

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 C₁₂-C₂₂
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 C₆-C₂₀ 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 C₄ and
2 about C₂₄.

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 SO₃, 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.

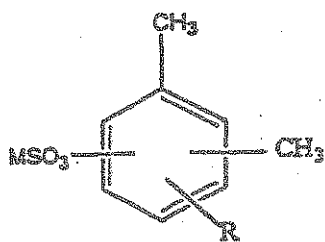
10 U.S. Patent No. 6,269,881 discloses an oil recovery process using a particular
11 class of alkylaryl sulfonates derived from an alpha-olefin stream having a
12 broad distribution of even carbon numbers ranging from 12 to 58. The
13 aromatic hydrocarbons used to produce the alkylaryl sulfonates may 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

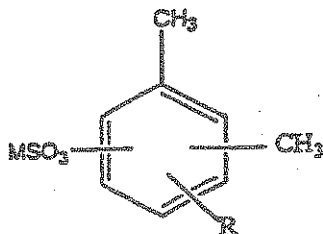
24 In a first aspect, there is provided alkylxylene sulfonates for enhanced oil
25 recovery processes, having the general formula :
26



wherein R is an alkyl group containing from 10 to 58 carbon atoms, M is a mono-valent cation, and the alkylxylene moiety is alkyl-ortho-xylene in at least 85 percent of the total alkylxylene sulfonates and wherein the alkylxylene moiety in the alkylxylene sulfonates contains greater than 70 weight percent of the 4-alkyl-1, 2-dimethyl benzene isomer and the attachment of the alkyl group to the xylene moiety in the alkylxylene sulfonates is at positions higher than the 2-position along the alkyl chain in at least 40 weight percent of the total alkylxylene sulfonates, and wherein the alkyl group contains a distribution of alkyl chain lengths wherein the alkyl chain lengths comprise from 40 to 80 weight percent C₁₂ to C₂₀ and 5 to 15 weight percent of C₃₂ to C₅₈.

In a second aspect, there is provided a method for enhanced oil recovery from a subterranean hydrocarbon containing formation, which method comprises:

(a) injecting into the formation an aqueous solution containing alkylxylene sulfonates effective for the recovery of crude oil wherein the alkylxylene sulfonates have the general formula:



as defined above; and

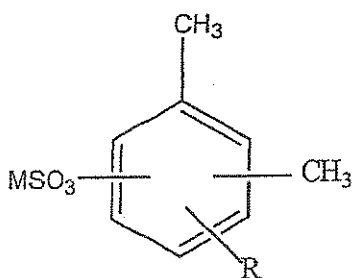
(b) displacing the crude oil with the aqueous solution injected into the formation to thereby recover hydrocarbons from a production well.

The present disclosure is directed to alkylxylene sulfonate for enhanced oil recovery (EOR) processes. The alkylxylene moiety in the alkylxylene sulfonate of the present disclosure 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 disclosure 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 disclosure. 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 disclosure 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 disclosure is directed to alkylxylene sulfonate for
17 enhanced oil recovery processes having the general formula:

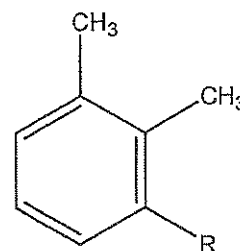
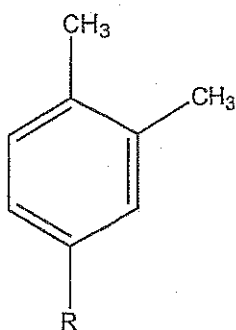


19 wherein R is an alkyl group containing from about 10 to about 58 carbon
20 atoms, M is a mono-valent cation, and the alkylxylene moiety in the
21 alkylxylene sulfonate is alkyl-ortho-xylene in at least 85 percent of the total
22 alkylxylene sulfonate, and wherein the alkylxylene moiety in the alkylxylene
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 disclosure.

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

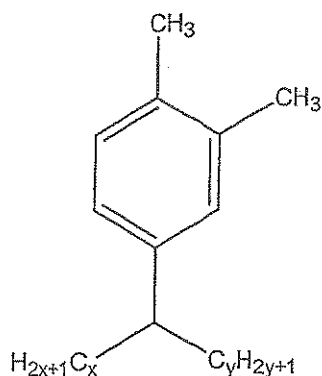
6 Preferably, the alkylxylene moiety in the alkylxylene sulfonate contains greater
7 than about 80 percent of the 4-alkyl-1,2-dimethyl benzene isomer. More
8 preferably, the alkylxylene moiety in the alkylxylene sulfonate contains at least
9 90 percent of the 4-alkyl-1,2-dimethyl benzene isomer. The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



