

1                                   **ALKYLXYLENE SULFONATES FOR**  
2                                   **ENHANCED OIL RECOVERY PROCESSES**

3    The present invention is directed to alkylxylene sulfonate for enhanced oil  
4    recovery processes. The alkylxylene moiety in the alkylxylene sulfonate  
5    contains a high percentage of the 4-alkyl-1,2-dimethyl benzene isomer and  
6    attachment of the alkyl group to the xylene ring at positions higher than the  
7    2-position on the alkyl carbon chain. The present invention is also directed to  
8    a method for enhancing the recovery of oil from a subterranean reservoir  
9    which method employs the alkylxylene sulfonate of the present invention. The  
10   alkylxylene sulfonate is employed in an aqueous media. The method  
11   optionally employs co-surfactants.

12                                   **BACKGROUND OF THE INVENTION**

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

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

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

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

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

1 solution containing the alkylaryl sulfonates which matches the salinity of the  
2 reservoir water.

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

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

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

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

22 EP 0 158 486 B1 discloses the use of polyalkyl aromatic sulfonates,  
23 particularly dialkyl aromatic sulfonates in steam recovery methods for  
24 enhancing oil recovery. The increase of the ratio of para-isomer to meta-  
25 isomer results in a significantly more hydrolytically, thermally stable surfactant  
26 under steam recovery operating conditions.

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

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

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

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

26 U.S. Patent No. 4,217,958 discloses the use of sacrificial agents, polybasic  
27 carboxylic acid or their water soluble salts, in admixture with a chemical oil

1 recovery agent, such as a surfactant, a polymer, and/or a micellar dispersion  
2 to reduce the adsorption of surfactants and/or the polymers on reservoir rock.

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

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

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

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

24 U.S. Patent No. 4,608,204 discloses a process for the preparation of a low  
25 viscosity aqueous alkyltoluene or alkylxylene sulfonate with the addition of  
26 sodium chloride during neutralization or after neutralization. Such low  
27 viscosity sulfonates are useful as surfactants in enhanced oil recovery

1 processes. When xylene is employed, a mixture of the three isomers, ortho-,  
2 meta- and para-, are preferred.

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

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

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

22 U.S. Patent No. 6,022,834 discloses an improved alkali surfactant flood  
23 process with ultra-low interfacial tension. The surfactant system contains  
24 (1) a mixture of anionic surfactants; (2) solvent(s); (3) a strong base; and  
25 (4) optionally, a nonionic surfactant or mixtures of nonionic surfactants or  
26 sulfates or carboxylates of these nonionic surfactants. The anionic  
27 surfactants are sulfonates derived from alkylbenzene, alkyl-naphthalene,

1 alkyltoluene or alkylxylene. The alkyl group consists of between about C<sub>4</sub> and  
2 about C<sub>24</sub>.

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

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

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

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

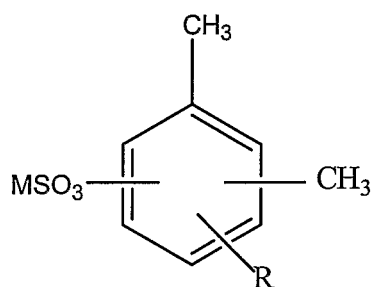
## 23 SUMMARY OF THE INVENTION

24 The present invention is directed to alkylxylene sulfonate for enhanced oil  
25 recovery (EOR) processes. The alkylxylene moiety in the alkylxylene  
26 sulfonate of the present invention contains greater than 70 percent of the

1 4-alkyl-1,2-dimethyl benzene isomer and wherein the attachment on the alkyl  
2 carbon chain to the xylene moiety at positions higher than the 2-position on  
3 the alkyl carbon chain is at least 40 percent. The present invention is also  
4 directed to a method for enhancing the recovery of oil from a subterranean  
5 reservoir which method employs the alkylxylene sulfonate of the present  
6 invention. The alkylxylene sulfonate is employed in an aqueous media. The  
7 method optionally employs co-surfactants, such as alcohols, alcohol ethers,  
8 polyalkylene glycols, poly(oxyalkylene)glycols and poly(oxyalkylene)glycol  
9 ethers, or mixtures thereof.

10 It has been discovered that the alkylxylene moiety in the alkylxylene sulfonate  
11 of the present invention containing greater than 70 percent of the 4-alkyl-1,2-  
12 dimethyl benzene isomer and wherein the attachment of the alkyl group to the  
13 xylene moiety in the alkylxylene sulfonate at positions higher than the  
14 2-position along the alkyl carbon chain is at least 40 percent provide an EOR  
15 surfactant having low Interfacial Tension (IFT).

16 In particular, the present invention is directed to alkylxylene sulfonate for  
17 enhanced oil recovery processes having the general formula:

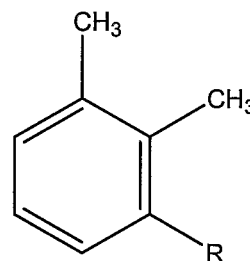
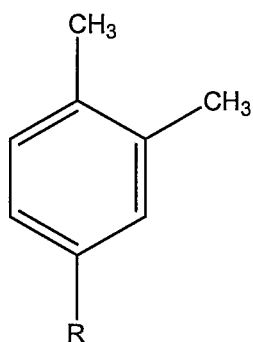


19 wherein R is an alkyl group containing from about 10 to about 58 carbon  
20 atoms, M is a mono-valent cation, and the alkylxylene moiety in the  
21 alkylxylene sulfonate is alkyl-ortho-xylene in at least 85 percent of the total  
22 alkylxylene sulfonate, and wherein the alkylxylene moiety in the alkylxylene  
23 sulfonate contains greater than about 70 percent of the 4-alkyl-1,2-dimethyl  
24 benzene isomer and the attachment of the alkyl group to the xylene moiety in

1 the alkylxylene sulfonate is at positions higher than the 2-position along the  
2 alkyl chain in at least 40 percent of the total alkylxylene sulfonate of the  
3 present invention.

4 Preferably, the alkylxylene moiety is alkyl-ortho-xylene in at least 95 percent  
5 of the total alkylxylene sulfonate.

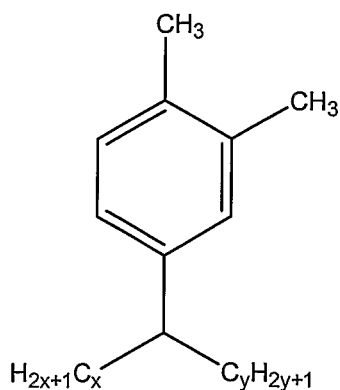
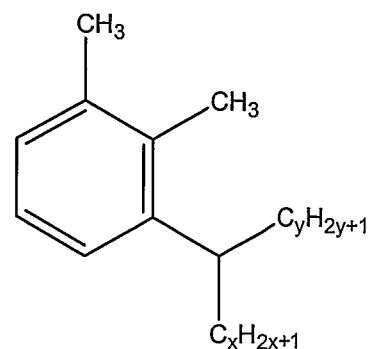
6 Preferably, the alkylxylene moiety in the alkylxylene sulfonate contains greater  
7 than about 80 percent of the 4-alkyl-1,2-dimethyl benzene isomer. More  
8 preferably, the alkylxylene moiety in the alkylxylene sulfonate contains at least  
9 90 percent of the 4-alkyl-1,2-dimethyl benzene isomer. The structures for the  
10 4-alkyl-1,2-dimethyl benzene and the 3-alkyl-1,2-dimethyl benzene are given  
11 below.



12 **4-alkyl-1,2dimethylbenzene**

**3-alkyl-1,2-dimethylbenzene**

13 Preferably, the attachment of the alkyl group to the xylene moiety is at  
14 positions higher than the 2-position along the alkyl chain in at least 45 percent  
15 of the total alkylxylene sulfonate and more preferably the attachment of the  
16 alkyl group to the xylene moiety is at positions higher than the 2-position  
17 along the alkyl chain in at least 60 percent of the total alkylxylene sulfonate.  
18 The structures for the various attachment positions on the carbon chain of the  
19 alkyl group to the xylene moiety are given below.

1     **4-alkyl-1,2-dimethylbenzene**

3-alkyl-1,2-dimethylbenzene

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

9     The mono-valent cation in the alkylxylene sulfonate is an alkali metal.  
 10    Preferably, the alkali metal is sodium. The mono-valent cation may be an  
 11    ammonium ion or an organic ammonium ion.

12    The alkyl group in the alkylxylene sulfonate of the present invention is derived  
 13    from a linear alpha olefin or isomerized olefin containing from about 10 to  
 14    about 58 carbon atoms. Preferably, the alkyl group is derived from a linear  
 15    alpha olefin or isomerized olefin containing from about 10 to about 40 carbon  
 16    atoms. More preferably, the alkyl group is derived from a linear alpha olefin or  
 17    isomerized olefin containing from about 12 to about 30 carbon atoms.

