

1                   **UNDER-NEUTRALIZED ALKYLXYLENE SULFONIC ACID**  
2                   **COMPOSITION FOR ENHANCED OIL RECOVERY PROCESSES**

3                                   FIELD OF THE INVENTION

4   The present invention is directed to an under-neutralized alkylxylene sulfonic  
5   acid composition for enhanced oil recovery processes. The present invention  
6   is also directed to a method for enhancing the recovery of oil from a  
7   subterranean reservoir which method employs the under-neutralized  
8   alkylxylene sulfonic acid compositions of the present invention. The  
9   under-neutralized alkylxylene sulfonic acid compositions are employed in an  
10   aqueous media. The method optionally employs suitable co-surfactants, such  
11   as alcohols, alcohol ethers, polyalkylene glycols and/or  
12   poly(oxyalkylene)glycols and poly(oxyalkylene)glycol ethers.

13                                   BACKGROUND OF THE INVENTION

14   Crude oil production from oil in subterranean reservoirs may involve use of  
15   various flooding methods as the natural forces that are used in the "primary  
16   recovery" process become depleted. A large portion of the crude oil may  
17   have to be driven out of the formation in "secondary" or "tertiary" recovery  
18   processes. In addition, some reservoirs may not have sufficient natural forces  
19   for oil production even by primary recovery processes. The production of  
20   crude oil using such flooding methods is one example of enhanced oil  
21   recovery processes.

22   One trend in the petroleum industry now is to plan exploitation of the oil field  
23   at the beginning of the project. Injecting a displacing fluid or gas may begin  
24   early, long before the complete depletion of the field by primary recovery  
25   techniques. Methods for improving displacement efficiency or sweep  
26   efficiency may be used at the very beginning of the first injection of a

1 displacing fluid or gas, rather than under secondary and tertiary recovery  
2 conditions.

3 The least expensive and easiest method of flooding a subterranean reservoir  
4 for the production of crude oil is by injecting a liquid or a gas into the well to  
5 force the oil to the surface. Water flooding is the most widely used fluid.  
6 However, water does not readily displace oil because of the immiscibility of  
7 water and oil and the high interfacial tension between the two liquids.

8 The addition of chemicals to modify the properties of the flooding liquid is well  
9 known in the art. Surfactants are one class of chemical compounds that have  
10 been used in aqueous media for enhanced oil recovery. Surfactants have  
11 been found to effectively lower the interfacial tension between oil and water  
12 and enabling the oil droplets to flow more easily through the channels of the  
13 reservoir.

14 Alkylaryl sulfonates have been used as surfactants for enhanced oil recovery.  
15 They have been used in surfactant flooding, alone or in conjunction with  
16 co-surfactants and/or sacrificial agents. Alkylaryl sulfonates are generally  
17 used not only because they are able to lower the interfacial tension between  
18 oil and water, but also because when used in conjunction with varying  
19 amounts of sodium chloride they exhibit different phase behavior. At low  
20 salinity, alkylaryl sulfonates have a tendency to stay in the aqueous phase,  
21 but at high salinity they tend to stay in the oil phase. Around mid-point  
22 salinity, a micro-emulsion forms in which appreciable amounts of oil and brine  
23 are in the micro-emulsion phase. It is at this mid-point salinity that the  
24 surfactant exhibits high oil recovery potential. The salinity of the water in  
25 subterranean hydrocarbon reservoirs may vary a great deal, for example, the  
26 Minas oil field in Indonesia has total dissolved salts of between 0.2 and  
27 0.3 weight percent. Other reservoirs may have salinities as high as or higher  
28 than 2.0 percent sodium chloride and over 0.5 percent calcium chloride and  
29 magnesium chloride. It is desirable to optimize the alkylaryl sulfonates for

1 surfactant flooding for enhanced oil recovery for a particular reservoir by  
2 determining the interfacial tension of the reservoir oil in an aqueous brine  
3 solution containing the alkylaryl sulfonates which matches the salinity of the  
4 reservoir water.

5 Generally, pure alkylaryl sulfonates, that is, those having a narrow range of  
6 molecular weights, are useful for recovery of light crude oils. Such alkylaryl  
7 sulfonates have been less useful for enhancing oil recovery of crude oils  
8 containing high wax content. Alkylaryl sulfonates having a broad spectrum of  
9 carbon chain lengths in the alkyl group are more desirable for use to recover  
10 waxy crude oils.

11 A number of patents and patent applications have discussed methods for  
12 enhanced oil recovery using surfactant flooding. In addition to the use of  
13 surfactants, there are a number of patent and patent applications discussing  
14 the use of co-surfactants and sacrificial agents for enhanced oil recovery.

15 EP 0 111 354 B1 discloses the use of alkylxylene sulfonate compounds  
16 derived from alkyl meta- and para-xylenes in methods for displacing oil from  
17 reservoirs of relatively higher salinities than those to which the conventional  
18 alkyl-ortho-xylene sulfonate compounds are limited.

19 EP 0 148 517 B1 discloses olefin sulfonate compositions comprising an  
20 aqueous solution containing 15 to 35 weight percent of a blend of a C<sub>12</sub>-C<sub>22</sub>  
21 linear alpha-olefin and an alkylaryl sulfonate wherein the aryl group is a  
22 benzene, toluene or xylene. The compositions are used in foam drive  
23 processes for enhanced oil recovery.

24 EP 0 158 486 B1 discloses the use of polyalkyl aromatic sulfonates,  
25 particularly dialkyl aromatic sulfonates in steam recovery methods for  
26 enhancing oil recovery. The increase of the ratio of para-isomer to

1 meta-isomer results in a significantly more hydrolytically, thermally stable  
2 surfactant under steam recovery operating conditions.

3 EP 0 413 374 B1 discloses the use of alkylxylene sulfonates and a glycol for  
4 enhanced oil recovery. The alkyl group containing 8 to 30 carbon atoms is  
5 attached to the aromatic ring from its 2-position to its mid-position. The glycol  
6 is used as a sacrificial agent.

7 GB 2 138 866 A discloses a micellar slug for use in the recovery of oil  
8 consisting essentially of a hydrocarbon, an aqueous medium, a surfactant and  
9 a co-surfactant. The surfactant containing, as essential constituents, an  
10 internal olefin sulfonate having 10 to 26 carbon atoms and at least one  
11 ethoxylate. The micellar slug has an improved salinity tolerance and  
12 hard-water resistance and is capable of forming micro-emulsions having low  
13 interfacial tension and good stability.

14 U.S. Patent No. 3,601,198 discloses the use of oil-soluble anionic  
15 surface-active agents or detergents, such as sulfonates, petroleum and  
16 synthetic, for a hydraulic fracturing operation. The synthetic sulfonates are  
17 alkaline earth metal salts of high molecular weight sulfonic acids and are  
18 produced using aromatics, such as benzene, toluene, xylene and  
19 naphthalene. The molecular weights of the sulfonates are in the range  
20 between 300 and about 750.

21 U.S. Patent No. 4,005,749 discloses the use of polyalkylene oxides as  
22 sacrificial agents prior to surfactant flooding in enhanced oil recovery process.  
23 The polyalkylene oxides have molecular weights of at least 1,200. The  
24 surfactant flood is an aqueous slug containing a surfactant exhibiting a lower  
25 molecular weight than that of the polyalkylene oxides. The sacrificial agent  
26 may also be used along with the surfactant flooding, but its concentration is  
27 lower than when used as a sacrificial agent.

1 U.S. Patent No. 4,217,958 discloses the use of sacrificial agents, polybasic  
2 carboxylic acid or their water soluble salts, in admixture with a chemical oil  
3 recovery agent, such as a surfactant, a polymer, and/or a micellar dispersion  
4 to reduce the adsorption of surfactants and/or the polymers on reservoir  
5 rocks.

6 U.S. Patent No. 4,452,708 discloses an oil recovery method using a particular  
7 class of alkylaryl sulfonate surfactants. The surfactants are derived from an  
8 extracted aromatic feedstock consisting essentially of benzene, toluene,  
9 xylene and lesser amounts of alkylbenzene alkylated with linear alpha-olefins  
10 to favor a second-carbon attachment. The sulfonates have a high oil  
11 solubilization parameters and their phase behavior is substantially  
12 independent of temperature over 120°F-250°F.

13 U.S. Patent No. 4,476,929 discloses the use of co-surfactants, a sulfoxide,  
14 having a maximum of 14 carbon atoms, in surfactant systems for enhanced oil  
15 recovery processes. The preferred surfactant is a petroleum sulfonate having  
16 average equivalent weights in the range of about 325 to 500.

17 U.S. Patent No. 4,452,308 discloses the use of polyalkylene glycols or  
18 copolymers thereof having molecular weights between 100 and 1,200 with  
19 chemical flooding. The concentration of the polyalkylene glycols used is  
20 0.01-0.5 weight percent. The preferred polyalkylene glycols are polyethylene  
21 and polypropylene glycols.

22 U.S. Patent No. 4,589,489 discloses the use of polyalkylene glycols or their  
23 copolymers for surfactant flooding or for preflushing. It is preferred to use  
24 polyethylene glycol having a molecular weight of from 800 to about 1,100.  
25 The concentration used is dependent on the subterranean formation, for  
26 example, between 1-100 kilograms per cubic meter.

1 U.S. Patent No. 4,608,204 discloses a process for the preparation of a low  
2 viscosity aqueous alkyltoluene or alkylxylene sulfonate with the addition of  
3 sodium chloride during neutralization or after neutralization. Such low  
4 viscosity sulfonates are useful as surfactants in enhanced oil recovery  
5 processes. When xylene is employed, a mixture of the three isomers, ortho-,  
6 meta- and para-, are preferred.

7 U.S. Patent No. 4,690,785 discloses low water neutralization energy-saving  
8 process to produce highly active alkylaryl sulfonate by combining an alkylaryl  
9 sulfonic acid with a salt-forming base, and utilizing the heat generated during  
10 the neutralization reaction to drive off the water present in the reaction  
11 mixture. The resulting free flowing alkylaryl sulfonate powder is at least  
12 90 percent active. When dissolved in water, the powdered product will have a  
13 pH of about 4.6 to about 11.5, usually about 7 or about 8.