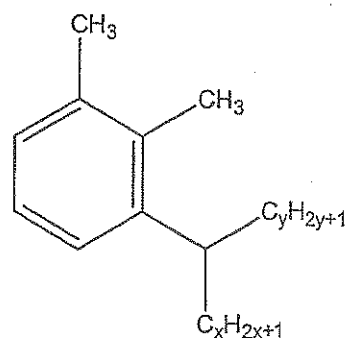
12 4-alkyl-1,2dimethylbenzene

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

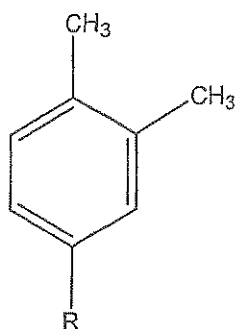
- 2 In the above structures, the values of x and y determine the attachment
3 position of the alkyl group to the xylene moiety on the carbon chain. For
4 example, for a C₁₂ alkyl group, the value of x equal to 2 and y equal to 9
5 corresponds to the attachment of the alkyl group at the 3-position on 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 C₁₀ and C₅₈.
- 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 disclosure 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 C₃₂ to C₅₈ 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 C₁₂ to C₂₀. A more preferred distribution of alkyl chain
4 lengths comprises from about 50 to about 70 percent C₁₂ to C₂₀.

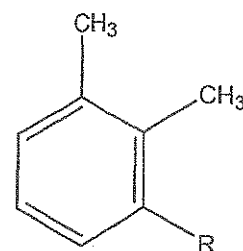
5 Another embodiment of the present disclosure is directed to alkylxylene
6 sulfonate for enhanced oil recovery processes, which composition is derived
7 from ortho-, meta- and para-xylene, and wherein the alkyl group contains from
8 about 10 to about 58 carbon atoms, and the alkylxylene moiety in the
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 disclosure.

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.

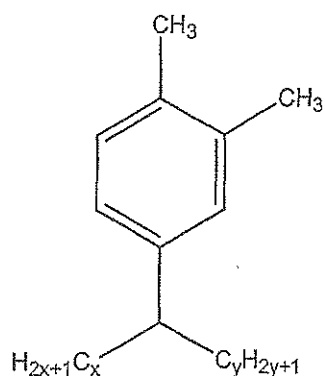


1 4-alkyl-1,2-dimethylbenzene

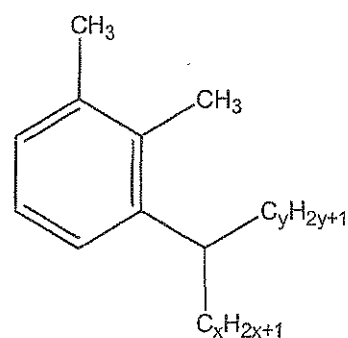


3-alkyl-1,2-dimethylbenzene

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 C₁₂ 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.

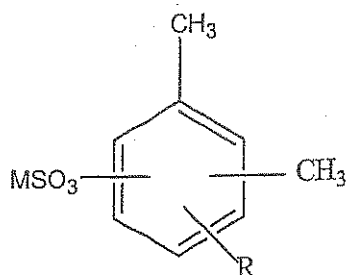
7 The alkyl group in the above alkylxylene sulfonate is derived from a linear
8 alpha olefin or an isomerized olefin containing from about 10 to about
9 58 carbon atoms. Preferably, the alkyl group is derived from a linear alpha
10 olefin or an isomerized olefin containing from about 10 to about 40 carbon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

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2

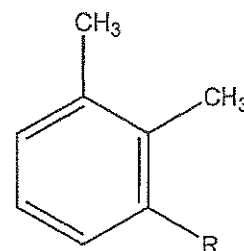
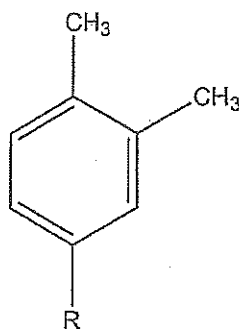
3 wherein R is an alkyl group containing from about 10 to about
 4 58 carbon atoms, M is a mono-valent cation, and the alkylxylene
 5 moiety in the alkylxylene sulfonate is alkyl-ortho-xylene in at least
 6 85 percent of the total alkylxylene sulfonate, and wherein the
 7 alkylxylene moiety in the alkylxylene 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 disclosure; 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.