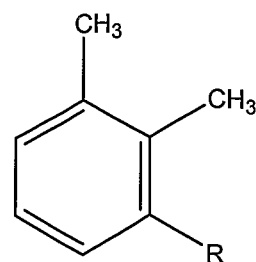
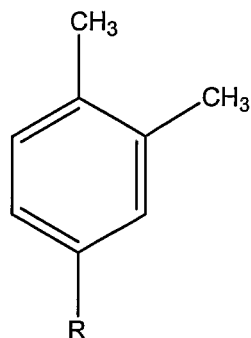
18    The alkyl group in the above alkylxylene sulfonate contains a broad  
 19    distribution of alkyl chain lengths. The upper heavier range C<sub>32</sub> to C<sub>58</sub> may  
 20    comprise from about 5 percent to about 15 percent of the alkyl groups and

1 more preferably from about 8 percent to about 12 percent of the alkyl groups.  
2 A preferred distribution of alkyl chain lengths comprises from about 40 to  
3 about 80 percent C<sub>12</sub> to C<sub>20</sub>. A more preferred distribution of alkyl chain  
4 lengths comprises from about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub>.

5 Another embodiment of the present invention is directed to alkylxylene  
6 sulfonate for enhanced oil recovery processes, which composition is derived  
7 from ortho-, meta- and para-xylene, and wherein the alkyl group contains from  
8 about 10 to about 58 carbon atoms, and the alkylxylene moiety in the  
9 alkylxylene sulfonate is alkyl-ortho-xylene in at least 85 percent of the total  
10 alkylxylene sulfonate, and wherein the alkylxylene moiety in the alkylxylene  
11 sulfonate contains greater than about 70 percent of the 4-alkyl-1,2-dimethyl  
12 benzene isomer and the attachment of the alkyl group to the xylene moiety in  
13 the alkylxylene sulfonate is at positions higher than the 2-position along the  
14 alkyl chain in at least 40 percent of the total alkylxylene sulfonate of the  
15 present invention.

16 Preferably, the alkylxylene moiety in the alkylxylene sulfonate is alkyl-ortho-  
17 xylene in at least 95 percent of the total alkylxylene sulfonate.

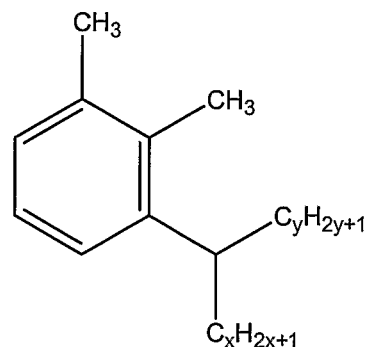
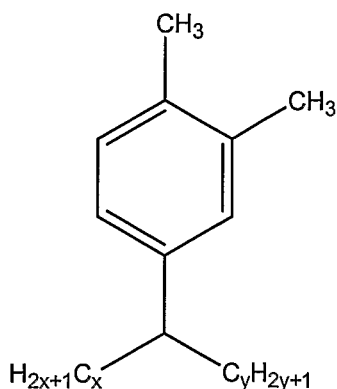
18 Preferably, the alkylxylene moiety in the alkylxylene sulfonate contains greater  
19 than about 80 percent of the 4-alkyl-1,2-dimethyl benzene isomer. More  
20 preferably, the alkylxylene moiety in the alkylxylene sulfonate contains at least  
21 90 percent of the 4-alkyl-1,2-dimethyl benzene isomer. The structures for the  
22 4-alkyl-1,2-dimethyl benzene and the 3-alkyl-1,2-dimethyl benzene are given  
23 below.



1 4-alkyl-1,2dimethylbenzene

3-alkyl-1,2-dimethylbenzene

2 Preferably, the attachment of the alkyl group to the xylene moiety in the above  
 3 alkylxylene sulfonate is at positions higher than the 2-position along the alkyl  
 4 chain in at least 45 percent of the total alkylxylene sulfonate. More preferably,  
 5 the attachment of the alkyl group to the xylene moiety is at positions higher  
 6 than the 2-position along the alkyl chain in at least 60 percent of the total  
 7 alkylxylene sulfonate. The structures for the various attachment positions on  
 8 the carbon chain of the alkyl group to the 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  
 11 position of the alkyl group to the xylene moiety on the carbon chain. For  
 12 example, for a C<sub>12</sub> alkyl group, the value of x equal to 2 and y equal to 9  
 13 corresponds to the attachment of the alkyl group at the 3-position on the alkyl

1 carbon chain. Thus, for  $x+y+1$  equal to between 10 and 58, knowing  $x$  and  $y$   
2 provides the attachment of the alkyl group to the xylene moiety for the  
3 corresponding chain lengths between  $C_{10}$  and  $C_{58}$ .

4 The mono-valent cation in the alkylxylene sulfonate is an alkali metal.  
5 Preferably, the alkali metal is sodium. The mono-valent cation may be an  
6 ammonium ion or an organic ammonium ion.

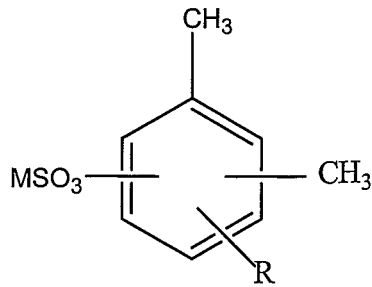
7 The alkyl group in the above alkylxylene sulfonate is derived from a linear  
8 alpha olefin or an isomerized olefin containing from about 10 to about  
9 58 carbon atoms. Preferably, the alkyl group is derived from a linear alpha  
10 olefin or an isomerized olefin containing from about 10 to about 40 carbon  
11 atoms. More preferably, the alkyl group is derived from a linear alpha olefin or  
12 an isomerized olefin containing from about 12 to about 30 carbon atoms.

13 The alkyl group in the above alkylxylene sulfonate contains a broad  
14 distribution of alkyl chain lengths. The upper heavier range  $C_{32}$  to  $C_{58}$  may  
15 comprise from about 5 percent to about 15 percent of the alkyl groups and  
16 more preferably from about 8 percent to about 12 percent of the alkyl groups.  
17 A preferred distribution of alkyl chain lengths comprises from about 40 to  
18 about 80 percent  $C_{12}$  to  $C_{20}$ . A more preferred distribution of alkyl chain  
19 lengths comprises from about 50 to about 70 percent  $C_{12}$  to  $C_{20}$ .

20 A further embodiment of the present invention is directed to a method for  
21 recovering crude oil from a subterranean hydrocarbon containing formation,  
22 which method comprises:

23 (a) injecting into the formation an aqueous solution containing an  
24 amount of an alkylxylene sulfonate or mixtures of alkylxylene  
25 sulfonates effective for the recovery of crude oil wherein the  
26 alkylxylene sulfonate has the general formula:

1



2

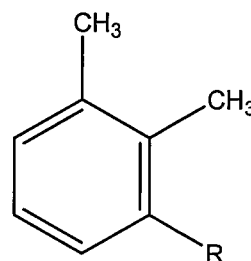
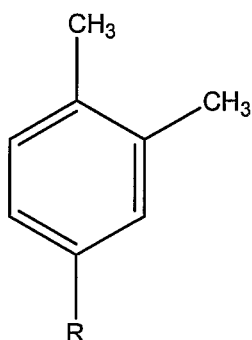
3 wherein R is an alkyl group containing from about 10 to about  
 4 58 carbon atoms, M is a mono-valent cation, and the alkylxylene  
 5 moiety in the alkylxylene sulfonate is alkyl-ortho-xylene in at least  
 6 85 percent of the total alkylxylene sulfonate, and wherein the  
 7 alkylxylene moiety in the alkylxylene sulfonate contains greater than  
 8 about 70 percent of the 4-alkyl-1,2-dimethyl benzene isomer and the  
 9 attachment of the alkyl group to the xylene moiety in the alkylxylene  
 10 sulfonate is at positions higher than the 2-position along the alkyl chain  
 11 in at least 40 percent of the total alkylxylene sulfonate of the present  
 12 invention; and

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

15 In step (a) in the above method, the alkylxylene sulfonate is present in the  
 16 range of about 0.03 weight percent to about 2.0 weight percent of the total  
 17 weight of the aqueous solution. Preferably, the composition is present in the  
 18 range of about 0.1 weight percent to about 1.5 weight percent of the total  
 19 weight of the aqueous composition. More preferably, the composition is  
 20 present in the range of about 0.3 weight percent to about 1.0 weight percent  
 21 of the total weight of the aqueous composition, and most preferably the  
 22 composition is present in the range of about 0.5 weight percent to about  
 23 0.8 weight percent of the total weight of the aqueous composition.

1 In the above method, the alkylxylene moiety in step (a) is preferably  
2 alkyl-ortho-xylene in at least 95 percent based on the total alkylxylene  
3 sulfonate.