14 U.S. Patent No. 4,873,025 discloses compositions comprising alkylxylene  
15 sulfonates in which a substantial portion of the alkylxylene sulfonate fraction  
16 has the C<sub>6</sub>-C<sub>20</sub> substituents, positioned directly opposite to the sulfonate  
17 moiety. Such compositions are derived from para-xylene or isomer mixtures  
18 comprising substantially para-xylene. These alkylxylene sulfonates are useful  
19 as surfactants, particularly in enhanced oil recovery techniques.

20 U.S. Patent No. 4,932,473 discloses a process for enhanced oil recovery  
21 employing one or more alkyltoluene sulfonates in an aqueous saline aqueous  
22 solution. The improvement comprises including into the said solutions one or  
23 more alkylpolysaccharide surfactants for enhancing the solubility of the  
24 alkyltoluene sulfonate. The composition enhances calcium and sodium ion  
25 tolerance of the alkyltoluene sulfonates.

26 U.S. Patent No. 6,022,834 discloses an improved alkali surfactant flood  
27 process with ultra-low interfacial tension. The surfactant system contains  
28 (1) a mixture of anionic surfactants; (2) solvent(s); (3) a strong base; and

1 (4) optionally, a nonionic surfactant or mixtures of nonionic surfactants or  
2 sulfates or carboxylates of these nonionic surfactants. The anionic  
3 surfactants are sulfonates derived from alkylbenzene, alkylnaphthalene,  
4 alkyltoluene or alkylxylene. The alkyl group consists of between about C<sub>4</sub> and  
5 about C<sub>24</sub>.

6 U.S. Patent No. 6,043,391 discloses new anionic surfactants and their method  
7 of preparation by simultaneously sulfonating and alkylating an aromatic  
8 hydrocarbon. The one-step preparation process involves sulfonating an  
9 alpha-olefin with SO<sub>3</sub>, followed by repeated hydrolysis and dehydration with  
10 water which results in the formation of an alkene sulfonic acid. This strong  
11 acid is used to alkylate aromatic compounds. Additional strong acid catalyst  
12 is beneficial to obtain useful yields of the final product.

13 U.S. Patent No. 6,269,881 discloses an oil recovery process using a particular  
14 class of alkylaryl sulfonates derived from an alpha-olefin stream having a  
15 broad distribution of even carbon numbers ranging from 12 to 58. The  
16 aromatic hydrocarbons used to produce the alkylaryl sulfonates may be  
17 benzene, toluene, xylene or mixtures thereof. The surfactant has ultra low  
18 interfacial tension with waxy crude oils.

19 WO 01/98432 A2 discloses a surfactant blend for lowering the interfacial  
20 tension between oil and aqueous fluid for enhanced oil recovery. The blend  
21 comprises at least one synthetic polyisobutylene and at least one surfactant  
22 consisting of sulfonate surfactants, alcohols and non-ionic surfactants.

23 A general treatise on enhanced oil recovery is Basic Concepts in Enhanced  
24 Oil Recovery Processes edited by M. Baviere (published for SCI by Elsevier  
25 Applied Science, London and New York, 1991).

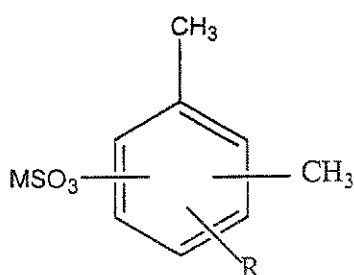
## SUMMARY OF THE INVENTION

There is disclosed an under-neutralized alkylxylene sulfonic acid composition for enhanced oil recovery (EOR) processes. There is also disclosed a method for enhancing the recovery of oil from a subterranean reservoir which method employs the under-neutralized alkylxylene sulfonic acid compositions of the present invention. The under-neutralized alkylxylene sulfonic acid compositions may be employed in an aqueous media. The method optionally employs suitable co-surfactants, such as alcohols, alcohol ethers, polyalkylene glycols, poly(oxyalkylene)glycols and/or poly(oxyalkylene)glycols ethers.

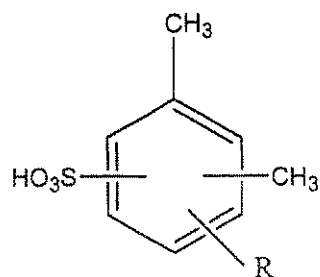
It has been discovered that the under-neutralized alkylxylene sulfonic acid disclosed herein provides an EOR surfactant having low IFT compared to the fully-neutralized alkylxylene sulfonic acid. This result is surprising since the surfactants used for EOR in the prior art are fully-neutralized sulfonates.

It has also been discovered that when the alkylxylene used to make the alkylxylene sulfonic acid of the present invention contains greater than 70 percent 4-alkyl-1,2-dimethylbenzene isomer, the alkylxylene sulfonic acid provides an EOR surfactant having low IFT.

In one aspect, there is provided an under-neutralized alkylxylene sulfonic acid composition for enhanced oil recovery processes, which composition is a mixture of compounds having the general formula:



(a)



(b)

1

2 wherein R is an alkyl group containing from about 10 to about 58 carbon  
 3 atoms, and M is a mono-valent cation, and wherein the alkylxylene moiety in  
 4 compounds (a) and (b) combined is alkyl-ortho-xylene in at least 85 percent  
 5 and compound (a) is present in the range of about 80 percent to about  
 6 98 percent based on the total under-neutralized alkylxylene sulfonic acid  
 7 composition.

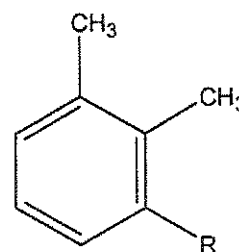
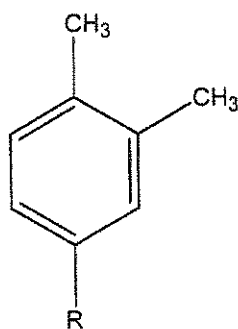
8 Preferably, the alkylxylene moiety in compounds (a) and (b) is  
 9 alkyl-ortho-xylene in at least 95 percent of the total under-neutralized  
 10 alkylxylene sulfonic acid composition.

11 Preferably, compound (a) is present in the range of about 85 percent to about  
 12 95 percent based on the total under-neutralized alkylxylene sulfonic acid  
 13 composition. More preferably, compound (a) is present in the range of about  
 14 87 percent to about 92 percent based on the total under-neutralized  
 15 alkylxylene sulfonic acid composition.

16 The mono-valent cation in the neutralized alkylxylene sulfonic acid compound  
 17 (a) is an alkali metal. Preferably, the alkali metal is sodium. The mono-valent  
 18 cation in the neutralized alkylxylene sulfonic acid compound may be an  
 19 ammonium ion or an organic ammonium ion.

20 The alkyl group in compounds (a) and (b) in the above under-neutralized  
 21 alkylxylene sulfonic acid composition is derived from a linear alpha olefin or

- 1 an isomerized olefin containing from about 10 to about 58 carbon atoms.  
2 Preferably, the alkyl group is derived from a linear alpha olefin or an  
3 isomerized olefin containing from about 10 to about 40 carbon atoms. More  
4 preferably, the alkyl group is derived from a linear alpha olefin or an  
5 isomerized olefin containing from about 12 to about 30 carbon atoms.
- 6 The alkylxylene moiety in compounds (a) and (b) combined in the  
7 under-neutralized alkylxylene sulfonic acid composition contains greater than  
8 about 70 percent of the 4-alkyl-1,2-dimethylbenzene isomer. Preferably, the  
9 alkylxylene moiety in compounds (a) and (b) combined in the  
10 under-neutralized alkylxylene sulfonic acid composition contains greater than  
11 about 80 percent of the 4-alkyl-1,2-dimethylbenzene isomer. More preferably,  
12 the alkylxylene moiety in compounds (a) and (b) combined in the  
13 under-neutralized alkylxylene sulfonic acid composition contains at least  
14 90 percent of the 4-alkyl-1,2-dimethylbenzene isomer. The structures for the  
15 4-alkyl-1,2-dimethylbenzene and the 3-alkyl-1,2-dimethylbenzene are given  
16 below.

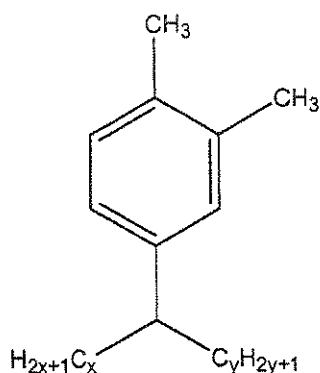


17 4-alkyl-1,2dimethylbenzene

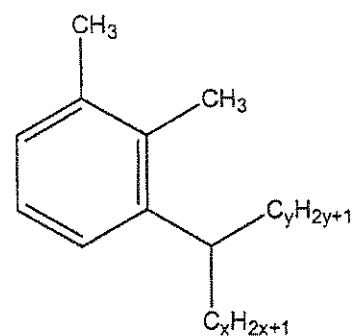
3-alkyl-1,2-dimethyl benzene

- 18 The attachment of the alkyl group to the xylene moiety in compounds (a) and  
19 (b) combined in the above under-neutralized alkylxylene sulfonic acid  
20 composition is at positions higher than the 2-position along the alkyl chain in  
21 at least 40 percent of the total under-neutralized alkylxylene sulfonic acid

1 composition. Preferably, the attachment of the alkyl group to the xylene  
 2 moiety is at positions higher than the 2-position along the alkyl chain in at  
 3 least 45 percent of the total under-neutralized alkylxylene sulfonic acid  
 4 composition. Preferably, the attachment of the alkyl group to the xylene  
 5 moiety is at positions higher than the 2-position along the alkyl chain in at  
 6 least 60 percent of the total under-neutralized alkylxylene sulfonic acid  
 7 composition. The structures for the various attachment positions on the  
 8 carbon chain of the alkyl group to the xylene moiety are given below.



