

5 **ALKALINE EARTH ALKYLARYL SULFONATES,**
 THEIR APPLICATION AS AN ADDITIVE FOR LUBRICATING OIL,
 AND METHODS OF PREPARATION

10 The present invention relates to alkaline earth alkylaryl sulfonates, their application
as detergent/dispersant additives for lubricating oils, and methods for preparing
those sulfonates.

BACKGROUND OF THE INVENTION

15 In prior art, methods are known for preparing weakly or strongly superalkalinized
sulfonates from sulfonic acids obtained by the sulfonation of different alkyl aryl
hydrocarbons and from an excess of alkaline earth base.

20 The alkyl aryl hydrocarbons subjected to the sulfonation reaction are obtained by
alkylation via the Friedel and Craft reaction of different aryl hydrocarbons,
particularly aromatic, with two different types of olefin:

- 25 • Branched olefins obtained by the oligo-polymerization of propylene to C₁₅ to C₄₂
hydrocarbons, particularly the propylene tetrapolymer dimerized to a C₂₄ olefin,
and
- Linear olefins obtained by the oligo-polymerization of ethylene to C₁₄ to C₄₀
hydrocarbons.

30 It is easy to obtain a good dispersion in the medium of the alkaline earth base not
fixed in the form of salt if the sulfonic acid is derived from a hydrocarbon obtained
by alkylation of an aryl hydrocarbon with a branched olefin. It is difficult if the
alkylation is effected with a linear olefin. It is particularly difficult for the alkylation of
an aryl hydrocarbon where a high percentage of the alkylaryl hydrocarbon has the
35 aryl substituent on positions 1 or 2 of the linear alkyl chain, due to the formation of
a skin in the open air.

This poor dispersion is especially pronounced if the medium also contains a high proportion of sulfonate, that is if it corresponds to a low Base Number (between 3
5 and 60), hence to a low content of free lime and the absence of carbon dioxide and carbonate.

In fact, during the alkylation reaction with benzene or another aromatic or aryl hydrocarbon, 25 mole% of the alkylaryl hydrocarbon has the aryl substituent on
10 positions 1 or 2 of the linear alkyl chain. Traditionally, aromatics attached at the 2-position of the alkyl group give the most absorption of water.

In the alkylation reaction of aromatics using normal alpha olefins (NAO), there are three competing reactions. They are (1) isomerization of the NAO, (2) alkylation of
15 the aromatic with the olefin, and (3) dimerization of the olefin.

When prepared by the method described, for example in French Patent No. 2,564,830, this high proportion of alkyl aryl hydrocarbon having an aryl radical on position 1 or 2 of the linear alkyl chain results in a sulfonate that exhibits
20 hygroscopic properties such that a superficial 'skin' is formed. This 'skin' makes this product unacceptable as an additive for lubricating oil.

Furthermore, the formation of this superficial skin is generally accompanied by a very low filtration rate, a high viscosity, a low incorporation of calcium, a
25 deterioration of anti-rust performance, and an undesirable turbid appearance, or even sedimentation, when the sulfonate thus prepared is added at the rate of 10% by weight to a standard lubricating oil and stored for examination.

The Applicant has carried out chromatographic analysis to identify each of the
30 different isomers differing by the position of the aryl radical on the carbon atom of the linear alkyl chain, and examined their respective influence on the properties of the corresponding alkyl aryl sulfonates of alkaline earth metals obtained from these different isomers.

35 The Applicant has thus discovered that he could overcome the aforementioned drawbacks, inasmuch as the mole % of the aryl hydrocarbon, other than benzene,

having the aryl substituent on positions 1 or 2 of the linear alkyl chain was between 0 and 13%, and preferably between 5 and 11%, and more particularly between 7 and 10%.

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This discovery was the subject of a French Patent Application filed 8 March 1995 under No. 95 02,709 by the Applicant.

Yet the Applicant had not succeeded in obtaining satisfactory results when the aryl
10 hydrocarbon was benzene, because, heretofore, he had never been able to prevent the formation of the skin with the use of this aromatic hydrocarbon, even if the hydrocarbon was alkylated with a very long chain linear mono olefin so that the mole% of the aryl hydrocarbon having the aryl substituent on positions 1 or 2 of the linear alkyl chain was between 0 and 13%, and preferably between 5 and 11%,
15 and more particularly between 7 and 10%.