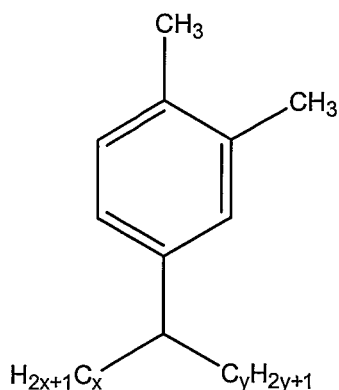
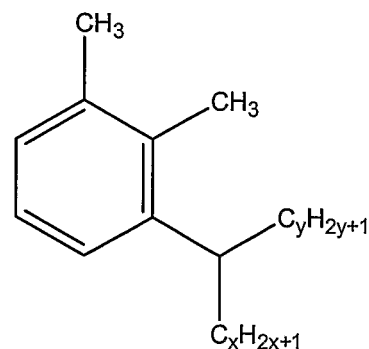
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6 preferably, the alkylxylene moiety in the alkylxylene sulfonate contains at least  
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9 below.



10 4-alkyl-1,2dimethylbenzene

3-alkyl-1,2-dimethylbenzene

11 Preferably, the attachment of the alkyl group to the xylene moiety in the above  
12 alkylxylene sulfonate is at positions higher than the 2-position along the alkyl  
13 chain in at least 45 percent of the total alkylxylene sulfonate. More preferably,  
14 the attachment of the alkyl group to the xylene moiety is at positions higher  
15 than the 2-position along the alkyl chain in at least 60 percent of the total  
16 alkylxylene sulfonate. The structures for the various attachment positions on  
17 the carbon chain of the alkyl group to the xylene moiety are given below.

1     **4-alkyl-1,2-dimethylbenzene**

3-alkyl-1,2-dimethylbenzene

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

9     The mono-valent cation in step (a) in the above method is an alkali metal.  
 10    Preferably, the alkali metal is sodium. The mono-valent cation may be an  
 11    ammonium ion or an organic ammonium ion.

12    The alkyl group in step (a) of the above method is derived from a linear alpha  
 13    olefin or an isomerized olefin containing from about 10 to about 58 carbon  
 14    atoms. Preferably, the alkyl group is derived from a linear alpha olefin or an  
 15    isomerized olefin containing from about 10 to about 40 carbon atoms. More  
 16    preferably, the alkyl group is derived from a linear alpha olefin or an  
 17    isomerized olefin containing from about 12 to about 30 carbon atoms.

18    The alkyl group in step (a) in the above method contains a broad distribution  
 19    of alkyl chain lengths. The upper heavier range C<sub>32</sub> to C<sub>58</sub> may comprise from  
 20    about 5 percent to about 15 percent of the alkyl groups and more preferably

1 from about 8 percent to about 12 percent of the alkyl groups. A preferred  
2 distribution of alkyl chain lengths comprises from about 40 to about 80 percent  
3 C<sub>12</sub> to C<sub>20</sub>. A more preferred distribution of alkyl chain lengths comprises from  
4 about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub>.

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

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

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

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

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

24 The aqueous solution in step (a) in the above method further employs a  
25 co-surfactant having a molecular weight in the range of about 60 to about  
26 1,200.

1 The co-surfactant in the above method may be an alcohol (primary,  
2 secondary, tertiary or mixtures thereof), an alcohol ether, a polyalkylene  
3 glycol, a poly(oxyalkylene) glycol, a poly(oxyalkylene)glycol ether or mixtures  
4 thereof. The poly(oxyalkylene) glycol ether may be any C<sub>1</sub>-C<sub>8</sub> mono-alkyl  
5 ether, such as ethylene or propylene glycol mono-alkyl or mono-phenyl ether,  
6 a di-ethylene or di-propylene glycol mono-alkyl or mono-phenyl ether, a  
7 tri-ethylene or tri-propylene glycol mono-alkyl or mono-phenyl ether,  
8 polyethylene glycol mono-phenyl ether, polypropylene glycol mono-phenyl  
9 ether or mixtures thereof.

10 Examples of the poly(oxyalkylene) glycol are poly(oxyethylene) glycol and  
11 poly(oxypropylene) glycol or mixtures thereof.

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

## 21 BRIEF DESCRIPTION OF THE DRAWINGS

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

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

3 Figure 3 is a plot of Equilibrated Interfacial Tensions, measured according to  
4 the method described below, versus sodium chloride concentration for  
5 samples of the alkylxylene sulfonate prepared using alkylxylene described in  
6 Examples 1A, 1B, 1C and 1D (using trifluoromethane sulfonic acid as the  
7 alkylation catalyst).

8 Figure 3 also shows IFT data for samples of the alkylxylene sulfonate  
9 prepared using alkylxylene described in Example 2 (using hydrogen fluoride  
10 as the alkylation catalyst), Example 3A (using aluminum trichloride as the  
11 alkylation catalyst) and Example 4 (using the ionic liquid alkylation catalyst).

## 12 DETAILED DESCRIPTION OF THE INVENTION

### 13 Definitions

14 As used herein, the following terms have the following meanings unless  
15 expressly stated to the contrary:

16

17 The terms "active" or "actives" as used herein refers to the concentration of  
18 sodium alkylxylene sulfonates in the Examples described in the present  
19 invention. The calculation of the actives content as sodium alkylxylene  
20 sulfonate is described in Example 6 and the data are summarized in Table II.

21

22 The term "alkylate" as used herein refers to the alkylxylene used to prepare  
23 the alkylxylene sulfonates of the present invention. The alkylxylene was  
24 prepared using xylene and linear alpha olefin or isomerized olefin containing  
25 from about 10 to about 58 carbon atoms. Preferably, the linear alpha olefin or  
26 isomerized olefin contains from about 10 to about 40 carbon atoms, and more  
27 preferably from about 12 to about 30 carbon atoms.

1 The term "alkali metal" as used herein refers to Group I A metals of the  
2 Periodic Table.

3

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

6 The term "co-surfactant" herein refers to nonionic surfactants that are used in  
7 conjunction with anionic surfactants in enhanced oil recovery processes.

8 Generally, nonionic surfactants have a somewhat higher tolerance to  
9 polyvalent ions, are water-soluble, and exhibit a wide range of low and stable  
10 interfacial tensions between alkaline brine and crude oil. They may also  
11 provide a reduction in viscosity of the surfactant.

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

18 The terms "Gas Chromatography" or "GC" as used herein refer to Gas Liquid  
19 Phase Chromatography.

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

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

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

9 The term "neutralized" as used herein refers to alkylxylene sulfonic acid  
10 neutralized with an inorganic or an organic base, such as an alkali metal  
11 hydroxide, oxide and/or alkoxide, ammonia, an organic amine or an alkanol  
12 amine.

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

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

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

22 It has surprisingly been discovered that in the alkylxylene sulfonate of the  
23 present invention the attachment position of the alkyl group to the xylene  
24 moiety is important for obtaining low interfacial tension. The best results were  
25 obtained when the alkylxylene moiety in the alkylxylene sulfonate contains  
26 greater than 70 percent the 4-alkyl-1,2-dimethyl benzene based on the total

1 alkylxylene sulfonate. Furthermore, the alkyl group attachment along the  
2 carbon chain of the alkyl group to the xylene moiety is also surprisingly  
3 important for obtaining low interfacial tension. Attachment of the alkyl group  
4 to the xylene moiety of the alkylxylene at positions higher than the 2-position  
5 along the alkyl carbon chain provides an EOR surfactant having low interfacial  
6 tension. It is preferred that at least 40 percent of the total alkylxylene  
7 sulfonate have the attachment at positions higher than the 2-position along  
8 the alkyl carbon chain. Gas Chromatography (GC) and  $^{13}\text{C}$ -Nuclear Magnetic  
9 Resonance spectroscopy ( $^{13}\text{C}$ -NMR) were used to determine the attachment  
10 position along the alkyl carbon chain.

11 Alkylxylene containing from about 10 to about 58 carbon atoms was prepared  
12 from ortho-xylene. Alkylation catalysts, hydrogen fluoride (HF),  
13 trifluoromethane sulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ), aluminum trichloride ( $\text{AlCl}_3$ ) and the  
14 ionic liquid catalyst, methyltributylammonium heptachloroaluminate, were  
15 used to alkylate ortho-xylene. The nature of the alkylation catalyst plays a key  
16 role in determining the alkylation position on the ortho-xylene ring.  $^{13}\text{C}$ -NMR  
17 analysis has shown that aluminum chloride and methyltributylammonium  
18 heptachloroaluminate typically give more than 90 percent yield of the 4-alkyl-  
19 1,2-dimethyl benzene (4-alkyl-ortho-xylene) based on the total amount of the  
20 alkylxylene produced. On the other hand, when hydrogen fluoride or  
21 trifluoromethane sulfonic acid is used as the alkylation catalyst, a mixture of  
22 4-alkyl-1,2-dimethyl benzene (4-alkyl-ortho-xylene) and 3-alkyl-1,2-dimethyl  
23 benzene (3-alkyl-ortho-xylene) is obtained. Typically, the yield of the 4-alkyl-  
24 1,2-dimethyl benzene (4-alkyl-ortho-xylene) is about 70 percent based on the  
25 total amount of the alkylxylene produced.