9 4-alkyl-1,2-dimethylbenzene



3,alkyl-1,2-dimethyl benzene

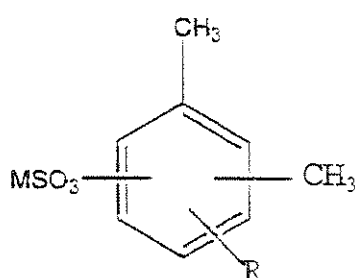
10 In the above structures, the values of x and y determine the attachment of the  
 11 alkyl group to the xylene moiety on the carbon chain. For example, for a C<sub>12</sub>  
 12 alkyl group, the value of x equal to 2 and y equal to 9 corresponds to the  
 13 attachment of the alkyl group at the 3-position on the alkyl carbon chain.  
 14 Thus, for x+y+1 equal to between 10 and 58, knowing x and y provides the  
 15 attachment of the alkyl group to the xylene moiety for the corresponding chain  
 16 lengths between C<sub>10</sub> and C<sub>58</sub>.

17 The alkyl group in compounds (a) and (b) in the above under-neutralized  
 18 alkylxylene sulfonic acid composition contains a broad distribution of alkyl  
 19 chain lengths. A preferred distribution of alkyl chain lengths comprise from  
 20 about 40 to about 80 percent C<sub>12</sub> to C<sub>20</sub>. A more preferred distribution of alkyl  
 21 chain lengths comprise from about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub>. The

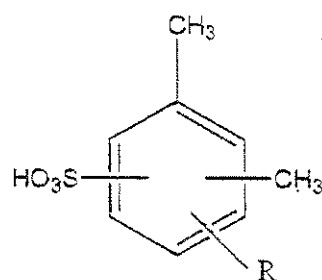
1 upper heavier range of alkyl chain lengths of C<sub>32</sub> to C<sub>58</sub> may comprise up to  
2 about 5 percent to about 15 percent of the alkyl groups, preferably upper  
3 heavier range of alkyl chain lengths of C<sub>32</sub> to C<sub>58</sub> may comprise up to about  
4 8 percent to about 12 percent of the alkyl groups.

5 In another aspect, there is provided a method for recovering crude oil from a subterranean  
6 hydrocarbon containing formation, which method comprises:  
7

8 (a) injecting into the formation an aqueous solution containing an  
9 amount of an under-neutralized alkyixylene sulfonic acid  
10 composition effective for the recovery of crude oil wherein the  
11 composition is a mixture of compounds having of the general  
12 formula:



(i)



(ii)

13  
14 wherein R is an alkyl group containing from about 10 to about  
15 58 carbon atoms, and M is a mono-valent cation, and wherein the  
16 alkyixylene moiety in compounds (a) and (b) combined is alkyl-  
17 ortho-xylene in at least 85 percent and compound (a) is present in  
18 the range of about 80 percent to about 98 percent based on the  
19 total under-neutralized alkyixylene sulfonic acid composition; and

1                   (b) displacing the crude oil with the aqueous solution injected into  
2                   the formation to thereby recover hydrocarbons from a  
3                   production well.

4   In step (a) in the above method, the under-neutralized alkylxylene sulfonic  
5   acid composition is present in the range of about 0.03 weight percent to about  
6   2.0 weight percent of the total weight of the aqueous solution. Preferably, the  
7   composition is present in the range of about 0.1 weight percent to about  
8   1.5 weight percent of the total weight of the aqueous composition. More  
9   preferably, the composition is present in the range of about 0.3 weight percent  
10   to about 1.0 weight percent of the total weight of the aqueous composition,  
11   and most preferably the composition is present in the range of about  
12   0.5 weight percent to about 0.8 weight percent of the total weight of the  
13   aqueous composition.

14   Preferably in the above method, the alkylxylene moiety in compounds (i) and  
15   (ii) in step (a) is alkyl-ortho-xylene in at least 95 percent based on the total  
16   under-neutralized alkylxylene sulfonic acid composition.

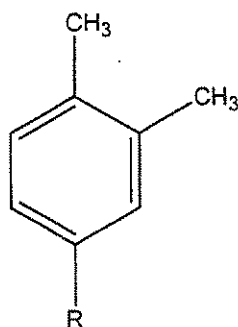
17   Preferably in the above method, compound (i) in step (a) is present in the  
18   range of about 85 percent to about 95 percent based on the total  
19   under-neutralized alkylxylene sulfonic acid composition. More preferably,  
20   compound (i) in step (a) is present in the range of about 87 percent to about  
21   92 percent based on the total under-neutralized alkylxylene sulfonic acid  
22   composition.

23   The mono-valent cation in compound (i) in step (a) in the above method is an  
24   alkali metal. Preferably, the alkali metal is sodium. The mono-valent cation in  
25   step (a) may be an ammonium ion or an organic ammonium ion.

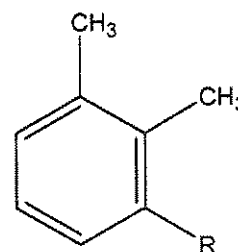
26   The alkyl group in compounds (i) and (ii) in step (a) of the above method is  
27   derived from a linear alpha olefin or an isomerized olefin containing from

1 about 10 to about 58 carbon atoms. Preferably, the alkyl group is derived  
2 from a linear alpha olefin or an isomerized olefin containing from about 10 to  
3 about 40 carbon atoms. More preferably, the alkyl group is derived from a  
4 linear alpha olefin or an isomerized olefin containing from about 12 to about  
5 30 carbon atoms.

6 The alkylxylene moiety in compounds (a) and (b) combined in the  
7 under-neutralized alkylxylene sulfonic acid composition contains greater than  
8 about 70 percent of the 4-alkyl-1,2-dimethylbenzene isomer. Preferably, the  
9 alkylxylene moiety in compounds (a) and (b) combined in the  
10 under-neutralized alkylxylene sulfonic acid composition contains greater than  
11 about 80 percent of the 4-alkyl-1,2-dimethylbenzene isomer. More preferably,  
12 the alkylxylene moiety in compounds (a) and (b) combined in the  
13 under-neutralized alkylxylene sulfonic acid composition contains at least  
14 90 percent of the 4-alkyl-1,2-dimethylbenzene isomer. The structures for the  
15 4-alkyl-1,2-dimethylbenzene and the 3-alkyl-1,2-dimethylbenzene are given  
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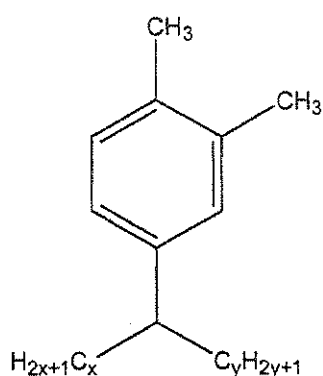
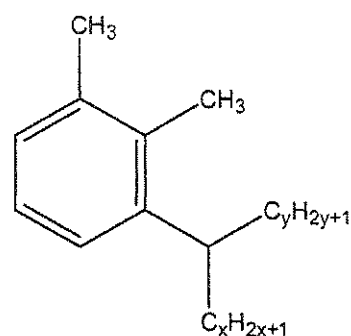
17 4-alkyl-1,2dimethylbenzene



3-alkyl-1,2-dimethyl benzene

18 In the above method, the alkyl group in compounds (i) and (ii) combined in  
19 step (a) is attached to the xylene moiety at positions higher than the 2-position  
20 along the alkyl chain in at least 40 percent based on the total  
21 under-neutralized alkylxylene sulfonic acid composition. Preferably, the alkyl

1 group is attached to the xylene moiety at positions higher than the 2-position  
 2 along the alkyl chain in at least 45 percent based on the total  
 3 under-neutralized alkylxylene sulfonic acid composition. More preferably, the  
 4 alkyl group is attached to the xylene moiety at positions higher than the  
 5 2-position along the alkyl chain in at least 60 percent based on the total  
 6 under-neutralized alkylxylene sulfonic acid composition. The structures for  
 7 the various attachment positions on the carbon chain of the alkyl group to the  
 8 xylene moiety are given below.

9 **4-alkyl-1,2-dimethylbenzene**

3-alkyl-1,2-dimethylbenzene

10 In the above structures, the values of x and y determine the attachment of the  
 11 alkyl group to the xylene moiety on the carbon chain. For example, for a C<sub>12</sub>  
 12 alkyl group, the value of x is 2 and y is 9 for the attachment of the alkyl group  
 13 at the 3-position on the alkyl carbon chain. Thus, for x+y+1 equal to 10 and  
 14 58, knowing x or y provides the attachment of the alkyl group to the xylene  
 15 moiety for the corresponding chain lengths between C<sub>10</sub> and C<sub>58</sub>.

16 The alkyl group in compounds (i) and (ii) in step (a) in the above method  
 17 contains a broad distribution of alkyl chain lengths. A preferred distribution of  
 18 alkyl chain lengths comprise from about 40 to about 80 percent C<sub>12</sub> to C<sub>20</sub>. A  
 19 more preferred distribution of alkyl chain lengths comprise from about 50 to  
 20 about 70 percent C<sub>12</sub> to C<sub>20</sub>. The upper heavier range of alkyl chain lengths of  
 21 C<sub>32</sub> to C<sub>58</sub> may comprise from about 5 percent to about 15 percent of the alkyl

1 groups, preferably upper heavier range of alkyl chain lengths of C<sub>32</sub> to C<sub>58</sub>  
2 may comprise from about 8 percent to about 12 percent of the alkyl groups.

3 The above method further employs, concurrently with or subsequent to the  
4 injection of the aqueous solution in step (a), injecting into the formation an  
5 amount of polymer effective for driving the aqueous solution of step (a) into  
6 the formation to displace the crude oil to thereby recover hydrocarbons from a  
7 production well.

8 In the above method, the polymer may be any suitable polymer, such as a  
9 polysaccharide, a polyacrylamide or a partially hydrolyzed polyacrylamide.

10 The above method further employs, concurrently or subsequent to the  
11 injection of the aqueous solution in step (a), injecting into the formation an  
12 amount of water effective for driving the aqueous solution of step (a) into the  
13 formation to displace the crude oil to thereby recover hydrocarbons from a  
14 production well.

15 The above method further employs, concurrently with or subsequent to the  
16 injection of the polymer, injecting into the formation an amount of water  
17 effective for driving the aqueous solution of step (a) or the above polymer into  
18 the formation to displace the crude oil to thereby recover hydrocarbons from a  
19 production well.

20 In the above method, the hydrocarbon in the subterranean formation may  
21 include a waxy crude oil.

22 The aqueous solution in step (a) in the above method further employs a  
23 co-surfactant having a molecular weight in the range of about 60 to about  
24 1,200.