As a result of more intensive studies, the Applicant had discovered that the aforementioned drawbacks could be overcome by using a mixture of alkyl aryl sulfonates of superalkalinized alkaline earth metals comprising:

- 20 (a) from 50% to 85% of a linear mono-alkyl phenyl sulfonate in which the linear alkyl chain contains between 14 and 40 carbon atoms, and between 0 and 13 mole% of the phenyl sulfonate radical of the alkaline earth metal is fixed on position 1 or 2 of the linear alkyl chain, and
(b) from 15% to 50% of a heavy alkyl aryl sulfonate selected from:
25 (i) dialkyl aryl sulfonates wherein both alkyl substituents are linear alkyl chains, of which the sum of the carbon atoms is from 16 to 40, or
(ii) mono or polyalkyl aryl sulfonates wherein the alkyl substituent or substituents are branched chains, wherein the sum of the carbon atoms is from 15 to 48 carbon atoms.

30

This mixture of alkyl aryl sulfonates has a maximum of 10 mole% of the phenyl sulfonate radical of the alkaline earth metal fixed on position 1 or 2 of the linear alkyl chain. This mixture has no skin formation after three days of storage in an open jar at room temperature. It has good calcium incorporation, a low viscosity,
35 good solubility, and good performances.

This discovery was the subject of a French Patent Application filed 5 September 1996 under No. 96 10,833 by the Applicant.

As a result of more intensive studies, the Applicant had discovered a mixture of alkyl phenyl sulfonates of alkaline earth metals having low color and no skin formation even after three days of storage in an open jar at room temperature.

5 That mixture comprises:

- (a) from 20% to 70% of a linear mono alkyl phenyl sulfonate in which the linear mono alkyl substituent contains from 14 to 40 carbon atoms and the mole% of the phenyl sulfonate radical fixed on position 1 or 2 of the linear alkyl chain is between 10% and 25%, and
- 10 (b) from 30% to 80% of a branched mono alkyl phenyl sulfonate in which the branched mono alkyl substituent contains from 14 to 18 carbon atoms.

This discovery was the subject of a European Patent Application filed 31 July 1998 under No. 98 401968.9 by the Applicant.

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SUMMARY OF THE INVENTION

The present invention provides a highly overbased alkaline earth alkylaryl sulfonate having improved compatibility and solubility, while having low color and
20 no skin formation.

In accordance with the present invention, there is provided an alkaline earth alkylarylsulfonate having a BN of at least 250, where the aryl radical is other than phenol, wherein the alkyl chain is a linear chain that contains between 14 and 40
25 carbon atoms, and wherein the mole percentage of the alkaline earth alkylaryl sulfonates having the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl is higher than 13 mole percent. The present invention also provides a lubricating oil composition containing the alkaline earth alkyarylsulfonates of this invention.

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Further provided by the present invention is a lubricating oil composition comprising the product produced by blending:

- (a) a major amount of a base oil of lubricating viscosity;
- (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl
35 sulfonates of this invention;
- (c) from 0 to 20% of at least one ashless dispersant;
- (d) from 0 to 5% of at least one zinc dithiophosphate;
- (e) from 0 to 10% of at least one oxidation inhibitor;

- (f) from 0 to 1% of at least one foam inhibitor; and
- (g) from 0 to 20% of at least one viscosity index improver.

5 The present invention also provides a concentrate comprising from about from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate of this invention and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said sulfonate.

10 While we have found that a too high concentration of 1-aryl or 2-aryl linear alkylaryl sulfonate causes skin formation in low overbased sulfonates (base Number 2 to 60), we have found that the higher BN (at least 250 BN) sulfonates are less sensitive to 2-aryl content in the alkylate because the 2-aryl content is diluted by the salts. Therefore, if the BN is high enough (at least 250), and the aryl radical is
15 not phenol, then the mole % of the aryl-sulfonate radical fixed on position 1 or 2 of the linear alkyl chain can be higher than 13%, preferably higher than 15% (more preferably between 20% and 30%) without any skin forming. This high mole percentage of 2-aryl gives a sulfonate having good water absorption properties due to the high level of salt (calcium carbonate).

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The alkyl chain of that alkaline earth alkylaryl sulfonate is a linear chain that contains between 14 and 40 carbon atoms, preferably from 20 to 24 carbon atoms or 20 to 24 carbon atoms.