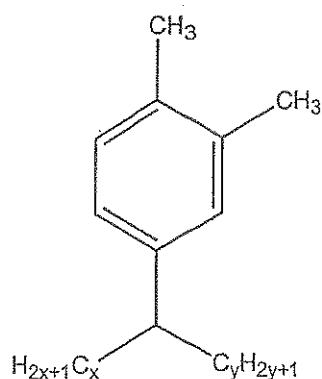
4 Preferably, the alkylxylene moiety in the alkylxylene sulfonate contains greater
5 than about 80 percent of the 4-alkyl-1,2-dimethyl benzene isomer. More
6 preferably, the alkylxylene moiety in the alkylxylene sulfonate contains at least
7 90 percent of the 4-alkyl-1,2-dimethyl benzene isomer. The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



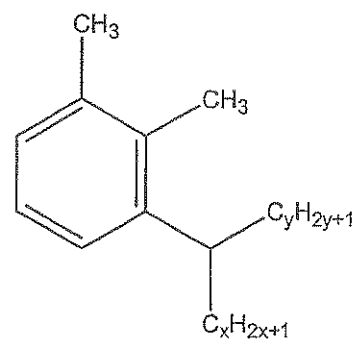
10 4-alkyl-1,2dimethylbenzene

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 C₁₂ 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 C₁₀ and C₅₈.

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 C₃₂ to C₅₈ 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 C₁₂ to C₂₀. A more preferred distribution of alkyl chain lengths comprises from
4 about 50 to about 70 percent C₁₂ to C₂₀.

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 C₁-C₈ 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 C₁₂
25 and C₁₄ 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}C -Nuclear Magnetic
9 Resonance spectroscopy (^{13}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 (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}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}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 (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

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Example 1A: Alkylation of Ortho-xylene with C₁₀-C₅₈ Normal Alpha Olefins

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Example 1B: Alkylation of Ortho-xylene with C₁₀-C₅₈ Isomerized Olefin

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28

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

1 of ortho-xylene and 600 grams of C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ Normal Alpha Olefin

8 Alkylxylene was prepared using hydrogen fluoride as alkylation catalyst.
9 Ortho-xylene was alkylated with of C₁₀-C₅₈ 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 5×10^5
14 pascal (72.52 psi). C₁₀-C₅₈ 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 C₁₀-C₅₈ Normal Alpha Olefins

Alkylxylene was prepared using aluminum trichloride alkylation catalyst by a contract manufacturer in a continuous process using ortho-xylene and C₁₀-C₅₈ normal alpha olefins.

Example 3B: Alkylation of Ortho-xylene with C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈ 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 C₁₀-C₅₈
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 ₃ H* (weight %)	H ₂ SO ₄ (weight %)	Acid Number (mg KOH/g)
Example 1A	CF ₃ SO ₃ H	86.8	0.77	128
Example 1A'	CF ₃ SO ₃ H	88.9	0.82	128
Example 1B	CF ₃ SO ₃ H	83.9	0.92	124
Example 1B'	CF ₃ SO ₃ H	84.4	0.91	124
Example 1C	CF ₃ SO ₃ H	83.7	0.96	124
Example 1C'	CF ₃ SO ₃ H	83.9	0.93	120
Example 1D	CF ₃ SO ₃ H	82.3	1.07	122
Example 1D'	CF ₃ SO ₃ 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 ₃	86.4	0.93	118
Example 3B	AlCl ₃	75.5	0.91	109
Example 3C	AlCl ₃	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.

13

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 H₂SO₄ 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:

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

22 W_{SA}: Weight of sulfonic acid sample (grams)

23 W%_{RSO₃H}: Weight percent of alkylxylene sulfonic acid determined by the
24 cyclohexylamine titration

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}C -Nuclear
6 Magnetic Resonance spectroscopy (^{13}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 C₁₂ and C₁₄ carbon alkyl chains. Quantitative
10 ¹³C-NMR on the other hand provides an average value for all carbon atoms
11 on the alkyl chain lengths.