25 The co-surfactant in the above method is an alcohol (primary, secondary,  
26 tertiary or mixtures thereof), an alcohol ether, a polyalkylene glycol, a

1 poly(oxyalkylene)glycol, a poly(oxyalkylene)glycol ether, or mixtures thereof.  
2 The poly(oxyalkylene)glycol ether may be any C<sub>1</sub>-C<sub>8</sub> mono-alkyl ether, such  
3 as ethylene or propylene glycol mono-alkyl or mono-phenyl ether, a  
4 di-ethylene or di-propylene glycol mono-alkyl or mono-phenyl ether, a  
5 tri-ethylene or tri-propylene glycol mono-alkyl or mono-phenyl ether,  
6 polyethylene glycol mono-phenyl ether, polypropylene glycol mono-phenyl  
7 ether, or mixtures thereof.

8 Examples of the poly(oxyalkylene)glycol are poly(oxyethylene)glycol and  
9 poly(oxypropylene)glycol, or mixtures thereof.

10 In the above method in step (a) the co-surfactant is in the range of about  
11 0.03 weight percent to about 2.0 weight percent of the total weight of the  
12 aqueous solution. Preferably, the co-surfactant is in the range of about  
13 0.1 weight percent to about 1.5 weight percent of the total weight of the  
14 aqueous composition. More preferably, the co-surfactant is in the range of  
15 about 0.3 weight percent to about 1.0 weight percent of the total weight of the  
16 aqueous composition, and most preferably the co-surfactant is in the range of  
17 about 0.5 weight percent to about 0.8 weight percent of the total weight of the  
18 aqueous composition.

#### 19 BRIEF DESCRIPTION OF THE DRAWINGS

20 Figure 1 is a chromatogram obtained by Gas Chromatography on a sample of  
21 the alkylxylene prepared using aluminum trichloride in Example 2. The weight  
22 percent of the attachment at carbon positions 2, 3, 4 and 4+ for C<sub>12</sub> and C<sub>14</sub>  
23 carbon chains can be calculated from the area under the resolved peaks  
24 shown in the chromatogram.

25 Figure 2 is similar to Figure 1 and was obtained on a sample of the  
26 alkylxylene prepared using trifluoromethane sulfonic acid in Example 1A.

1 Figure 3 is a plot of the data collected using the Equilibrated Interfacial  
2 Tension Method described below on samples of alkylxylene sulfonic acids  
3 prepared using alkylxylene prepared in Examples 1A, 1B and 1C (using  
4 trifluoromethane sulfonic acid as the alkylation catalyst).

5 Figure 4 is a plot of the data collected using the Equilibrated Interfacial  
6 Tension Method, described below, on samples of alkylxylene sulfonic acids  
7 prepared using alkylxylene prepared in Example 2 (using aluminum trichloride  
8 as the alkylation catalyst).

## 9 DETAILED DESCRIPTION OF THE INVENTION

### 10 DEFINITIONS

11 As used herein, the following terms have the following meanings unless  
12 expressly stated to the contrary:

13

14 The terms "active" or "actives" as used herein refers to the concentration of  
15 sodium alkylxylene sulfonates and the sulfonic acids described in the present  
16 invention. The calculation of the actives content is described in Example 4  
17 and the data are summarized in Table II.

18

19 The term "alkylate" as used herein refers to the alkylxylene used to prepare  
20 the fully-neutralized and under-neutralized sulfonic acids of the present  
21 invention. The alkylxylene was prepared using xylene and linear alpha olefin  
22 or isomerized olefin containing from about 10 to about 58 carbon atoms.  
23 Preferably, the linear alpha olefin or isomerized olefin contains from about  
24 10 to about 40 carbon atoms, and more preferably from about 12 to about  
25 30 carbon atoms.

26

27 The term "alkali metal" as used herein refers to Group IA metals of the  
28 Periodic Table.

1 The term "alkoxide" means a compound which can be formed as the reaction  
2 product of an alcohol and a reactive metal.

3 The term "co-surfactant" herein refers to nonionic surfactants that are used in  
4 conjunction with anionic surfactants in enhanced oil recovery processes.  
5 Generally, nonionic surfactants have a somewhat higher tolerance to  
6 polyvalent ions, are water-soluble, and exhibit a wide range of low and stable  
7 interfacial tensions between alkaline brine and crude oil. They may also  
8 provide a reduction in viscosity of the surfactant.

9 The terms "enhanced oil recovery" or "EOR" as used herein refer to  
10 processes for enhancing the recovery of hydrocarbons from subterranean  
11 reservoirs. Techniques for improving displacement efficiency or sweep  
12 efficiency may be used for the exploitation of an oil field by introducing  
13 displacing fluids or gas into injection wells to drive oil through the reservoir to  
14 producing wells.

15 The terms "Gas Chromatography" or "GC" as used herein refer to Gas Liquid  
16 Phase Chromatography.

17 The term "isomerized olefin" as used herein refers to an alpha olefin that has  
18 been subjected to isomerization conditions which results in an alternation of  
19 the distribution of the olefin species present and/or the introduction of  
20 branching along the alkyl chain.

21 The terms "interfacial tension" or "IFT" as used herein refer to the surface  
22 tension between oil and water. To achieve high enhanced oil recovery, it is  
23 necessary to reduce the interfacial tension between the oil and the water in  
24 the reservoir to about 0.01 dyne per centimeter. These ultra-low interfacial  
25 tensions are measured using a spinning drop tensiometer. Interfacial tension  
26 may also be measured by any known method for measuring interfacial  
27 tension.

1 The term "micro-emulsion" as used herein refers to a stable, micellar solution  
2 of oil, water, a surfactant and optionally one or more electrolytes.  
3 Micro-emulsions are defined as those emulsions having an average particle  
4 size of about a few nanometers in diameter.

5 The term "neutralized" as used herein refers to alkylxylene sulfonic acid  
6 neutralized with an inorganic or an organic base, such as an alkali metal  
7 hydroxide, oxide and/or alkoxide, ammonia, an organic ammonium cation or  
8 an alkanol ammonium cation.

9 The terms "optimum salinity" or "midpoint salinity" as used herein refer to the  
10 amount of salt in the aqueous phase required to minimize the interfacial  
11 tension and maximize the recovery of oil.

12 The term "under-neutralized" as used herein refers to alkylxylene sulfonic acid  
13 neutralized with an inorganic or an organic base, and wherein the remaining  
14 non-neutralized alkylxylene sulfonic acid is at least 2 weight percent based on  
15 the total weight of the neutralized alkylxylene sulfonic acid composition. The  
16 percentage of neutralization as defined herein is the weight of the base used  
17 divided by the weight of the base necessary to neutralize all the alkylxylene  
18 sulfonic acid expressed as a percentage.

19 The term "waxy crude oil" as used herein refers to crude oil usually consisting  
20 of a variety of light and intermediate hydrocarbons, such as paraffins and  
21 aromatic hydrocarbons, wax paraffins and a variety of other heavy organic  
22 compounds, such as resins and asphaltenes.

23 Unless otherwise specified, all percentages are in weight percent and the  
24 pressure is atmospheric pressure.

25 The present invention is directed to an under-neutralized alkylxylene sulfonic  
26 acid composition for enhanced oil recovery processes. It has surprisingly

1    been discovered that the under-neutralized alkylxylene sulfonic acid  
2    composition of the present invention provides a lower interfacial tension  
3    compared to the 100 percent neutralized alkylxylene sulfonic acid. A marked  
4    decrease in interfacial tension is observed with a 10 percent reduction in  
5    neutralization of the alkylxylene sulfonic acids. This result was unexpected  
6    since prior art uses of alkylaryl sulfonates for surfactant flooding for enhanced  
7    oil recovery techniques employ fully-neutralized, or carbonated, over-based  
8    alkylaryl sulfonic acids. Another reason this result was surprising is the well  
9    known prior art use of alkaline flooding in enhanced oil recovery processes.  
10   Alkaline agents, such as sodium hydroxide, have been added during water  
11   flooding and these agents react with the naturally occurring organic acids in  
12   the crude oil to produce surface active agents that reduce interfacial tension  
13   (similarly to surfactants) between the oil and the water in the reservoir.

14   Alkylxylene containing from about 10 to about 58 carbon atoms were  
15   prepared from xylene. Alkylation catalysts trifluoromethane sulfonic acid  
16   ( $\text{CF}_3\text{SO}_3\text{H}$ ) and aluminum trichloride ( $\text{AlCl}_3$ ) were used for alkylating xylene.  
17   The nature of the alkylation catalyst plays a key role in determining the  
18   alkylation position on the xylene ring.  $^{13}\text{C}$ -NMR analysis has shown that  
19   aluminum trichloride typically gives more than 90 percent yield of the  
20   4-alkyl-1,2-dimethylbenzene (4-alkyl-ortho-xylene) based on the total amount  
21   of the alkylxylene produced. On the other hand, when trifluoromethane  
22   sulfonic acid is used as the alkylation catalyst, a mixture of 4-alkyl-1,2-  
23   dimethylbenzene (4-alkyl-ortho-xylene) and 3-alkyl-1,2-dimethylbenzene  
24   (3-alkyl-ortho-xylene) is obtained. Typically, the yield of the 3-alkyl-1,2-  
25   dimethylbenzene (3-alkyl-ortho-xylene) is about 30 percent based on the total  
26   amount of the alkylxylene produced.

27   From the IFT data, it has been surprisingly discovered that the  
28   under-neutralized alkylxylene sulfonic acids prepared using the 4-alkyl-1,2-  
29   dimethylbenzene (4-alkyl-ortho-xylene) gave lower IFT data than the IFT data

1 obtained for under-neutralized alkylxylene sulfonic acids prepared using the  
2 3-alkyl-1,2-dimethylbenzene (3-alkyl-ortho-xylene).

3 Similarly, a surprising discovery was made from the IFT data that the  
4 attachment position along the carbon chain of the alkyl group to the xylene  
5 moiety is important for obtaining lower IFT data. Attachment of the alkyl  
6 group to the xylene moiety at positions higher than the 2-position along the  
7 alkyl carbon chain provides an EOR surfactant having lower IFT. It is  
8 preferred that at least 40 percent of the total under-neutralized alkylxylene  
9 sulfonic acid composition has the attachment at positions higher than the  
10 2-position along the alkyl carbon chain. Gas Chromatography (GC) and  
11  $^{13}\text{C}$ -Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR) were used to determine the  
12 attachment position along the alkyl carbon chain.