25 Preferably, the alkaline earth alkylaryl sulfonate has a mono-alkylate content of at least 87% and an iodine number of less than 1.0.

Preferably, the alkaline earth alkylaryl sulfonate is derived from a C₁₄-C₄₀ normal alpha olefin, more preferably from a C₂₀₋₂₈ or C₂₀-C₂₄ normal alpha olefin.

30

This alkaline earth alkylaryl sulfonate is preferably derived from an alkylate formed by the reaction of benzene and normal alpha olefin in the presence of hydrogen fluoride, preferably in a one-stage reactor. Preferably, the alkylaryl sulfonate is formed in the presence of methanol and xylene, but preferably in the absence of
35 chlorine.

Preferably, the alkaline earth alkylaryl sulfonate is used as a detergent/dispersant additive for lubricating oils. A lubricating oil formulation would contain a major

amount of a base oil of lubricating viscosity and a minor amount (preferably from 0.5 to 40%) of the alkaline earth alkylaryl sulfonate of the present invention. In addition, the lubricating oil formulation would typically contain from 0 to 20% of at least one ashless dispersant, from 0 to 5% of at least one zinc dithiophosphate, from 0 to 10% of at least one oxidation inhibitor, from 0 to 1% of at least one foam inhibitor; and from 0 to 20% of at least one viscosity index improver.

This lubricating oil composition can be made by blending a major amount of a base oil of lubricating viscosity and from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate of the present invention, preferably with from 0 to 20% of at least one ashless dispersant, from 0 to 5% of at least one zinc dithiophosphate, from 0 to 10% of at least one oxidation inhibitor, from 0 to 1% of at least one foam inhibitor; and from 0 to 20% of at least one viscosity index improver.

A concentrate can be formed comprising from about 0.5% to 90% of the alkaline earth alkylaryl sulfonate of the present invention and from about 10% to 90% of an organic liquid diluent compatible with the sulfonate.

The present invention is based at least in part on the discovery that the higher the amount of alkylaryl sulfonates having the aryl sulfonate attached at the 1 or 2 position of the alkyl group ("1+2 attachment"), the more significant are the improvements in the performance of the sulfonate, especially those linked to the increase of linearity of the molecule. Examples of (1+2) attachment of 29 or 30 weight percent with benzene and toluene are provided below. Very high BN of 500 and even more can be obtained. The alkylation of the aromatic compound can be conducted in presence of HF as catalyst or in a fixed bed using zeolite Y, for example, as catalyst, conditions giving the highest (1+2) attachment are targeted.

The sulfonates of the present invention have the following advantages/properties:

- Better solubility/compatibility ;
- Higher BN (500 and even more) obtained without any deterioration of solubility/compatibility ;

- 5
- Possibility of using higher molecular weight linear alpha olefin (NAO C₂₀₋₂₈ instead of NAO C₂₀₋₂₄) because alkylation reaction is favored relative to isomerization ;
- 10
- Possibility to use the alkylate of the invention associated with another alkylates (co-sulfonation or mixture of sulfonic acid can be used);
 - Less dispersant required in MCL formulation ;
 - Good hydrolytic stability and rate of neutralization

15 The alkylaryl sulfonate is formed in the presence of methanol and xylene or other alcohol(s) and possibly a diluent. Possibly, a chloride is used.

DETAILED DESCRIPTION OF THE INVENTION

- 20 In its broadest aspect, the present invention involves an alkaline earth alkylaryl sulfonate, its application as a detergent/dispersant additive for lubricating oils, and methods for preparing said mixture.

25 Prior to discussing the invention in further detail, the following terms will be defined:

DEFINITIONS

30 As used herein the following terms have the following meanings unless expressly stated to the contrary:

The term "alkaline earth metal" refers to calcium, barium, magnesium, and strontium.

- 35 The term "alkaline earth alkylaryl sulfonate" refers to an alkaline earth metal salt of an alkylaryl sulfonic acid. In other words, it is an alkaline earth metal salt of an aryl that is substituted with (1) an alkyl group and (2) a sulfonic acid group that is capable of forming a metal salt.