26 It has also been observed that the attachment position along the carbon chain  
27 of the alkyl group to the xylene moiety is important for obtaining lower IFT  
28 data. Attachment of the alkyl group to the xylene moiety at positions higher  
29 than the 2-position along the alkyl carbon chain provides an EOR surfactant  
30 having lower IFT. It is preferred that at least 40 percent of the total

1 alkylxylene sulfonate composition has attachment at positions higher than the  
2 2-position along the alkyl carbon chain. GC and  $^{13}\text{C}$ -NMR were used to  
3 determine the attachment position along the alkyl carbon chain.

4 Alkylxylene sulfonate containing more than 40 percent attachment at positions  
5 higher than the 2-position along the alkyl carbon chain may be obtained by  
6 the use of pre-isomerized olefins containing internal double bonds.

7 It has been discovered that when the alkylxylene is prepared using the  
8 alkylation catalyst trifluoromethane sulfonic acid ( $\text{CF}_3\text{SO}_3\text{H}$ ), the resultant  
9 alkylxylene sulfonate of the present invention has an optimum salinity at  
10 0.5 percent sodium chloride. On the other hand, when aluminum trichloride  
11 ( $\text{AlCl}_3$ ) is used for preparing the alkylxylene sulfonate of the present invention,  
12 the optimum salinity is 0.3 percent sodium chloride. The ionic liquid alkylation  
13 catalyst methyltributylammoniumchloride exhibits an optimum salinity at  
14 0.4 percent sodium chloride. Thus, the alkylxylene sulfonate of the present  
15 invention may be effectively used for enhanced oil recovery in reservoirs with  
16 salinities varying between 0.2 to 0.5 percent.

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 amount of the alkylxylene  
20 sulfonate or mixtures of alkylxylene sulfonates of the present invention  
21 effective for enhancing the recovery of crude oil.

22 In addition to the use of an aqueous solution containing the alkylxylene  
23 sulfonate of the present method for enhancing the recovery of crude oil,  
24 optionally, an amount of polymer may be injected, concurrently with or  
25 subsequent to the injection of the aqueous solution, effective for driving the  
26 aqueous solution of the alkylxylene sulfonate into the formation to displace the  
27 crude oil into the formation to recover hydrocarbons from a production well.

1 The injection of the polymer may be followed by an injection of an amount of  
2 water effective for driving the polymer into the formation to recover  
3 hydrocarbons from a production well. Alternately, the injection of an amount  
4 of water effective for driving the alkylxylene sulfonate of the present invention  
5 into the formation to recover hydrocarbons from a production well may be  
6 performed without the prior injection of the polymer. Another alternative  
7 involves the use of water along with the polymer for driving the alkylxylene  
8 sulfonate of the present invention into the formation to recover hydrocarbons  
9 from a production well.

10 In the above method, the hydrocarbon in the subterranean formation may be  
11 a waxy crude oil.

12 Any suitable co-surfactants may optionally be used with the alkylxylene  
13 sulfonate of the present invention. Examples of such suitable co-surfactants  
14 are alcohols, alcohol ethers, polyalkylene glycols, poly(oxyalkylene)glycols  
15 and poly(oxyalkylene)glycol ethers may optionally be used along with the  
16 alkylxylene sulfonate of this invention for surfactant flooding.

#### 17 Preparation of Alkylxylenes

18 The alkylxylenes used for the preparation of the neutralized alkylxylene  
19 sulfonic acids of the present invention may be prepared with normal alpha  
20 olefins and isomerized olefins by any method known to a person skilled in the  
21 art.

22 Typically, alkylxylenes may be prepared using acid catalysts (Bronsted or  
23 Lewis acids), such as hydrogen fluoride, trifluoromethane sulfonic acid or  
24 aluminum trichloride. Trifluoromethane sulfonic acid can mimic hydrogen  
25 fluoride in alkylation reactions and its use is preferred in the laboratory to  
26 avoid the hazardous handling of hydrogen fluoride. Example 1 shows that the  
27 data obtained using trifluoromethane sulfonic acid as the alkylation catalyst

1 correlates well with the data obtained in Example 2 using hydrogen fluoride as  
2 the alkylation catalyst.

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

7 The alkylation process may be carried out in batch or continuous mode. In  
8 the batch mode, a typical method is to use a stirred autoclave or glass flask,  
9 which may be heated or cooled to the desired reaction temperature. At the  
10 end of the reaction, the catalyst is either recycled (when hydrogen fluoride is  
11 used) or hydrolyzed (when aluminum trichloride is used) or removed by  
12 washing (when trifluoromethane sulfonic acid is used).

#### 13 Procedure for Isomerization of Normal Alpha Olefins

14 The isomerization of normal alpha olefins is achieved using at least two types  
15 of acidic catalysts, solid or liquid. A solid catalyst preferably has at least one  
16 metal oxide and an average pore size of less than 5.5 angstroms. More  
17 preferably, the solid catalyst is a molecular sieve with a one-dimensional pore  
18 system, such as SM-3, MAPO-11, SPO-11, SSZ-32, ZSM-23, MAPO-39,  
19 SAPO-39, ZSM-22 or SSZ-20. Other possible solid acidic catalysts useful for  
20 isomerization include ZSM-35, SUZ4, NU-23, NU-87 and natural or synthetic  
21 ferrierites. These molecular sieves are well known in the art and are  
22 discussed in Rosemarie Szostak's Handbook of molecular Sieves (New York,  
23 Van Nostrand Reinhold, 1992 and U.S. Pat. No. 5,282,858, which are hereby  
24 incorporated by reference for all purposes. A liquid type of isomerization  
25 catalyst that can be used is iron pentacarbonyl ( $\text{Fe}(\text{CO})_5$ ).

26 The process for the isomerization of normal alpha olefins may be carried out  
27 in batch or continuous mode. The process temperatures can range from 50°C

1 to 250°C. In the batch mode, a typical method is to use a stirred autoclave or  
2 glass flask, which may be heated to the desired reaction temperature. A  
3 continuous process is most efficiently carried out in a fixed bed process.  
4 Space rates in a fixed bed process can range from 0.1 to 10 or more weight  
5 hourly space velocity.

6 In a fixed bed process, the isomerization catalyst is charged to the reactor and  
7 activated or dried at a temperature of at least 150°C under vacuum or flowing  
8 inert, dry gas. After activation, the temperature of the isomerization catalyst is  
9 adjusted to the desired reaction temperature and a flow of the olefin is  
10 introduced into the reactor. The reactor effluent containing the partially-  
11 branched, isomerized olefins is collected. The resulting partially-branched,  
12 isomerized olefins contain a different olefin distribution (alpha olefin, beta  
13 olefin; internal olefin, tri-substituted olefin, and vinylidene olefin) and  
14 branching content than the unisomerized olefin and conditions are selected in  
15 order to obtain the desired olefin distribution and the degree of branching.

#### 16 Procedure for Sulfonation of Alkylxylene

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

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

#### 23 Procedure for Neutralization of Alkylxylene Sulfonic acids

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

1 Generally, the neutralization reaction is carried out in an in-line mixing reactor  
2 in which the alkylxylene sulfonic acid and an organic or inorganic base are  
3 mixed and the temperature is maintained between about 20°C and 80°C. The  
4 amount of alkali metal used is based on the acid number determined for each  
5 alkylxylene sulfonic acid.

6

7

### EXAMPLES

8

#### Example 1

9

#### Preparation of Alkylxylene using

10

#### Trifluoromethane Sulfonic Acid Alkylation Catalyst

11

12

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

13 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
14 catalyst. To a 3 liter glass reactor were charged, under nitrogen,  
15 904.09 grams of ortho-xylene and 595.91 grams of C<sub>10</sub>-C<sub>58</sub> normal alpha  
16 olefin and allowed to mix. The mixture was heated to 60°C. Next,  
17 41.71 grams of trifluoromethane sulfonic acid was added to the reaction  
18 mixture while stirring. A strong exotherm was observed with a temperature  
19 increase to 122°C. The reaction mixture was allowed to cool to room  
20 temperature for 4 hours and 30 minutes. After this cooling period, the  
21 reaction was quenched with cold distilled water followed by three consecutive  
22 water washes to remove the acid catalyst from the organic phase. The  
23 organic phase containing the alkylxylene product was dried over magnesium  
24 sulfate and the excess ortho-xylene was distilled under reduced pressure  
25 using a Rotovap evaporator to recover the alkylxylene product.

26

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

27 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
28 catalyst. To a 3 liter glass reactor were charged, under nitrogen, 852 grams

1 of ortho-xylene and 600 grams of C<sub>10</sub>-C<sub>58</sub> isomerized olefin (normal alpha  
2 olefin content about 75 percent of the total olefin) and allowed to mix. The  
3 reaction mixture was heated to 40°C. Next, 42 grams of trifluoromethane  
4 sulfonic acid was added to the reaction mixture while stirring. A strong  
5 exotherm was observed with a temperature increase to 90°C. The reaction  
6 mixture was allowed to cool 60°C and held at this temperature for 2 hours.  
7 After this cooling period, the reaction was quenched and the alkylxylene was  
8 recovered as described above in Example 1A.