13 Under-neutralized sulfonic acid composition containing more than 40 percent  
14 attachment at positions higher than the 2-position along the alkyl carbon chain  
15 may be obtained by the use of pre-isomerized olefins containing internal  
16 double bonds.

17 The present invention is also directed to a method for enhancing the recovery  
18 of oil from a subterranean reservoir which method comprises injecting into the  
19 formation an aqueous solution containing an effective amount of the  
20 under-neutralized alkylxylene sulfonic acid composition of the present  
21 invention. The under-neutralized alkylxylene sulfonic acid composition is a  
22 mixture of compound (a) mono-valent cation neutralized alkylxylene sulfonic  
23 acid and compound (b) alkylxylene sulfonic acid.

24 Any suitable co-surfactants may be used with the alkylxylene sulfonic acids of  
25 the present invention. Examples of such co-surfactants are alcohols, alcohol  
26 ethers, polyalkylene glycols, poly(oxyalkylene)glycols and  
27 poly(oxyalkylene)glycols ethers, which may be optionally used along with the

1 under-neutralized alkylxylene sulfonic acid composition of this invention for  
2 surfactant flooding.

### 3 Preparation of Alkylxylenes

4 The alkylxylenes used for the preparation of the under-neutralized alkylxylene  
5 sulfonic acids of the present invention may be prepared with normal alpha  
6 olefins and isomerized olefins by any method known to a person skilled in the  
7 art.

8 Typically, alkylxylene may be prepared using acid catalysts (Bronsted or  
9 Lewis acids), such as hydrogen fluoride, trifluoromethane sulfonic acid or  
10 aluminum trichloride. Trifluoromethane sulfonic acid mimics hydrogen fluoride  
11 in alkylation reactions and its use is preferred in the laboratory to avoid the  
12 hazardous handling of hydrogen fluoride.

13 The alkylation reaction is typically carried out with a xylene and an olefin in  
14 molar ratios from 1:15 to 25:1. Process temperatures can range from about  
15 0°C to about 200°C. As the olefins have a high boiling point, the process is  
16 preferably carried out in the liquid phase.

17 The alkylation process may be carried out in batch or continuous mode. In  
18 the batch mode, a typical method is to use a stirred autoclave, which may be  
19 heated or cooled to the desired reaction temperature. At the end of the  
20 reaction, the catalyst is either recycled or hydrolyzed.

### 21 Procedure for Isomerization of Normal Alpha Olefins

22 The isomerization of normal alpha olefins is achieved using at least two types  
23 of acidic catalysts, solid or liquid. A solid catalyst preferably has at least one  
24 metal oxide and an average pore size of less than 5.5 angstroms. More  
25 preferably, the solid catalyst is a molecular sieve with a one-dimensional pore  
26 system, such as SM-3, MAPO-11, SPO-11, SSZ-32, ZSM-23, MAPO-39,

1 SAPO-39, ZSM-22 or SSZ-20. Other possible solid acidic catalysts useful for  
2 isomerization include ZSM-35, SUZ4, NU-23, NU-87 and natural or synthetic  
3 ferrierites. These molecular sieves are well known in the art and are  
4 discussed in Rosemarie Szostak's *Handbook of Molecular Sieves* (New York,  
5 Van Nostrand Reinhold, 1992 and U.S. Pat. No. 5,282,858, which are hereby  
6 incorporated by reference for all purposes. A liquid type of isomerization  
7 catalyst that can be used is iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ).

8 The process for the isomerization of normal alpha olefins may be carried out  
9 in batch or continuous mode. The process temperatures can range from 50°C  
10 to 250°C. In the batch mode, a typical method is to use a stirred autoclave or  
11 glass flask, which may be heated to the desired reaction temperature. A  
12 continuous process is most efficiently carried out in a fixed bed process.  
13 Space rates in a fixed bed process can range from 0.1 to 10 or more weight  
14 hourly space velocity.

15 In a fixed bed process, the isomerization catalyst is charged to the reactor and  
16 activated or dried at a temperature of at least 150°C under vacuum or flowing  
17 inert, dry gas. After activation, the temperature of the isomerization catalyst is  
18 adjusted to the desired reaction temperature and a flow of the olefin is  
19 introduced into the reactor. The reactor effluent containing the partially-  
20 branched, isomerized olefins is collected. The resulting partially-branched,  
21 isomerized olefins contain a different olefin distribution (alpha olefin, beta  
22 olefin, internal olefin, tri-substituted olefin, and vinylidene olefin) and  
23 branching content than the unisomerized olefin and conditions are selected in  
24 order to obtain the desired olefin distribution and the degree of branching.

#### 25 Procedure for Sulfonation of Alkylxylene

26 Sulfonation of alkylxylene may be carried out by any method known to a  
27 person skilled in the art.

1 The sulfonation reaction is typically carried out in a continuous falling film  
2 tubular reactor maintained at about 55°C. The alkylxylene is placed in the  
3 reactor along with the sulfur trioxide diluted with air. The molar ratio of  
4 alkylxylene to sulfur trioxide is maintained at about 1.05:1.

5 Procedure for Neutralization of Alkylxylene Sulfonic acids

6 Neutralization of alkylxylene sulfonic acids may be carried out in a continuous  
7 or batch process by any method known to a person skilled in the art to  
8 produce alkylxylene sulfonates.

9  
10 Generally, the neutralization reaction is carried out in an in-line mixing reactor  
11 in which the alkylxylene sulfonic acid and an organic or inorganic base are  
12 mixed. The reaction mixture temperature is maintained at about 20°C. The  
13 amount of alkali metal used is based on the acid number determined for each  
14 alkylxylene sulfonic acid.

15  
16 EXAMPLES

17  
18 Example 1

19 Preparation of Alkylxylene using  
20 Trifluoromethane Sulfonic Acid Alkylation Catalyst

21  
22 Example 1A: Alkylation of Ortho-xylene with C<sub>10</sub>-C<sub>58</sub> Normal Alpha Olefins

23 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
24 catalyst. To a 3 liter glass reactor were charged, under nitrogen,  
25 904.09 grams of ortho-xylene and 595.91 grams of C<sub>10</sub>-C<sub>58</sub> normal alpha  
26 olefin and allowed to mix. The mixture was heated to 60°C. Next,  
27 41.71 grams of trifluoromethane sulfonic acid was added to the reaction  
28 mixture while stirring. A strong exotherm was observed with a temperature  
29 increase to 122°C. The reaction mixture was allowed to cool to room

1 temperature for 4 hours and 30 minutes. After this cooling period, the  
2 reaction was quenched with cold distilled water, followed by three consecutive  
3 water washes to remove the acid catalyst from the organic phase. The  
4 organic phase containing the alkylxylene product was dried over magnesium  
5 sulfate and the excess ortho-xylene was distilled under reduced pressure  
6 using a Rotovap evaporator to recover the alkylxylene product.

7 Example 1B: Alkylation of Ortho-xylene with C<sub>10</sub>-C<sub>58</sub> Isomerized Olefin

8 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
9 catalyst. To a 3 liter glass reactor were charged, under nitrogen, 852 grams  
10 of ortho-xylene and 600 grams of C<sub>10</sub>-C<sub>58</sub> isomerized olefin (normal alpha  
11 olefin content about 75 percent of the total olefin) and allowed to mix. The  
12 reaction mixture was heated to 40°C. Next, 42 grams of trifluoromethane  
13 sulfonic acid was added to the reaction mixture while stirring. A strong  
14 exotherm was observed with a temperature increase to 90°C. The reaction  
15 mixture was allowed to cool 60°C and held at this temperature for 2 hours.  
16 After this cooling period, the reaction was quenched and the alkylxylene was  
17 recovered as described above in Example 1A.

18 Example 1C: Alkylation of Ortho-xylene with C<sub>10</sub>-C<sub>58</sub> Isomerized Olefin

19 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
20 catalyst. To a 3 liter glass reactor were charged, under nitrogen, 852 grams  
21 of ortho-xylene and 600 grams of C<sub>10</sub>-C<sub>58</sub> isomerized olefin (normal alpha  
22 olefin content about 40 percent of the total olefin) and allowed to mix. The  
23 reaction mixture was heated to 40°C. Next, 42 grams of trifluoromethane  
24 sulfonic acid was added to the reaction mixture while stirring. A strong  
25 exotherm was observed with a temperature increase to 90°C. The reaction  
26 mixture was allowed to cool 60°C and held at this temperature for 2 hours.  
27 After this cooling period, the reaction was quenched and the alkylxylene was  
28 recovered as described above in Example 1A.

1 Example 2

2 Preparation of Alkylxylene using Aluminum Trichloride Alkylation Catalyst

3 Alkylation of Ortho-xylene with C<sub>10</sub>-C<sub>58</sub> Normal Alpha Olefins

4 Alkylxylene was prepared using aluminum trichloride alkylation catalyst by a  
5 contract manufacturer in a continuous process using ortho-xylene and C<sub>10</sub>-C<sub>58</sub>  
6 normal alpha olefins.

7 Example 3

8 Preparation of Alkylxylene Sulfonic Acids

9 Alkylxylene sulfonic acids were prepared using the alkylxylenes prepared in  
10 Examples 1 and 2 above.

11 Sulfonation of the alkylxylene was performed in a continuous falling film flow  
12 reactor by contacting the alkylxylene with a stream of air and sulfur trioxide.  
13 The molar ratio of the alkylxylene to sulfur trioxide was about 1:0.94. The  
14 reactor jacket temperature was maintained around 55°C. The sulfonic acid  
15 product was titrated potentiometrically with a standardized cyclohexylamine  
16 solution to determine the weight percent of the sulfonic acid and the sulfuric  
17 acid in the samples. The total acid number was also determined using the  
18 ASTM Test No. D-664. The results are summarized below in Table I. Two  
19 samples of the alkylxylene prepared in Examples 1A, 1B and 1C were  
20 sulfonated as described above. The duplicate samples of these alkylxylene  
21 sulfonic acids are shown as 1A', 1B' and 1C' in Table I below.

