compounds, Claims 29, 30), in which n is 1-20 and M is a metal ion.

The applicant's attention is drawn to the fact that claims, or parts of claims, relating to inventions in respect of which no international search report has been established need not be the subject of an international preliminary examination (Rule 66.1(e) PCT). The applicant is advised that the EPO policy when acting as an International Preliminary Examining Authority is normally not to carry out a preliminary examination on matter which has not been searched. This is the case irrespective of whether or not the claims are amended following receipt of the search report or during any Chapter II procedure.

INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/GB 01/03953

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
EP 0832965	A	01-04-1998	EP 0832965 A1	01-04-1998
			AU 4738997 A	17-04-1998
			BR 9713474 A	11-04-2000
			JP 2000503066 T	14-03-2000
			PL 332646 A1	27-09-1999
			WO 9813455 A1	02-04-1998
WO 9800498	A	08-01-1998	BR 9710072 A	10-08-1999
			CN 1228113 A	08-09-1999
			EP 0907702 A1	14-04-1999
			JP 2000500186 T	11-01-2000
			WO 9800498 A1	08-01-1998
			US 6239093 B1	29-05-2001
US 3832408	A	27-08-1974	US 3860625 A	14-01-1975
GB 1563089	A	19-03-1980	AU 506059 B2	13-12-1979
			AU 1556676 A	12-01-1978
			BE 843719 A1	03-01-1977
			DE 2629849 A1	20-01-1977
			DK 299576 A	05-01-1977
			FR 2316222 A1	28-01-1977
			IT 1063137 B	11-02-1985
			NL 7607321 A	06-01-1977
			NO 762270 A	05-01-1977
			SE 7607568 A	05-01-1977
			ZA 7603959 A	29-06-1977
US 2944900	A	12-07-1960	NONE	
JP 51128912	A	10-11-1976	JP 58033867 B	22-07-1983
JP 2000256549	A	19-09-2000	NONE	
FR 2733982	A	15-11-1996	FR 2733982 A1	15-11-1996
			AU 5903696 A	29-11-1996
			WO 9635663 A1	14-11-1996