The term "the mole % of the aryl sulfonate radical fixed on position 1 or 2 of the linear alkyl chain" refers to the mole percentage of all the aryl sulfonate radicals fixed on a linear alkyl chain that are fixed at the 1st or 2nd position of the linear alkyl chain. The 1st position of the linear alkyl chain is the position at the end of the chain. The 2nd position of the linear alkyl chain is the position immediately next to the 1st position.

The term "1-aryl" refers to an aryl sulfonate radical fixed on a linear alkyl chain at the 1st position of the linear alkyl chain.

The term "2-aryl" refers to an aryl sulfonate radical fixed on a linear alkyl chain at the 2nd position of the linear alkyl chain.

The term "monoalkylate content" is the weight percentage of the alkylate that is not dialkylate $[100 \times \text{monoalkylate} / (\text{monoalkylate} + \text{dialkylate})]$.

The term "Iodine Number" is the absorption value (Hübl Number or Wijs number), which is the quantity of iodine, in grams, absorbed by 100 grams of fat or oil under specified conditions. It indicates the amount of double bonds present.

The term "Base Number" or "BN" refers to the amount of base equivalent to milligrams of KOH in one gram of sample. Thus, higher BN numbers reflect more alkaline products, and therefore a greater alkalinity reserve. The BN of a sample can be determined by ASTM Test No. D2896 or any other equivalent procedure.

The term "overbased alkaline earth alkylaryl sulfonate" refers to a composition comprising a diluent (e.g., lubricating oil) and alkylaryl sulfonate wherein additional alkalinity is provided by a stoichiometric excess of an alkaline earth metal base, based on the amount required to react with the acidic moiety of the detergent. Enough diluent should be incorporated in the overbased detergent to ensure easy handling at safe operating temperatures.

The term "highly overbased alkaline earth alkylaryl sulfonate" refers to an overbased alkaline earth alkylaryl sulfonate having a BN of 250 or more. Generally a carbon dioxide treatment is required to obtain high BN overbased detergent compositions. It is believed that this forms a colloidal dispersion of metal base.

Unless otherwise specified, all percentages are in weight percent, all ratios are molar ratios, and all molecular weights are number average molecular weights.

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STARTING OLEFINS

The most important point is to have a high mole percentage of the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl chain because a long and linear alkyl chain favors solubilization (incorporation) of the micelles of high overbased
10 sulfonates in the diluent oil. For this reason, usually a normal alpha olefin C₂₀₋₂₄ or C₂₀₋₂₈ is used (because about 90% of the double bonds are between carbon 1 and carbon 2 of the alkyl chain of olefin).

During the alkylation step there are two competitive reactions : migration of the
15 double bond and alkylation (which is favored by a large molar excess of aromatic versus olefin).

So, for obtaining a high mole percentage of the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl chain, there are two important points :
20

1. A large molar excess of aromatic versus olefin at alkylation step (condition required in any case).
2. Usually normal alpha olefin, but isomerized normal alpha olefins can also give
25 improved compatibility and solubility, if the level of branching obtained during isomerization step is not high. The isomerization step is conducted on a fixed bed zeolite Y in order to obtain the appropriate structure regarding the level of double bonds between carbon 1 and carbon 2 of the alkyl chain of the olefin (alpha content) and a low level of branching. In very specific conditions, a migration of
30 double bond from inside to the end (alpha position) of the alkyl chain is observed (it is called back migration of the double bound).

ALKYLATES

- 35 The structure of the alkylates (linear and long alkyl chain) which gives a high mole percentage of arylsulfonate radical on position 1 or 2 of the linear alkyl chain is the most important for improvement of compatibility, solubility, foaming, dispersion and reduction of sediment in the final package where alkylaryl sulfonates are mixed with

sulfurized overbased alkylphenates. So the improvement is the most significant if sulfonic acid is only from an alkylate having a high mole percentage of the aromatic radical on position 1 or 2 of the linear alkyl chain. This improvement is still
5 significant if such an alkylate is mixed with another heavy alkylate such as : dialkyl benzene where the amount of carbon of the both alkyl chains is between C₁₄ and C₆₀ and preferably between C₁₈ and C₄₀; a mono or poly alkyl-aryl-sulfonate in which the aryl radical may be a phenyl (substituted or not) such as phenyl, tolyl, xylyl, ethyl phenyl or cumenyl in which the alkyl groups are branched or linear
10 chain having a total number of carbons of at least on average 15 and up to 48; alkyl naphthalene, a petroleum fraction or polyisobutene having a molecular weight preferably between 400 and 2300. The alkyl chain of the alkylate is coming from dehydrogenation of paraffin or from polymerization of ethylene, propylene, butene-1 or isobutene. This mixture can be obtained by co-sulfonation, sulfonation of a
15 mixture of alkylates or mixing of sulfonic acid.