Table I

| Example     | Catalyst                          | RSO <sub>3</sub> H*<br>(weight %) | H <sub>2</sub> SO <sub>4</sub><br>(weight %) | Acid Number<br>(mg KOH/g) |
|-------------|-----------------------------------|-----------------------------------|----------------------------------------------|---------------------------|
| Example 1A  | CF <sub>3</sub> SO <sub>3</sub> H | 86.8                              | 0.77                                         | 128                       |
| Example 1A' | CF <sub>3</sub> SO <sub>3</sub> H | 88.9                              | 0.82                                         | 128                       |
| Example 1B  | CF <sub>3</sub> SO <sub>3</sub> H | 83.9                              | 0.92                                         | 124                       |
| Example 1B' | CF <sub>3</sub> SO <sub>3</sub> H | 84.4                              | 0.91                                         | 124                       |
| Example 1C  | CF <sub>3</sub> SO <sub>3</sub> H | 83.7                              | 0.96                                         | 124                       |
| Example 1C' | CF <sub>3</sub> SO <sub>3</sub> H | 83.9                              | 0.93                                         | 120                       |
| Example 2   | AlCl <sub>3</sub>                 | 86.4                              | 0.93                                         | 118                       |

\*An average molecular weight of 453 grams per mole is assumed for all sulfonic acids.

#### Example 4

##### Preparation of Under-neutralized and Fully-neutralized Alkylxylene Sulfonic Acids

Under-neutralized alkylxylene sulfonic acids and the Comparative fully-neutralized alkylxylene sulfonic acids were prepared using the alkylxylene sulfonic acid prepared in Example 3 above.

Neutralization of the sulfonic acid was performed in a beaker with magnetic stirring. The sulfonic acid was heated to about 40°C to lower the viscosity of the sulfonic acid. Next, a 50 weight percent aqueous solution of sodium hydroxide was slowly added to the reaction mixture. The temperature of the reaction mixture was maintained below 80°C to limit the evaporation of water. The sodium hydroxide added was calculated based on the acid number obtained for each sulfonic acid. To prepare the 100 percent neutralized sulfonic acid, the exact amount of sodium hydroxide necessary for the

1 neutralization of all the acid species in the sulfonic acid samples, sulfonic acid  
 2 and H<sub>2</sub>SO<sub>4</sub> was added to the reaction mixture based on the Total Acid  
 3 Number analysis results obtained for the sulfonic acids reported in Table I  
 4 above. For the 90 percent neutralized Examples (the under-neutralized  
 5 Examples), 10 percent less sodium hydroxide than calculated for 100 percent  
 6 neutralization was employed to perform the neutralization. For the  
 7 100 percent neutralized Examples, the Comparative Examples, a 100 percent  
 8 of the calculated sodium hydroxide was employed.

9 The active content of the sodium alkylxylene sulfonate was calculated using  
 10 the formula given below:  
 11

$$12 \quad \% \text{ active as sodium sulfonate} = \frac{W_{SA} * W\%_{RSO_3H} * \frac{Mw_{RSO_3Na}}{Mw_{RSO_3H}}}{W_{SA} + W_{NaOH \text{ sol}} * \left(1 + \frac{0.5 * 18}{40}\right)}$$

13 W<sub>SA</sub>: Weight of sulfonic acid sample (grams)  
 14 W%<sub>RSO<sub>3</sub>H</sub>: Weight percent of alkylxylene sulfonic acid determined by the  
 15 cyclohexylamine titration  
 16 Mw<sub>RSO<sub>3</sub>Na</sub>: Molecular weight of the alkylxylene sodium sulfonate (grams per  
 17 mole)  
 18 Mw<sub>RSO<sub>3</sub>H</sub>: Molecular weight of the alkylxylene sulfonic acid (grams per  
 19 mole)  
 20 W<sub>NaOH sol</sub>: Weight of the NaOH solution (50 weight %) used for the  
 21 neutralization surfactant having low IFT.

22

23 For the under-neutralized Examples, the remaining sulfonic acid is considered  
 24 as active. Since less sodium hydroxide solution was used to neutralized the  
 25 under-neutralized Examples, their active content is slightly higher than the  
 26 100% neutralized Examples, the Comparative Examples. 475 g/mol and

1 453 g/mol were used as average molecular weight of the alkylxylene sodium  
2 sulfonate and the alkylxylene sulfonic acid, respectively.

3 The neutralization and active content data collected for the under-neutralized  
4 and fully-neutralized Examples is given below in Table II.

6 Table II

7

| Example        | Neutralization<br>Based on<br>TAN<br>(mol %) | Weight of<br>Sulfonic<br>Acid<br>(g) | Total Acid<br>Number-TAN<br>(mg KOH/g) | NaOH<br>(50%<br>weight in<br>H <sub>2</sub> O) | Active<br>Content<br>(weight %) |
|----------------|----------------------------------------------|--------------------------------------|----------------------------------------|------------------------------------------------|---------------------------------|
| Comparative 1A | 100                                          | 241                                  | 128                                    | 43.99                                          | 76.2                            |
| Example 1A     | 90                                           | 241                                  | 128                                    | 39.56                                          | 77.6                            |
| Comparative 1B | 100                                          | 240                                  | 124                                    | 42.44                                          | 72.7                            |
| Example 1B     | 90                                           | 240                                  | 124                                    | 38.19                                          | 74.0                            |
| Comparative 1C | 100                                          | 240                                  | 120                                    | 42.44                                          | 72.7                            |
| Example 1C     | 90                                           | 240                                  | 120                                    | 38.19                                          | 74.0                            |
| Comparative 2A | 100                                          | 240                                  | 118                                    | 40.38                                          | 75.1                            |
| Example 2A     | 90                                           | 240                                  | 118                                    | 36.35                                          | 76.4                            |

8  
9  
10 Example 5

11 Determination of the Attachment Position on the Alkyl Carbon Chain  
12 to the Xylene Moiety

13 The attachment position on the alkyl carbon chain to the xylene moiety was  
14 determined by Gas Chromatograph (GC) and quantitative <sup>13</sup>C-Nuclear  
15 Magnetic Resonance spectroscopy (<sup>13</sup>C-NMR).

16 Since the resolution of the peaks obtained in GC decreases with the retention  
17 time, it is possible to accurately quantify the attachment position of alkyl group

1 on the xylene ring only for 12 and 14 carbon atoms on the alkyl chains.

2 Quantitative  $^{13}\text{C}$ -NMR on the other hand provides an average value for all

3 carbon atoms on the alkyl chain lengths.

4  $^{13}\text{C}$ -NMR and GC also give the attachment position of the alkyl chain on the

5 ortho-xylene ring. It appears that when aluminum trichloride is used to

6 catalyze the alkylation of ortho-xylene, the isomer formed primarily is

7 4-alkyl-1,2-dimethylbenzene, whereas when trifluoromethane sulfonic acid is

8 used as alkylation catalysts, a mixture of 3-alkyl-1,2-dimethylbenzene and

9 4-alkyl-1,2-dimethylbenzene is obtained. Figures 1 and 2 show the GC

10 chromatograms obtained for the alkylate portion of the  $\text{C}_{12}$  and  $\text{C}_{14}$

11 ortho-xylene sulfonic acids prepared in Examples 2 and 1A, respectively. The

12 percent of the 4-alkyl-1,2-dimethyl benzene was calculated based by

13 averaging the area of the GC peaks for the 2-position attachment on the alkyl

14 chain for  $\text{C}_{12}$  and  $\text{C}_{14}$ . The attachment position of the xylene ring on the alkyl

15 carbon chain of the alkyl group was also calculated. The results of the GC

16 chromatography obtained for Examples 1A, 1B, 1C and 2 are given below in

17 Table III. The data show that percent of the 4-alkyl-1,2-dimethylbenzene is

18 much lower in Examples 1A, 1B and 1C when the alkylation catalyst is

19 trifluoromethane sulfonic acid than in Example 2 when aluminum trichloride is

20 used as the alkylation catalyst.

21 The results obtained by GC and  $^{13}\text{C}$ -NMR for the alkylxylene prepared above

22 in Examples 1 and 2 are given below in Table III.

1

Table III

| Example     | Alkylation Catalyst               | 4-alkyl-1,2-dimethyl-benzene<br>(% of total alkyl-ortho-xylene) | Alkyl Chain Attachment position |      |      |      |      |
|-------------|-----------------------------------|-----------------------------------------------------------------|---------------------------------|------|------|------|------|
|             |                                   |                                                                 | 2                               | 3    | 4    | 4+   | 3-4+ |
| Example 1A  | CF <sub>3</sub> SO <sub>3</sub> H | 73                                                              | 35.8                            | 21.1 | 17.9 | 25.2 | 64.2 |
| Example 1B  | CF <sub>3</sub> SO <sub>3</sub> H | 71                                                              | 33.9                            | 22.2 | 18.7 | 25.2 | 66.1 |
| Example 1C  | CF <sub>3</sub> SO <sub>3</sub> H | 65                                                              | 27.9                            | 21.2 | 20.3 | 30.6 | 72.1 |
| Example 2A  | AlCl <sub>3</sub>                 | >95                                                             | 50.1                            | 21.9 | 11.9 | 16.1 | 49.9 |
| Example 2A* | AlCl <sub>3</sub>                 | >95                                                             | 46.5                            | 18.8 | 14.9 | 19.8 | 53.5 |

2

3 \*The alkyl chain attachment position to the xylene moiety was determined by  
 4 <sup>13</sup>C-NMR for the alkylxylene prepared in Example 2A.

5

Example 6

6

Determination of Interfacial Tension

7 The performance of the under-neutralized alkylxylene sulfonic acids and the  
 8 fully-neutralized alkylxylene sulfonic acids prepared above in Example 4 was  
 9 determined by measuring the interfacial tension. The interfacial tension was  
 10 determined using Minas crude oil (a waxy crude oil) having a pour point  
 11 around 35°C and aqueous solutions of the under-neutralized alkylxylene  
 12 sulfonic acids and the fully-neutralized alkylxylene sulfonic acids. A spinning  
 13 drop tensiometer was used to measure the interfacial tension at 93°C using  
 14 the method described below.