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

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

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

21 Alkylxylene was prepared using trifluoromethane sulfonic acid alkylation  
22 catalyst. To a 3 liter glass reactor were charged, under nitrogen, 852 grams  
23 of ortho-xylene and 600 grams of C<sub>10</sub>-C<sub>58</sub> isomerized olefin (normal alpha  
24 olefin content about 5 percent of the total olefin) and allowed to mix. The  
25 reaction mixture was heated to 40°C. Next, 42 grams of trifluoromethane  
26 sulfonic acid was added to the reaction mixture while stirring. A strong  
27 exotherm was observed with a temperature increase to 90°C. The reaction  
28 mixture was allowed to cool 60°C and held at this temperature for 2 hours.

1 After this cooling period, the reaction was quenched and the alkylxylene was  
2 recovered as described above in Example 1A.

3

### Example 2

4

#### Preparation of Alkylxylene using

5

#### Hydrogen Fluoride Alkylation Catalyst

6

7

#### Example 2: Alkylation of Ortho-xylene with C<sub>10</sub>-C<sub>58</sub> Normal Alpha Olefin

8

Alkylxylene was prepared using hydrogen fluoride as alkylation catalyst.

9

Ortho-xylene was alkylated with of C<sub>10</sub>-C<sub>58</sub> normal alpha olefin in a continuous

10

process alkylation pilot plant. The pilot plant consisted of a stirred,

11

heat-jacketed reactor (1.15 liters) in series with a settler (25 liters). The settler

12

is for separating the organic phase from the phase containing the hydrofluoric

13

acid and is maintained under nitrogen pressure of approximately  $5 \times 10^5$

14

pascal (72.52 psi). C<sub>10</sub>-C<sub>58</sub> normal alpha olefins heated to approximately

15

50°C was pumped into the reactor heated to approximately 64°C at a rate of

16

approximately 16.3 grams per minute. Simultaneously with the addition of the

17

normal alpha olefins, hydrofluoric acid was charged to the reactor at a rate of

18

approximately 1.7 grams per minutes along with ortho-xylene at a rate of

19

approximately 58 grams per minute. The charge mole ratio of the

20

ortho-xylene to the normal alpha olefins was 10 and the charge mole ratio of

21

the hydrofluoric acid to the normal alpha olefins was 1.5. The residence time

22

in the reactor was approximately 15 minutes. The resulting product mixture

23

was passed into the unheated settler and depressurized to atmospheric

24

pressure. The organic layer was recovered from the settler and the excess

25

ortho-xylene removed by distillation to obtain the alkylated ortho-xylene.

26

### Example 3

### Preparation of Alkylxylene using Aluminum Trichloride Alkylation Catalyst

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

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

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

Into a 3 liter glass reactor were charged, under nitrogen, 711.3 grams of ortho-xylene and while stirring 35.7 grams of aluminum trichloride was added to the reaction mixture. Next, 357.7 grams of C<sub>10</sub>-C<sub>58</sub> normal alpha olefin was added to the reactor over 3 hours in order to control the temperature increase due to the exothermic reaction. The temperature of the reaction mixture never exceeded 21°C. At the end of the olefin addition, the reaction mixture was maintained at about 20°C with continued stirring for one hour. After this period, the reaction was quenched and the alkylxylene was recovered as described above in Example 1A except that a 3.0 weight percent ammonium hydroxide aqueous solution was used for the first two washes of the organic phase to remove the aluminum from the organic phase by solubilizing it in the aqueous phase.

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

To a 3 liter glass reactor were charged, under nitrogen, 682.8 grams of ortho-xylene and while stirring 28.6 grams of aluminum trichloride was added to the reaction mixture. The temperature of the reaction mixture at this time was about 20°C. Next, 572.4 grams of C<sub>10</sub>-C<sub>58</sub> normal alpha olefin was added to the reactor over about 15 minutes. The temperature of the reaction mixture

1 spiked to 76°C. The reaction mixture was cooled to about 60°C and the  
2 alkylation reaction was allowed to proceed at this temperature for two hours.  
3 After this period, the reaction was quenched and the alkylxylene was  
4 recovered as described above in Example 3B.

5 Example 4

6 Preparation of Alkylxylene using an Ionic Liquid Alkylation Catalyst

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

8 An ionic liquid alkylation catalyst was prepared by mixing 1 mole of  
9 methyltributylammoniumchloride with 2 moles of aluminum chloride under  
10 nitrogen. From the reaction was obtained 36.6 milliliters of the ionic liquid  
11 alkylation catalyst as a brown ionic liquid. The ionic liquid alkylation catalyst  
12 was charged to a glass reactor under nitrogen. To 183.2 grams of C<sub>10</sub>-C<sub>58</sub>  
13 normal alpha olefin was mixed 166.8 grams of ortho-xylene. The mixture was  
14 added slowly to the ionic liquid alkylation catalyst while stirring at room  
15 temperature over about 15 minutes. The temperature of the reaction mixture  
16 spiked to 80°C because of the exothermic reaction. The reaction mixture was  
17 allowed to slowly cool down to room temperature while being stirred for an  
18 additional 2 hours. Next, the reaction mixture was washed 3 times with water  
19 and the alkylxylene was recovered as described above in Example 3B.

20 Example 5

21 Preparation of Alkylxylene Sulfonic Acids

22 Alkylxylene sulfonic acids were prepared using the alkylxylenes prepared in  
23 Examples 1-4 above.

24 Sulfonation of the alkylxylene was performed in a continuous falling film flow  
25 reactor by contacting the alkylxylene with a stream of air and sulfur trioxide.  
26 The molar ratio of the alkylxylene to sulfur trioxide was about 1:0.94. The  
27 reactor jacket temperature was maintained around 55°C. The sulfonic acid

1 product was titrated potentiometrically with a standardized cyclohexylamine  
 2 solution to determine the weight percent of the sulfonic acid and the sulfuric  
 3 acid in the samples. The total acid number was also determined using the  
 4 ASTM Test No. D-664. The results are summarized below in Table I. Two  
 5 samples of the alkylxylene prepared in Examples 1A, 1B, 1C, 1D and 2 were  
 6 sulfonated as described above. The duplicate samples of these alkylxylene  
 7 sulfonates are shown as 1A', 1B', 1C', 1D' and 2' in Tables I and II below.

8 Table I

9

| 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 1D  | CF <sub>3</sub> SO <sub>3</sub> H | 82.3                              | 1.07                                         | 122                       |
| Example 1D' | CF <sub>3</sub> SO <sub>3</sub> H | 82.5                              | 1.10                                         | 125                       |
| Example 2   | HF                                | 90.5                              | 0.62                                         | 126                       |
| Example 2'  | HF                                | 86.8                              | 0.71                                         | 124                       |
| Example 3A  | AlCl <sub>3</sub>                 | 86.4                              | 0.93                                         | 118                       |
| Example 3B  | AlCl <sub>3</sub>                 | 75.5                              | 0.91                                         | 109                       |
| Example 3C  | AlCl <sub>3</sub>                 | 78.7                              | 1.04                                         | 113                       |
| Example 4   | Ionic Liquid                      | 89.3                              | 0.82                                         | 129                       |

10  
 11 \*An average molecular weight of 453 grams per mole is assumed for all the  
 12 sulfonic acids.

1

Example 6

2

Preparation of Alkylxylene Sulfonates

3

4 The alkylxylene sulfonates were prepared using the alkylxylene sulfonic acids  
5 prepared in Example 5 above.

6

Neutralization of the sulfonic acid was performed in a beaker with magnetic  
7 stirring. The sulfonic acid was heated to about 40°C to lower the viscosity of  
8 the sulfonic acid. Next, a 50 weight percent solution of sodium hydroxide was  
9 slowly added to the reaction mixture. The temperature of the reaction mixture  
10 was maintained below 80°C to control the evaporation of water. The sodium  
11 hydroxide added was calculated based on the acid number obtained for each  
12 sulfonic acid. To prepare the alkylxylene sulfonates, the exact amount of  
13 sodium hydroxide necessary for the neutralization of all the acid species in the  
14 sulfonic acid samples, sulfonic acid and H<sub>2</sub>SO<sub>4</sub> was added to the reaction  
15 mixture based on the Total Acid Number analysis results obtained for the  
16 sulfonic acids reported in Table II below. An exact quantity of sodium  
17 hydroxide was employed to obtain exactly a 100 percent neutralization of the  
18 alkylxylene sulfonic acids.