¹³C-NMR and GC also give the attachment position of the alkyl chain on the ortho-xylene ring. It appears that when aluminum trichloride is used to catalyze the alkylation of ortho-xylene, the isomer formed primarily is 4-alkyl-1,2-dimethyl benzene, whereas when trifluoromethane sulfonic acid or hydrogen fluoride are used as alkylation catalysts a mixture of 3-alkyl-1,2-dimethyl benzene and 4-alkyl-1,2-dimethyl benzene is obtained. Figures 1 and 2 show the C₁₂ and C₁₄ portion of the gas chromatograms obtained for the alkylate prepared in Examples 1A and 3A, respectively. The percent of the 4-alkyl-1,2-dimethyl benzene was calculated based by averaging the area of the GC peaks for the 2-position attachment on the alkyl chain for C₁₂ and C₁₄. The attachment position of the xylene ring on the alkyl carbon chain of the alkyl group was also calculated. The GC results obtained for Examples 1-4 are given below in Table III. The data show that percent of the 4-alkyl-1,2-dimethyl benzene is much lower in Examples 1 and 2 when the alkylation catalyst is trifluoromethane sulfonic acid or hydrogen fluoride than in Examples 3 and 4 when aluminum trichloride or ionic liquid catalyst is used as 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 (% of total alkyl-ortho-xylene)	Alkyl Chain Attachment position				
			2	3	4	4+	3-4+
Example 1A	CF ₃ SO ₃ H	73	35.8	21.1	17.9	25.2	64.2
Example 1B	CF ₃ SO ₃ H	71	33.9	22.2	18.7	25.2	66.1
Example 1C	CF ₃ SO ₃ H	65	27.9	21.2	20.3	30.6	72.1
Example 1D	CF ₃ SO ₃ 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 ₃	> 95	50.1	21.9	11.9	16.1	49.9
Example 3A*	AlCl ₃	> 95	46.5	18.8	14.9	19.8	53.5
Example 3B	AlCl ₃	> 95	63.4	21.9	7.8	7.0	36.7
Example 3C	AlCl ₃	> 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 ¹³C-NMR for the alkylxylene prepared in Example 3A.

Example 8

Determination of Interfacial Tension

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

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

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

Equilibrated Interfacial Tension Method

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

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

2 ω 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 (% of total alkyl-ortho-xylene)	3, 4 & 4+ Position on Carbon Chain* (% of total attachment)	Salinity (weight % NaCl) 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 (comparative)	65	72.1	3.34	1.21	1.05	0.118	0.018
Example 2 (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 (Na^+)	900	39.13
Calcium (Ca^{+2})	20	1.0
Magnesium (Mg^{+2})	5	0.42
Total Cation		40.55
Chloride (Cl^-)	800	22.57
Bicarbonate (HCO_3^-)	1100	18.03
Sulfate (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

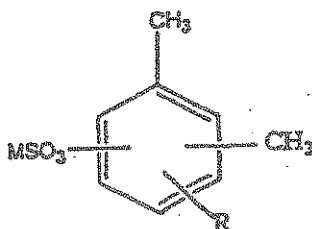
Table V

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

2

CLAIMS:

1. Alkylxylene sulfonates for enhanced oil recovery processes, having the general formula :



5 wherein R is an alkyl group containing from 10 to 58 carbon atoms, M is a mono-valent cation, and the alkylxylene moiety is alkyl-ortho-xylene in at least 85 percent of the total alkylxylene sulfonates and wherein the alkylxylene moiety in the alkylxylene sulfonates contains greater than 70 weight percent of the 4-alkyl-1, 2-dimethyl benzene isomer and the attachment of the alkyl group to the xylene moiety in the alkylxylene sulfonates is at
10 positions higher than the 2-position along the alkyl chain in at least 40 weight percent of the total alkylxylene sulfonates, and wherein the alkyl group contains a distribution of alkyl chain lengths wherein the alkyl chain lengths comprise from 40 to 80 weight percent C₁₂ to C₂₀ and 5 to 15 weight percent of C₃₂ to C₅₈.

15 2. The alkylxylene sulfonates of claim 1, wherein the alkylxylene moiety is alkyl-ortho-xylene in at least 95 weight percent of the total alkylxylene sulfonates.

3. The alkylxylene sulfonates of claim 1, wherein the alkylxylene moiety in the alkylxylene sulfonates contains greater than about 80 weight percent of the 4-alkyl-1, 2-dimethyl benzene isomer.

4. The alkylxylene sulfonates of claim 3, wherein the alkylxylene moiety in the alkylxylene sulfonates contains at least 90 weight percent of the 4-alkyl-1, 2-dimethyl benzene isomer.
- 5 5. The alkylxylene sulfonates of claim 1, wherein the alkyl group on the xylene moiety is attached at positions higher than the 2-position along the alkyl chain in at least 45 weight percent of the total alkylxylene sulfonates.
6. The alkylxylene sulfonates of claim 5, wherein the alkyl group on the xylene moiety is attached at positions higher than the 2-position along the alkyl chain in at least 60 weight percent of the total alkylxylene sulfonates.
- 10 7. The alkylxylene sulfonates of claim 1, wherein the mono-valent cation is an alkali metal.
8. The alkylxylene sulfonates of claim 7, wherein the alkali metal is sodium.
9. The alkylxylene sulfonates of claim 1, wherein the mono-valent cation is an ammonium ion or an organic ammonium ion.
- 15 10. The alkylxylene sulfonates of claim 1, wherein the alkyl group is derived from a linear alpha olefin or an isomerized olefin containing from about 10 to about 58 carbon atoms.
11. The alkylxylene sulfonates of claim 10, wherein the alkyl group is derived from a linear alpha olefin or an isomerized olefin containing from about 10 to about 40 carbon atoms.
- 20 12. The alkylxylene sulfonates of claim 11, wherein the alkyl group is derived from a linear alpha olefin or an isomerized olefin containing from about 12 to about 30 carbon atoms.