15

Equilibrated Interfacial Tension Method

16 A 5 milliliter sample of a solution of alkylxylene sulfonic acid, water, a  
 17 co-surfactant and sodium chloride was added to an equal volume of crude oil

1 in a glass tube. The test tube was tightly sealed and shaken. The test tube  
2 was allowed to equilibrate for one month at 93°C. At the end of the  
3 equilibration period, an aliquot of the aqueous phase was loaded into the  
4 glass tube of the spinning tensiometer. Next, a small drop of the upper oil  
5 phase is injected into the glass tube. The tube is spun and the interfacial  
6 tension between the aqueous solution and the oil is determined using the  
7 B. Vonnegut equation for elongated droplets given in B. Vonnegut in *Review*  
8 *Scientific Instruments*, 13 (1942) 6:

9 
$$IFT = \frac{\omega^2 R^3 \Delta \rho}{4}$$

10  $\omega$  being the rotational speed,  $R$  the radius of the droplet, and  $\Delta \rho$  the density  
11 difference between the oil and the aqueous solution. It takes typically 1 to  
12 3 hours for the system to reach equilibrium.

13 Samples of the under-neutralized sulfonic acids and the fully-neutralized  
14 alkylxylene sulfonic acids described above in Example 4 were prepared with  
15 0.24 weight percent (on actives basis) of the under-neutralized sulfonic acids  
16 and the fully-neutralized alkylxylene sulfonic acids and 0.067 weight percent  
17 sec-butyl alcohol as co-surfactant. The interfacial tension data were collected  
18 in the presence of sodium chloride solutions between 0.1 percent to  
19 0.5 percent.

20 The results of the interfacial tension determination are given below in  
21 Table IV.

22 The IFT data for the under-neutralized alkylxylene sulfonic acids was  
23 compared to the data for the fully-neutralized alkylxylene sulfonic acids and  
24 the percent reduction of IFT was calculated by using the following formula:

25

$$1 \quad \% \text{ IFT reduction} = \left(1 - \frac{\text{IFT}_{(90\% \text{ neutralized SA})}}{\text{IFT}_{(100\% \text{ neutralized SA})}}\right) \times 100$$

2 SA = sulfonic acid

3 Table IV

| Example                     | 4-alkyl-1,2-dimethyl benzene<br>(% of total alkyl attachment) | Neutral-ization<br>(%) | Salinity (weight % NaCl)<br>IFT (dynes/cm) |           |             |             |             |
|-----------------------------|---------------------------------------------------------------|------------------------|--------------------------------------------|-----------|-------------|-------------|-------------|
|                             |                                                               |                        | 0.1                                        | 0.2       | 0.3         | 0.4         | 0.5         |
| Comparative 1A              | 73                                                            | 100                    | 2.75                                       | 0.81      | 0.28        | 0.051       | 0.006       |
| Example 1A                  | 73                                                            | 90                     | 0.75                                       | 0.36      | 0.09        | 0.016       | 0.004       |
| <b>Reduction in IFT (%)</b> |                                                               | --                     | <b>73</b>                                  | <b>56</b> | <b>68</b>   | <b>68</b>   | <b>27</b>   |
| Comparative 1B              | 71                                                            | 100                    | 5.61                                       | 0.97      | 0.67        | 0.154       | 0.008       |
| Example 1B                  | 71                                                            | 90                     | 1.15                                       | 0.61      | 0.34        | 0.080       | 0.00037     |
| <b>Reduction in IFT (%)</b> |                                                               | --                     | <b>79</b>                                  | <b>37</b> | <b>37</b>   | <b>48</b>   | <b>95</b>   |
| Comparative 1C              | 65                                                            | 100                    | 3.34                                       | 1.21      | 1.05        | 0.15        | 0.018       |
| Example 1C                  | 65                                                            | 90                     | 10.71                                      | 0.25      | 0.34        | 0.08        | 0.004       |
| <b>Reduction in IFT (%)</b> |                                                               |                        | <b>(221)</b>                               | <b>79</b> | <b>68</b>   | <b>47</b>   | <b>78</b>   |
| Comparative 2               | > 95                                                          | 100                    | 1.71                                       | 0.009     | 0.002       | 0.09        | 0.089       |
| Example 2                   | > 95                                                          | 90                     | 1.09                                       | 0.00088   | 0.05        | 0.11        | 0.13        |
| <b>Reduction in IFT (%)</b> |                                                               | --                     | <b>36</b>                                  | <b>90</b> | <b>(25)</b> | <b>(22)</b> | <b>(46)</b> |

4

5 The data in Table IV show a significant decrease in interfacial tension  
 6 between the under-neutralized alkylxylene sulfonic acids of the present  
 7 invention and oil compared to the fully-neutralized alkylxylene sulfonic acid.  
 8 The interfacial tension between the fully-neutralized alkylxylene sulfonic acid  
 9 composition prepared using trifluoromethane sulfonic acid and oil is higher  
 10 compared to that obtained for the under-neutralized alkylxylene sulfonic acid  
 11 composition at all salinities tested except for Example 1C at 0.1 weight  
 12 percent NaCl. At ultra low salinity of 0.1 percent NaCl, the measured IFT is  
 13 high and the system is not at the optimum salinity.

14

15 The IFT data for the under-neutralized and fully-neutralized alkylxylene  
 16 sulfonic acids prepared using aluminum trichloride show that the optimum  
 17 salinity is at about 0.2 weight percent NaCl because all the IFT values at

1 salinities above this are much higher. At 0.3 weight percent NaCl and higher  
2 salinities, the fully-neutralized sample gave lower IFT values than the  
3 under-neutralized sample. The lowest IFT value of 0.00088 dynes per  
4 centimeter was obtained at 0.2 weight percent NaCl for the under-neutralized  
5 sample of Example 2, whereas the fully-neutralized sample of Example 2  
6 gave an IFT value of 0.009 dynes per centimeter at this salinity. The lowest  
7 IFT value obtained for the under-neutralized alkylxylene sulfonic acid  
8 prepared using aluminum trichloride was 0.00088 dynes per centimeter at  
9 0.2 weight percent NaCl compared to 0.002 dynes per centimeter at  
10 0.3 weight percent NaCl obtained for the fully-neutralized alkylxylene sulfonic  
11 acids prepared using aluminum trichloride.

12

13 The optimum salinity for the fully-neutralized alkylxylene sulfonic acids and  
14 the under-neutralized alkylxylene sulfonic acids prepared using  
15 trifluoromethane sulfonic acid is higher than that observed for the  
16 fully-neutralized alkylxylene sulfonic acids and the under-neutralized  
17 alkylxylene sulfonic acids prepared using aluminum trichloride, 0.5 percent  
18 sodium chloride and 0.2-0.3 percent sodium chloride, respectively.

19

20 Figure 3 shows a graph for the IFT data for the fully-neutralized and the  
21 90 percent neutralized alkylxylene sulfonic acids prepared using  
22 trifluoromethane sulfonic acid and Figure 4 shows a graph for the IFT data for  
23 the fully-neutralized and the 90 percent neutralized alkylxylene sulfonic acids  
24 prepared using aluminum trichloride. The graphs clearly show the reduction  
25 in IFT when the alkylxylene sulfonic acids are neutralized only 90 percent  
26 instead of 100 percent.

27

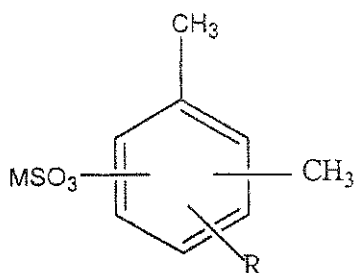
28 The data in Table IV also show that the under-neutralized alkylxylene sulfonic  
29 acid, obtained by alkylation with aluminum trichloride, having greater than  
30 95 percent of the alkylxylene moiety as the 4-alkyl-1,2-dimethylbenzene  
31 (4-alkyl-ortho-xylene) isomer is better for enhanced oil recovery of waxy crude  
32 oil in reservoirs with salinities between 0.2 percent and 0.3 percent as found

- 1 in the Minas oil fields in Indonesia than the under-neutralized alkylxylene
- 2 sulfonic acid, obtained with trifluoromethane sulfonic acid, having between
- 3 65-73 percent of the alkylxylene as the 4-alkyl-1,2-dimethylbenzene
- 4 (4-alkyl-ortho-xylene).

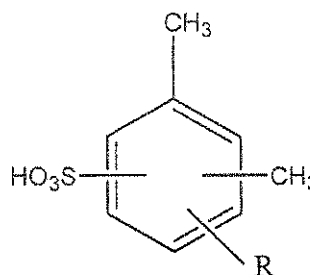
## 1 WHAT IS CLAIMED IS:

2

- 3 1. An under-neutralized alkylxylene sulfonic acid composition for  
4 enhanced oil recovery processes, which composition is a mixture of  
5 compounds having the general formula:



(a)



(b)

6

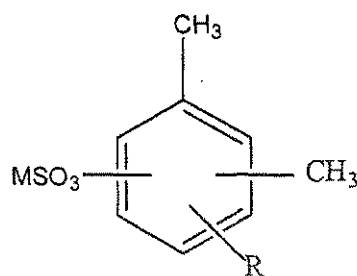
- 7 wherein  $\text{R}$  is an alkyl group containing from about 10 to about  
8 58 carbon atoms, and  $\text{M}$  is a mono-valent cation, and wherein the  
9 alkylxylene moiety in compounds (a) and (b) combined is alkyl-ortho-  
10 xylene in at least 85 percent of the total under-neutralized alkylxylene  
11 sulfonic acid composition and compound (a) is present in the range of  
12 about 80 percent to about 98 percent based on the total  
13 under-neutralized alkylxylene sulfonic acid composition.

- 14 2. The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
15 wherein the alkylxylene moiety in compounds (a) and (b) combined is  
16 alkyl-ortho-xylene in at least 95 percent of the total under-neutralized  
17 alkylxylene sulfonic acid composition.

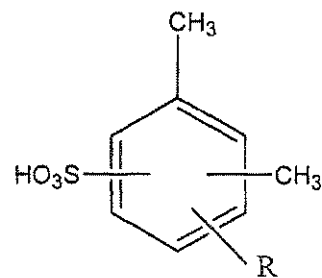
- 18 3. The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
19 wherein compound (a) is present in the range of about 85 percent to  
20 about 95 percent based on the total under-neutralized alkylxylene  
21 sulfonic acid composition.