19 The active content of the sodium alkylxylene sulfonate was calculated using  
20 the formula given below:

$$21 \quad \% \text{ active as sodium sulfonate} = \frac{W_{SA} * W\%_{RSO_3H} * \frac{Mw_{RSO_3Na}}{Mw_{RSO_3H}}}{W_{SA} + W_{NaOH \text{ sol}} * (1 + \frac{0.5 * 18}{40})}$$

22 W<sub>SA</sub>: Weight of sulfonic acid sample (grams)

23 W%<sub>RSO<sub>3</sub>H</sub>: Weight percent of alkylxylene sulfonic acid determined by the  
24 cyclohexylamine titration

- 1 Mw  $\text{RSO}_3\text{Na}$ : Molecular weight of the alkylxylene sodium sulfonate (grams per  
 2 mole)  
 3 Mw  $\text{RSO}_3\text{H}$ : Molecular weight of the alkylxylene sulfonic acid (grams per  
 4 mole)  
 5  $W_{\text{NaOH sol}}$ : Weight of the NaOH solution (50 weight %) used for the  
 6 neutralization surfactant having low IFT.  
 7  
 8 The average molecular weight of 475 g/mol was used for the alkylxylene  
 9 sodium sulfonate.

10 The neutralization and actives content data collected for the neutralized  
 11 alkylxylene sulfonates prepared in Example 6 are summarized below in  
 12 Table II.

13 Table II

| Example     | Alkylation catalyst              | Weight of Sulfonic Acid (g) | Total Acid Number-TAN (mg KOH/g) | NaOH (50% weight in $\text{H}_2\text{O}$ ) | Active Content (weight %) |
|-------------|----------------------------------|-----------------------------|----------------------------------|--------------------------------------------|---------------------------|
| Example 1A  | $\text{CF}_3\text{SO}_3\text{H}$ | 241                         | 128                              | 44.0                                       | 74.4                      |
| Example 1A' | $\text{CF}_3\text{SO}_3\text{H}$ | 241                         | 128                              | 44.0                                       | 76.2                      |
| Example 1B  | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 124                              | 42.4                                       | 72.3                      |
| Example 1B' | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 124                              | 42.4                                       | 72.7                      |
| Example 1C  | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 124                              | 41.1                                       | 72.7                      |
| Example 1C' | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 120                              | 42.44                                      | 72.1                      |
| Example 1D  | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 122                              | 41.8                                       | 71.1                      |
| Example 1D' | $\text{CF}_3\text{SO}_3\text{H}$ | 240                         | 125                              | 42.8                                       | 71.0                      |
| Example 2   | HF                               | 240                         | 126                              | 43.1                                       | 77.7                      |
| Example 2'  | HF                               | 246                         | 124                              | 41.8                                       | 74.8                      |
| Example 3A  | $\text{AlCl}_3$                  | 240                         | 118                              | 40.4                                       | 75.1                      |
| Example 3B  | $\text{AlCl}_3$                  | 50                          | 109                              | 7.76                                       | 66.5                      |
| Example 3C  | $\text{AlCl}_3$                  | 50                          | 113                              | 8.09                                       | 68.9                      |
| Example 4   | Ionic Liquid                     | 241                         | 129                              | 44.3                                       | 76.4                      |

14

1 Example 7  
2 Determination of the Attachment Position on the Alkyl Carbon Chain  
3 to the Xylene Moiety

4 The attachment position on the alkyl carbon chain to the xylene moiety was  
5 determined by Gas Chromatography (GC) and quantitative  $^{13}\text{C}$ -Nuclear  
6 Magnetic Resonance spectroscopy ( $^{13}\text{C}$ -NMR).

7 Since the resolution of the peaks obtained in GC decreases with the retention  
8 time, it is possible to accurately quantify the attachment position of alkyl group  
9 on the xylene ring only for  $\text{C}_{12}$  and  $\text{C}_{14}$  carbon alkyl chains. Quantitative  
10  $^{13}\text{C}$ -NMR on the other hand provides an average value for all carbon atoms  
11 on the alkyl chain lengths.

12  $^{13}\text{C}$ -NMR and GC also give the attachment position of the alkyl chain on the  
13 ortho-xylene ring. It appears that when aluminum trichloride is used to  
14 catalyze the alkylation of ortho-xylene, the isomer formed primarily is  
15 4-alkyl-1,2-dimethyl benzene, whereas when trifluoromethane sulfonic acid or  
16 hydrogen fluoride are use as alkylation catalysts a mixture of 3-alkyl-1,2-  
17 dimethyl benzene and 4-alkyl-1,2-dimethyl benzene is obtained. Figures 1  
18 and 2 show the  $\text{C}_{12}$  and  $\text{C}_{14}$  portion of the gas chromatograms obtained for  
19 the alkylate prepared in Examples 1A and 3A, respectively. The percent of  
20 the 4-alkyl-1,2-dimethyl benzene was calculated based by averaging the area  
21 of the GC peaks for the 2-position attachment on the alkyl chain for  $\text{C}_{12}$  and  
22  $\text{C}_{14}$ . The attachment position of the xylene ring on the alkyl carbon chain of  
23 the alkyl group was also calculated. The GC results obtained for  
24 Examples 1-4 are given below in Table III. The data show that percent of the  
25 4-alkyl-1,2-dimethyl benzene is much lower in Examples 1 and 2 when the  
26 alkylation catalyst is trifluoromethane sulfonic acid or hydrogen fluoride than in  
27 Examples 3 and 4 when aluminum trichloride or ionic liquid catalyst is used as  
28 the alkylation catalyst.

1 The GC data obtained for Examples 3B and 3C in Table III also show that the  
 2 alkylation reaction is temperature dependent. The samples prepared in  
 3 Examples 3B and 3C were treated similarly except that the temperature of the  
 4 alkylation reaction in 3B was controlled at about 20°C by addition of the  
 5 normal alpha olefin over a 3 hour period to prevent the temperature from  
 6 increasing due to the exotherm of the alkylation reaction. In contrast, in  
 7 Example 3C, the normal alpha olefin was added over about 15 minutes and  
 8 the temperature spiked to 76°C with the result that the sample in Example 3C  
 9 contains nearly twice as much of the 3-4+ alkyl chain attachment compared to  
 10 the sample prepared in Example 3B. The 3-4+ alkyl chain attachment in  
 11 Examples 3B and 3C is 36.7 and 68.1 percent of the total attachment,  
 12 respectively. It is believed that the alkylation catalysts, such as aluminum  
 13 trichloride, also catalyze isomerization of the olefin to produce olefins  
 14 containing a higher percentage of internal double bonds and at high  
 15 temperatures the isomerization reaction proceeds at a faster rate than at low  
 16 temperatures.

17 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 1D  | CF <sub>3</sub> SO <sub>3</sub> H | 71                                                              | 16.1                            | 11.9 | 21.9 | 50.1 | 83.9 |
| Example 2   | HF                                | 64                                                              | 25.9                            | 20.1 | 20   | 34   | 74.1 |
| Example 3A  | AlCl <sub>3</sub>                 | > 95                                                            | 50.1                            | 21.9 | 11.9 | 16.1 | 49.9 |
| Example 3A* | AlCl <sub>3</sub>                 | > 95                                                            | 46.5                            | 18.8 | 14.9 | 19.8 | 53.5 |
| Example 3B  | AlCl <sub>3</sub>                 | > 95                                                            | 63.4                            | 21.9 | 7.8  | 7.0  | 36.7 |
| Example 3C  | AlCl <sub>3</sub>                 | > 95                                                            | 32.0                            | 19.4 | 16.8 | 31.9 | 68.1 |
| Example 4   | Ionic Liquid                      | > 95                                                            | 30.3                            | 16.3 | 19.3 | 34.2 | 69.7 |

18

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

1

Example 8

2

Determination of Interfacial Tension

3 The performance of the alkylxylene sulfonates prepared above in Example 6  
4 was determined by measuring the interfacial tension. The alkylxylene  
5 sulfonates in Example 6 were prepared using the alkylxylene sulfonic acids  
6 prepared in Example 5, which in turn were prepared using the alkylxylenes  
7 prepared in Examples 1-4.

8 Alkylxylene sulfonates prepared from alkylxylenes prepared in Example 1C,  
9 Example 2 and Example 3B were used for comparison since they are outside  
10 the scope of the alkylxylene sulfonates of the present invention.

11 The interfacial tension was determined using Minas crude oil (a waxy crude  
12 oil) having a pour point around 35°C and aqueous solutions of the alkylxylene  
13 sulfonates. A spinning drop tensiometer was used to measure the interfacial  
14 tension at 93°C. Two methods described below were used to measure the  
15 interfacial tension:

16

Equilibrated Interfacial Tension Method

17 A 5 milliliter sample of a solution of alkylxylene sulfonate, water, a  
18 co-surfactant and sodium chloride was added to an equal volume of crude oil  
19 in a glass tube. The test tube was tightly sealed and shaken. The test tube  
20 was allowed to equilibrate for one month at 93°C. At the end of the  
21 equilibration period, an aliquot of aqueous phase was loaded into the glass  
22 tube of the spinning tensiometer. Next, a small drop of the upper oil phase is  
23 injected into the glass tube. The tube is spun and the interfacial tension  
24 between the aqueous solution and the oil is determined using the B. Vonnegut  
25 equation for elongated droplets given in B. Vonnegut in *Review Scientific*  
26 *Instruments*, 13 (1942) 6:

1 
$$IFT = \frac{\omega^2 R^3 \Delta \rho}{4}$$

2  $\omega$  being the rotational speed,  $R$  the radius of the droplet, and  $\Delta \rho$  the density  
3 difference between the oil and the aqueous solution. It takes typically 1 to  
4 3 hours for the system to reach equilibrium.