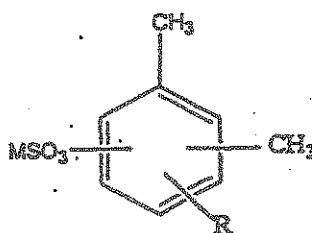
13. The alkylxylene sulfonates of claim 1, wherein the alkyl chain lengths comprise from 50 to 70 weight percent C_{12} to C_{20} and 5 weight percent to 15 weight percent of C_{32} to C_{58} .

5 14. The alkylxylene sulfonates of claim 13, wherein the alkyl chain lengths comprise 8 weight percent to 12 weight percent of C_{32} to C_{58} .

15. A method for enhanced oil recovery from a subterranean hydrocarbon containing formation, which method comprises:

(a) injecting into the formation an aqueous solution containing alkylxylene sulfonates effective for the recovery of crude oil wherein the alkylxylene sulfonates have the general formula:

10



as defined in any one of claims 1 to 14; and

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

15

16. The method of claim 15, wherein in step (a) the alkylxylene sulfonate is present in the range of 0.03 weight percent to 2.0 weight percent of the total weight of the aqueous solution.

17. The method of claim 16, wherein the alkylxylene sulfonate is present in the range of 0.1 weight percent to 1.5 weight percent of the total weight of the aqueous solution.

20

1 18. The method of claim 17, wherein the alkylxylene sulfonate is present in
2 the range of 0.3 weight percent to 1.0 weight percent of the total weight
3 of the aqueous solution.

4 19. The method of claim 18, wherein the alkylxylene sulfonate is present in
5 the range of 0.5 weight percent to 0.8 weight percent of the total weight
6 of the aqueous solution.

7 20. The method of claim 15, wherein the hydrocarbon in the subterranean
8 formation is a waxy crude oil.

9 21. The method of claim 15, wherein the method further comprises,
10 concurrently with or subsequent to the injection of the aqueous solution
11 in step (a), injecting into the formation an amount of polymer effective
12 for driving the aqueous solution of step (a) into the formation to
13 displace the crude oil to thereby recover hydrocarbons from a
14 production well.

15 22. The method of claim 21, wherein the polymer is a polysaccharide, an
16 acrylamide or a partially hydrolyzed polyacrylamide.

17 23. The method of claim 15, wherein the method further comprises,
18 concurrently with or subsequent to the injection of the aqueous solution
19 in step (a), injecting into the formation an amount of water effective for
20 driving the aqueous solution of step (a) into the formation to displace
21 the crude oil to thereby recover hydrocarbons from a production well.

22 24. The method of claim 21, wherein the method further employs,
23 concurrently with or subsequent to the injection of the polymer,
24 injecting into the formation an amount of water effective for driving the
25 aqueous solution of step (a) into the formation to displace the crude oil
26 to thereby recover hydrocarbons from a production well.

- 1 25. The method of claim 15, wherein the aqueous solution in step (a)
2 further contains a co-surfactant having a molecular weight in the range
3 of 60 to 1,200.
- 4 26. The method of claim 25, 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 27. The method of claim 26, 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 28. The method of claim 26, wherein the poly(oxyalkylene) glycol is a
13 poly(oxyethylene) glycol or a poly(oxypropylene) glycol or mixtures
14 thereof.
- 15 29. The method of claim 25, wherein in step (a) the co-surfactant is present
16 in the range of 0.03 weight percent to 2.0 weight percent of the total
17 weight of the aqueous solution.
- 18 30. The method of claim 29, wherein the co-surfactant is present in the
19 range of 0.1 weight percent to 1.5 weight percent of the total weight of
20 the aqueous solution.
- 21 31. The method of claim 30, wherein the co-surfactant is present in the
22 range of 0.3 weight percent to 1.0 weight percent of the total weight of
23 the aqueous solution.
- 24 32. The method of claim 31, wherein the co-surfactant is present in the
25 range of 0.5 weight percent to 0.8 weight percent of the total weight of
26 the aqueous solution.