- 1     4.     The under-neutralized alkylxylene sulfonic acid composition of claim 3,  
2           wherein compound (a) is present in the range of about 87 percent to  
3           about 92 percent based on the total under-neutralized alkylxylene  
4           sulfonic acid composition.
- 5     5.     The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
6           wherein the mono-valent cation is an alkali metal.
- 7     6.     The under-neutralized alkylxylene sulfonic acid composition of claim 5,  
8           wherein the alkali metal is sodium.
- 9     7.     The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
10          wherein the mono-valent cation is an ammonium ion or an organic  
11          ammonium ion.
- 12    8.     The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
13          wherein the alkyl group is derived from a linear alpha olefin or an  
14          isomerized olefin containing from about 10 to about 58 carbon atoms.
- 15    9.     The under-neutralized alkylxylene sulfonic acid composition of claim 8,  
16          wherein the alkyl group is derived from a linear alpha olefin or an  
17          isomerized olefin containing from about 10 to about 40 carbon atoms.
- 18    10.    The under-neutralized alkylxylene sulfonic acid composition of claim 9,  
19          wherein the alkyl group is derived from a linear alpha olefin or an  
20          isomerized olefin containing from about 12 to about 30 carbon atoms.
- 21    11.    The under-neutralized alkylxylene sulfonic acid composition of claim 1,  
22          wherein the alkylxylene moiety in compounds (a) and (b) combined  
23          contains greater than about 70 percent of the 4-alkyl-1,2-dimethyl  
24          benzene isomer.

12. The under-neutralized alkylxylene sulfonic acid composition of claim 11, wherein the alkylxylene moiety in compounds (a) and (b) combined contains greater than about 80 percent of the 4-alkyl-1, 2-dimethyl benzene isomer.
13. The under-neutralized alkylxylene sulfonic acid composition of claim 12, wherein the alkylxylene moiety in compounds (a) and (b) combined contains at least 90 percent of the 4-alkyl-1, 2-dimethyl benzene isomer.
14. The under-neutralized alkylxylene sulfonic acid composition of claim 1, wherein the alkyl group contains a distribution of alkyl chain lengths wherein the alkyl chain lengths comprise from about 40 to about 80 percent  $C_{12}$  to  $C_{20}$  and about 5 percent to about 15 percent of  $C_{32}$  to  $C_{58}$ .
15. The under-neutralized alkylxylene sulfonic acid of claim 14, wherein the distribution of alkyl chain lengths comprise from about 50 to about 70 percent  $C_{12}$  to  $C_{20}$  and about 5 percent to about 15 percent of  $C_{32}$  to  $C_{58}$ .
16. The under-neutralized alkylxylene sulfonic acid of claim 15, wherein the distribution of alkyl chain lengths comprise about 8 percent to about 12 percent of  $C_{32}$  to  $C_{58}$ .
17. A method for recovering crude oil from a subterranean hydrocarbon containing formation, which method comprises:
  - (a) injecting into the formation an aqueous solution containing an amount of an under-neutralized alkylxylene sulfonic acid composition effective for the recovery of crude oil wherein the composition is a mixture of compounds having of the general formula:



(i)



(ii)

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2

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8

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wherein R is an alkyl group containing from about 10 to about 58 carbon atoms, and M is a mono-valent cation, and wherein the alkylxylene moiety in compounds (i) and (ii) combined is alkyl-ortho-xylene in at least 85 percent of the total under-neutralized alkylxylene sulfonic acid composition and compound (i) is present in the range of about 80 percent to about 98 percent based on the total under-neutralized alkylxylene sulfonic acid composition; and

10

11

12

(b) displacing the crude oil with the aqueous solution injected into the formation to thereby recover hydrocarbons from a production well.

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18. The method of claim 17, wherein in step (a) the under-neutralized alkylxylene sulfonic acid composition is present in the range of about 0.03 weight percent to about 2.0 weight percent of the total weight of the aqueous solution.

17

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19

20

19. The method of claim 18, wherein the under-neutralized alkylxylene sulfonic acid composition is present in the range of about 0.1 weight percent to about 1.5 weight percent of the total weight of the aqueous solution.

- 1    20.    The method of claim 19, wherein the under-neutralized alkylxylene  
2           sulfonic acid composition is present in the range of about 0.3 weight  
3           percent to about 1.0 weight percent of the total weight of the aqueous  
4           solution.
- 5    21.    The method of claim 20, wherein the under-neutralized alkylxylene  
6           sulfonic acid composition is present in the range of about 0.5 weight  
7           percent to about 0.8 weight percent of the total weight of the aqueous  
8           solution.
- 9    22.    The method of claim 17, wherein compound (i) in step (a) is present in  
10          the range of about 85 percent to about 95 percent based on the total  
11          under-neutralized alkylxylene sulfonic acid composition.
- 12   23.    The method of claim 22, wherein compound (i) in step (a) is present in  
13          the range of about 87 percent to about 92 percent based on the total  
14          under-neutralized alkylxylene sulfonic acid composition.
- 15   24.    The method of claim 17, wherein in compound (i) the mono-valent  
16          cation is an alkali metal.
- 17   25.    The method of claim 24, wherein the alkali metal is sodium.
- 18   26.    The method of claim 17, wherein the mono-valent cation in  
19          compound (i) is an ammonium ion or an organic ammonium ion.
- 20   27.    The method of claim 19, wherein in step (a) the alkyl group in  
21          compounds (i) and (ii) is derived from a linear alpha olefin or an  
22          isomerized olefin containing from about 10 to about 58 carbon atoms.
- 23   28.    The method of claim 27, wherein in step (a) the alkyl group in  
24          compounds (i) and (ii) is derived from a linear alpha olefin or an  
25          isomerized olefin containing from about 10 to about 40 carbon atoms.

- 1     29.     The method of claim 28, wherein in step (a) the alkyl group in  
2             compounds (i) and (ii) is derived from a linear alpha olefin or an  
3             isomerized olefin containing from about 12 to about 30 carbon atoms.
- 4     30.     The method of claim 17, wherein the alkylxylene moiety in  
5             compounds (i) and (ii) combined in step (a) contains greater than about  
6             70 percent of the 4-alkyl-1,2-dimethyl benzene isomer.
- 7     31.     The method of claim 30, wherein the alkylxylene moiety in  
8             compounds (i) and (ii) combined in step (a) contains greater than about  
9             80 percent of the 4-alkyl-1,2-dimethylbenzene isomer.
- 10    32.     The method of claim 31, wherein the alkylxylene moiety in  
11             compounds (i) and (ii) combined in step (a) contains at least 90 percent  
12             of the 4-alkyl-1,2-dimethylbenzene isomer.
- 13    33.     The method of claim 17, wherein in step (a) the alkyl group in  
14             compounds (i) and (ii) contains a distribution of alkyl chain lengths and  
15             wherein the alkyl chain lengths comprise from about 40 to about  
16             80 percent C<sub>12</sub> to C<sub>20</sub> and about 5 percent to about 15 percent of C<sub>32</sub> to  
17             C<sub>58</sub>.
- 18    34.     The method of claim 33, wherein the distribution of alkyl chain lengths  
19             comprise from about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub> and about  
20             5 percent to about 15 percent of C<sub>32</sub> to C<sub>58</sub>.
- 21    35.     The method of claim 34, wherein the distribution of alkyl chain lengths  
22             comprise about 8 percent to about 12 percent of C<sub>32</sub> to C<sub>58</sub>.
- 23    36.     The method of claim 17, wherein the hydrocarbon in the subterranean  
24             formation is a waxy crude oil.

- 1    37.    The method of claim 17, wherein the method further comprises,  
2           concurrently with or subsequent to the injection of the aqueous solution  
3           of step (a), injecting into the formation an amount of polymer effective  
4           for driving the aqueous solution of step (a) into the formation to  
5           displace the crude oil to thereby recover hydrocarbons from a  
6           production well.
- 7    38.    The method of claim 37, wherein the polymer is a polysaccharide, an  
8           acrylamide or a partially hydrolyzed polyacrylamide.
- 9    39.    The method of claim 17, wherein the method further comprises,  
10           concurrently with or subsequent to the injection of the aqueous solution  
11           of step (a), injecting into the formation an amount of water effective for  
12           driving the aqueous solution of step (a) into the formation to displace  
13           the crude oil to thereby recover hydrocarbons from a production well.
- 14   40.    The method of claim 37, wherein the method further employs,  
15           concurrently with or subsequent to the injection of the polymer,  
16           injecting into the formation an amount of water effective for driving the  
17           aqueous solution of step (a) into the formation to displace the crude oil  
18           to thereby recover hydrocarbons from a production well.
- 19   41.    The method of claim 17, wherein the aqueous solution in step (a)  
20           further contains a co-surfactant having a molecular weight in the range  
21           of about 60 to about 1,200.
- 22   42.    The method of claim 41, wherein the co-surfactant is an alcohol, an  
23           alcohol ether, a polyalkylene glycol, a poly(oxyalkylene)glycol, a  
24           poly(oxyalkylene)glycol ether, or mixtures thereof.
- 25   43.    The method of claim 42, wherein the poly(oxyalkylene) glycol ether is  
26           an ethylene glycol mono-alkyl or mono-phenyl ether, a di-ethylene

1 glycol mono-alkyl or mono-phenyl ether, a tri-ethylene glycol  
2 mono-alkyl or a mono-phenyl ether, a polyethylene glycol mono-phenyl  
3 ether, a polypropylene glycol mono-phenyl ether, or mixtures thereof.

4 44. The method of claim 43, wherein the poly(oxyalkylene) glycol is a  
5 poly(oxyethylene) glycol or a poly(oxypropylene) glycol, or mixtures  
6 thereof.

7 45. The method of claim 41, wherein in step (a) the co-surfactant is in the  
8 range of about 0.03 weight percent to about 2.0 weight percent of the  
9 total weight of the aqueous solution.

10 46. The method of claim 45, wherein the co-surfactant is present in the  
11 range of about 0.1 weight percent to about 1.5 weight percent of the  
12 total weight of the aqueous solution.

13 47. The method of claim 46, wherein the co-surfactant is present in the  
14 range of about 0.3 weight percent to about 1.0 weight percent of the  
15 total weight of the aqueous solution.

16 48. The method of claim 47, wherein the co-surfactant is present in the  
17 range of about 0.5 weight percent to about 0.8 weight percent of the  
18 total weight of the aqueous solution.