5 Fresh Interfacial Tension Method

6 Interfacial tension is measured as described above except without the  
7 equilibrium period of one month at 93°C. The glass tube of the spinning  
8 tensiometer is filled as described above with a solution of alkylxylene  
9 sulfonate, water, a co-surfactant and sodium chloride and sealed. A drop of  
10 oil is injected into the sealed glass tube. The tube is spun and the interfacial  
11 tension is recorded until a stable value is obtained, which takes generally 1 to  
12 3 hours. Although this method can be used to obtain interfacial tension data  
13 in only a few hours, the data obtained by this method tend to be higher than  
14 those obtained using the Equilibrated Interfacial Tension Method described  
15 above.

16 Interfacial tension data for the alkylxylene sulfonates prepared above in  
17 Example 6 were determined using the Equilibrated Interfacial Tension Method  
18 described above. Samples were prepared with 0.24 weight percent (on active  
19 basis) of the alkylxylene sulfonate and 0.067 weight percent sec-butyl alcohol  
20 as co-surfactant. The interfacial tension data were collected in the presence  
21 of sodium chloride solutions between 0.1 percent to 0.5 percent.

22 The results of the interfacial tension determination are given below in  
23 Tables IV and V.

Table IV

| Example                     | 4-alkyl-1,2-dimethyl- benzene<br>(% of total alkyl-ortho-xylene) | 3, 4 & 4+<br>Position on<br>Carbon<br>Chain*<br>(% of total<br>attachment) | Salinity (weight % NaCl)<br>IFT (dynes/cm) |       |       |         |         |
|-----------------------------|------------------------------------------------------------------|----------------------------------------------------------------------------|--------------------------------------------|-------|-------|---------|---------|
|                             |                                                                  |                                                                            | 0.1                                        | 0.2   | 0.3   | 0.4     | 0.5     |
| Example 1A                  | 73                                                               | 64.2                                                                       | 2.75                                       | 0.81  | 0.28  | 0.051   | 0.006   |
| Example 1B                  | 71                                                               | 66.1                                                                       | 5.61                                       | 0.97  | 0.67  | 0.154   | 0.00075 |
| Example 1D                  | 71                                                               | 83.9                                                                       | 1.88                                       | 0.49  | 0.047 | 0.00035 | 0.00022 |
| Example 1C<br>(comparative) | 65                                                               | 72.1                                                                       | 3.34                                       | 1.21  | 1.05  | 0.118   | 0.018   |
| Example 2<br>(comparative)  | 64                                                               | 74.1                                                                       | 5.67                                       | 0.91  | 0.48  | 0.034   | 0.0275  |
| Example 3A                  | > 95                                                             | 49.9                                                                       | 1.71                                       | 0.009 | 0.002 | 0.09    | 0.089   |
| Example 4                   | > 95                                                             | 69.7                                                                       | 0.49                                       | 0.03  | 0.009 | 0.00078 | 0.00083 |

\* The percent attachment in the 3, 4 and 4+ positions plus the percent attachment in the 2-position is a 100 percent.

1 Fresh interfacial tension data were used to compare the alkylxylene  
 2 sulfonates prepared from the alkylxylene prepared in Examples 3B and 3C.  
 3 Samples were prepared with 0.60 weight percent (on active basis) of the  
 4 alkylxylene sulfonate and 0.17 weight percent sec-butyl alcohol as co-  
 5 surfactant.

6 The fresh interfacial tension data were collected using a synthetic Minas oil  
 7 field brine instead of the sodium chloride solution used in the equilibrated  
 8 interfacial tension experiments described above. The composition of the  
 9 synthetic Minas brine is given below:

| Component                        | Milligrams per liter | Milliequivalents per liter |
|----------------------------------|----------------------|----------------------------|
| Sodium ( $\text{Na}^+$ )         | 900                  | 39.13                      |
| Calcium ( $\text{Ca}^{+2}$ )     | 20                   | 1.0                        |
| Magnesium ( $\text{Mg}^{+2}$ )   | 5                    | 0.42                       |
| Total Cation                     |                      | 40.55                      |
| Chloride ( $\text{Cl}^-$ )       | 800                  | 22.57                      |
| Bicarbonate ( $\text{HCO}_3^-$ ) | 1100                 | 18.03                      |
| Sulfate ( $\text{SO}_4^{-2}$ )   | 18                   | 0.38                       |
| Total Anion                      |                      | 40.98                      |

10

11 Results of the fresh interfacial tension measurement summarized in Table V  
 12 below show that the alkylxylene sulfonate prepared from the alkylxylene  
 13 prepared in Example 3C is four times better than the alkylxylene prepared  
 14 from the alkylxylene prepared in Example 3B. The data show that even when  
 15 the 4-alkyl-1,2-dimethyl benzene isomer is very high in the alkylxylene  
 16 sulfonates, greater than 95 percent of the total attachment, the interfacial  
 17 tension is high if the amount of the 3, 4 and 4+ attachment on the alkyl carbon  
 18 chain is low.

1

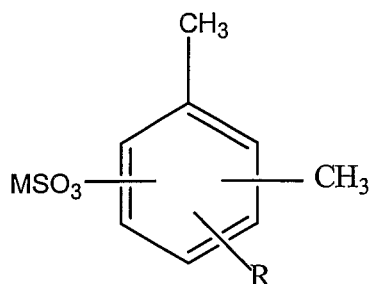
Table V

| Example                     | 4-alkyl-1,2-dimethyl benzene<br>(% of total alkyl-ortho-xylene) | 3,4 & 4+ Position<br>on Alkyl Carbon<br>Chain<br>(% of total<br>attachment) | Fresh IFT<br>in synthetic Minas<br>brine<br>(dynes/cm) |
|-----------------------------|-----------------------------------------------------------------|-----------------------------------------------------------------------------|--------------------------------------------------------|
| Example 3B<br>(comparative) | > 95                                                            | 36.7                                                                        | 0.45                                                   |
| Example 3C                  | > 95                                                            | 68.1                                                                        | 0.11                                                   |

2

## 1 WHAT IS CLAIMED IS:

- 2 1. An alkylxylene sulfonate for enhanced oil recovery processes, having  
 3 the general formula:



- 4
- 5 wherein R is an alkyl group containing from about 10 to about  
 6 58 carbon atoms, M is a mono-valent cation, and the alkylxylene  
 7 moiety is alkyl-ortho-xylene in at least 85 percent of the total  
 8 alkylxylene sulfonate and wherein the alkylxylene moiety in the  
 9 alkylxylene sulfonate contains greater than about 70 percent of the  
 10 4-alkyl-1,2-dimethyl benzene isomer and the attachment of the alkyl  
 11 group to the xylene moiety in the alkylxylene sulfonate is at positions  
 12 higher than the 2-position along the alkyl chain in at least 40 percent of  
 13 the total alkylxylene sulfonate.
- 14 2. The alkylxylene sulfonate of claim 1, wherein the alkylxylene moiety is  
 15 alkyl-ortho-xylene in at least 95 percent of the total alkylxylene  
 16 sulfonate.
- 17 3. The alkylxylene sulfonate of claim 1, wherein the alkylxylene moiety in  
 18 the alkylxylene sulfonate contains greater than about 80 percent of the  
 19 4-alkyl-1,2-dimethyl benzene isomer.
- 20 4. The alkylxylene sulfonate of claim 3, wherein the alkylxylene moiety in  
 21 the alkylxylene sulfonate contains at least 90 percent of the  
 22 4-alkyl-1,2-dimethyl benzene isomer.

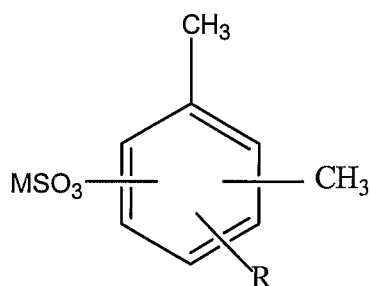
- 1     5.     The alkylxylene sulfonate of claim 1, wherein the alkyl group on the  
2           xylene moiety is attached at positions higher than the 2-position along  
3           the alkyl chain in at least 45 percent of the total alkylxylene sulfonate.
- 4     6.     The alkylxylene sulfonate of claim 5, wherein the alkyl group on the  
5           xylene moiety is attached at positions higher than the 2-position along  
6           the alkyl chain in at least 60 percent of the total alkylxylene sulfonate.
- 7     7.     The alkylxylene sulfonate of claim 1, wherein the mono-valent cation is  
8           an alkali metal.
- 9     8.     The alkylxylene sulfonate of claim 7, wherein the alkali metal is sodium.
- 10    9.     The alkylxylene sulfonate of claim 1, wherein the mono-valent cation is  
11          an ammonium ion or an organic ammonium ion.
- 12    10.    The alkylxylene sulfonate of claim 1, wherein the alkyl group is derived  
13          from a linear alpha olefin or an isomerized olefin containing from about  
14          10 to about 58 carbon atoms.
- 15    11.    The alkylxylene sulfonate of claim 10, wherein the alkyl group is  
16          derived from a linear alpha olefin or an isomerized olefin containing  
17          from about 10 to about 40 carbon atoms.
- 18    12.    The alkylxylene sulfonate of claim 11, wherein the alkyl group is  
19          derived from a linear alpha olefin or an isomerized olefin containing  
20          from about 12 to about 30 carbon atoms.
- 21    13.    The alkylxylene sulfonate of claim 1, wherein the alkyl group contains a  
22          distribution of alkyl chain lengths wherein the alkyl chain lengths  
23          comprise from about 40 to about 80 percent C<sub>12</sub> to C<sub>20</sub> and about  
24          5 percent to about 15 percent of C<sub>32</sub> to C<sub>58</sub>.

1 14. The alkylxylene sulfonate of claim 13, wherein the alkyl chain lengths  
2 comprise from about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub> and about  
3 5 percent to about 15 percent of C<sub>32</sub> to C<sub>58</sub>.

4 15. The alkylxylene sulfonate of claim 14, wherein the alkyl chain lengths  
5 comprise about 8 percent to about 12 percent of C<sub>32</sub> to C<sub>58</sub>.

6 16. A method for recovering crude oil from a subterranean hydrocarbon  
7 containing formation, which method comprises:

8 (a) injecting into the formation an aqueous solution containing an  
9 amount of alkylxylene sulfonate or a mixture of alkylxylene  
10 sulfonates effective for the recovery of crude oil wherein the  
11 alkylxylene sulfonate has the general formula:



12

13 wherein R is an alkyl group containing from about 10 to about  
14 58 carbon atoms, M is a mono-valent cation, and the alkylxylene  
15 moiety is alkyl-ortho-xylene in at least 85 percent of the total  
16 alkylxylene sulfonate, and wherein the alkylxylene moiety in the  
17 alkylxylene sulfonate contains greater than about 70 percent of the  
18 4-alkyl-1,2-dimethyl benzene isomer and the attachment of the alkyl  
19 group to the xylene moiety in the alkylxylene sulfonate is at positions  
20 higher than the 2-position along the alkyl chain in at least 40 percent of  
21 the total alkylxylene sulfonate; and

- 1 (b) displacing the crude oil with the aqueous solution injected into the  
2 formation to thereby recover hydrocarbons from a production well.
- 3 17. The method of claim 16, wherein in step (a) the alkylxylene sulfonate is  
4 present in the range of about 0.03 weight percent to about 2.0 weight  
5 percent of the total weight of the aqueous solution.
- 6 18. The method of claim 17, wherein the alkylxylene sulfonate is present in  
7 the range of about 0.1 weight percent to about 1.5 weight percent of  
8 the total weight of the aqueous solution.
- 9 19. The method of claim 18, wherein the alkylxylene sulfonate is present in  
10 the range of about 0.3 weight percent to about 1.0 weight percent of  
11 the total weight of the aqueous solution.
- 12 20. The method of claim 19, wherein the alkylxylene sulfonate is present in  
13 the range of about 0.5 weight percent to about 0.8 weight percent of  
14 the total weight of the aqueous solution.
- 15 21. The method of claim 16, wherein the alkylxylene moiety in step (a) is  
16 alkyl-ortho-xylene in at least 95 percent of the total alkylxylene  
17 sulfonate.
- 18 22. The method of claim 16, wherein the alkylxylene sulfonate contains  
19 greater than about 80 percent of the 4-alkyl-1,2-dimethyl benzene  
20 isomer.
- 21 23. The method of claim 22, wherein the alkylxylene moiety in the  
22 alkylxylene sulfonate contains at least 90 percent of the  
23 4-alkyl-1,2-dimethyl benzene isomer.

- 1     24.     The method of claim 16, wherein in step (a) the alkyl group is attached  
2             to the xylene moiety at positions higher than the 2-position along the  
3             alkyl chain in at least 45 percent of the total alkylxylene sulfonate.
- 4     25.     The method of claim 24, wherein in step (a) the alkyl group is attached  
5             to the xylene moiety at positions higher than the 2-position along the  
6             alkyl chain in at least 60 percent of the total alkylxylene sulfonate.
- 7     26.     The method of claim 16, wherein in step (a) the mono-valent cation is  
8             an alkali metal.
- 9     27.     The method of claim 26, wherein the alkali metal is sodium.
- 10    28.     The method of claim 16, wherein in step (a) the mono-valent cation is  
11             an ammonium ion or an organic ammonium ion.
- 12    29.     The method of claim 16, wherein in step (a) the alkyl group is derived  
13             from a linear alpha olefin or an isomerized olefin containing from about  
14             10 to about 58 carbon atoms.
- 15    30.     The method of claim 29, wherein in step (a) the alkyl group is derived  
16             from a linear alpha olefin or an isomerized olefin containing from about  
17             10 to about 40 carbon atoms.
- 18    31.     The method of claim 30, wherein in step (a) the alkyl group is derived  
19             from a linear alpha olefin or an isomerized olefin containing from about  
20             12 to about 30 carbon atoms.
- 21    32.     The method of claim 16, wherein in step (a) the alkyl group contains a  
22             distribution of alkyl chain lengths and wherein the alkyl chain lengths  
23             comprise from about 40 to about 80 percent C<sub>12</sub> to C<sub>20</sub> and about  
24             5 percent to about 15 percent of C<sub>32</sub> to C<sub>58</sub>.

- 1     33.     The method of claim 32, wherein in step (a) the chain lengths comprise  
2             from about 50 to about 70 percent C<sub>12</sub> to C<sub>20</sub> and about 5 percent to  
3             about 15 percent of C<sub>32</sub> to C<sub>58</sub>.
- 4     34.     The method of claim 33, wherein in step (a) the chain lengths comprise  
5             about 8 percent to about 12 percent of C<sub>32</sub> to C<sub>58</sub>.
- 6     35.     The method of claim 16, wherein the hydrocarbon in the subterranean  
7             formation is a waxy crude oil.
- 8     36.     The method of claim 16, wherein the method further comprises,  
9             concurrently with or subsequent to the injection of the aqueous solution  
10            in step (a), injecting into the formation an amount of polymer effective  
11            for driving the aqueous solution of step (a) into the formation to  
12            displace the crude oil to thereby recover hydrocarbons from a  
13            production well.
- 14    37.     The method of claim 36, wherein the polymer is a polysaccharide, an  
15            acrylamide or a partially hydrolyzed polyacrylamide.
- 16    38.     The method of claim 16, wherein the method further comprises,  
17            concurrently with or subsequent to the injection of the aqueous solution  
18            in step (a), injecting into the formation an amount of water effective for  
19            driving the aqueous solution of step (a) into the formation to displace  
20            the crude oil to thereby recover hydrocarbons from a production well.
- 21    39.     The method of claim 36, wherein the method further employs,  
22            concurrently with or subsequent to the injection of the or the polymer,  
23            injecting into the formation an amount of water effective for driving the  
24            aqueous solution of step (a) into the formation to displace the crude oil  
25            to thereby recover hydrocarbons from a production well.

- 1     40.     The method of claim 16, wherein the aqueous solution in step (a)  
2             further contains a co-surfactant having a molecular weight in the range  
3             of about 60 to about 1,200.
- 4     41.     The method of claim 40, wherein the co-surfactant is an alcohol, an  
5             alcohol ether, a polyalkylene glycol, a poly(oxyalkylene) glycol, a  
6             poly(oxyalkylene) glycol ether, or mixtures thereof.
- 7     42.     The method of claim 41, wherein the poly(oxyalkylene) glycol ether is  
8             an ethylene glycol mono-alkyl or mono-phenyl ether, a di-ethylene  
9             glycol mono-alkyl or mono-phenyl ether, a tri-ethylene glycol  
10            mono-alkyl or mono-phenyl ether, a polyethylene glycol mono-phenyl  
11            ether, polypropylene glycol mono-phenyl ether, or mixtures thereof.
- 12    43.     The method of claim 41, wherein the poly(oxyalkylene) glycol is a  
13             poly(oxyethylene) glycol or a poly(oxypropylene) glycol or mixtures  
14             thereof.
- 15    44.     The method of claim 40, wherein in step (a) the co-surfactant is present  
16             in the range of about 0.03 weight percent to about 2.0 weight percent  
17             of the total weight of the aqueous solution.
- 18    45.     The method of claim 44, wherein the co-surfactant is present in the  
19             range of about 0.1 weight percent to about 1.5 weight percent of the  
20             total weight of the aqueous solution.
- 21    46.     The method of claim 45, wherein the co-surfactant is present in the  
22             range of about 0.3 weight percent to about 1.0 weight percent of the  
23             total weight of the aqueous solution.
- 24    47.     The method of claim 46, wherein the co-surfactant is present in the  
25             range of about 0.5 weight percent to about 0.8 weight percent of the  
26             total weight of the aqueous solution.