ALKYLARYL SULFONATES

The alkylaryl sulfonates of the present invention are highly overbased alkaline
20 earth alkylaryl sulfonates having linear alkyl groups, and having a high mole % of the aryl-sulfonate radical fixed on position 1 or 2 of the linear alkyl chain (higher than 13%, preferably higher than 20%). These alkylaryl sulfonates have improved compatibility and solubility, while having low color and no skin formation.

25 It is essential that the alkylaryl sulfonates be highly overbased (BN of at least 250), in order to diluent the 2-aryl content sufficiently so that skin formation will not result.

It is also essential that the aryl radical is not phenol, since highly overbased
30 alkylphenoxy sulfonates having a high 2-aryl content tend to be too viscous for easy handling. Preferably, it is an alkyl benzene sulfonate, an alkyl toluene sulfonate, or an alkyl ortho-xylene sulfonate.

The linear alkyl chain contains between 14 and 40 carbon atoms, preferably from
35 20 to 28 or 20 to 24 carbon atoms. Preferably, the alkaline earth alkylaryl sulfonate is derived from a C₁₄-C₄₀ normal alpha olefin, more preferably from a C₂₀-C₂₈ or C₂₀₋₂₄ normal alpha olefin.

Preferably, the alkaline earth alkylaryl sulfonate has a monoalkylate content of at least 87% and an Iodine number of less than 1.0.

- 5 French Patent No. 2.564.830 to the company Orogil whose corresponding application was published in 1985, and which corresponds to US Patent No. 4,764,295 describes alkylaryl sulfonates of alkaline earth metals resulting from alkylation by a linear olefin.
- 10 The alkaline earth alkylaryl sulfonate can be derived from an alkylate formed by the reaction of benzene and normal alpha olefin in the presence of hydrogen fluoride, preferably in a one-stage reactor. Preferably, the alkaline earth alkylaryl sulfonate is formed in the presence of methanol and xylene, or other alcohol(s) and possibly a diluent. Possibly, a chloride is used.
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OTHER ADDITIVE COMPONENTS

- 20 The following additive components are examples of components that can be favorably employed in combination with the mixture of alkylaryl sulfonates of alkaline earth metals in the compositions of the present invention:
- (1) **Ashless dispersants:** alkenyl succinimides, alkenyl succinimides modified with other organic compounds, and alkenyl succinimides modified with
- 25 boric acid, alkenyl succinic ester.
- (2) **Detergents:** sulfurized or unsulfurized alkyl or alkenyl phenates, sulfurized or unsulfurized metal salts of multi-hydroxy alkyl or alkenyl aromatic compounds, alkyl or alkenyl hydroxy aromatic sulfonates, sulfurized or unsulfurized alkyl or alkenyl salicylates, sulfurized or unsulfurized alkyl or alkenyl naphthenates,
- 30 metal salts of alkanolic acids, metal salts of an alkyl or alkenyl multiacid, and chemical and physical mixtures thereof.
- (3) **Oxidation inhibitors:**
- 1) Phenol type phenolic oxidation inhibitors:
- 4,4'-methylenebis(2,6-di-tert-butylphenol),
- 35 4,4'-bis(2,6-di-tert-butylphenol), 4,4'-bis(2-methyl-6-tert-butylphenol),
- 2,2'-(methylenebis(4-methyl-6-tert-butylphenol),
- 4,4'-butylidenebis(3-methyl-6-tert-butylphenol),
- 4,4'-isopropylidenebis(2,6-di-tert-butylphenol),

- 2,2'-methylenebis(4-methyl-6-nonylphenol),
 2,2'-isobutylidene-bis(4,6-dimethylphenol),
 2,2'-methylenebis(4-methyl-6-cyclohexylphenol), 2,6-di-tert-butyl-4-methylphenol,
 5 2,6-di-tert-butyl-4-ethylphenol,
 2,4-dimethyl-6-tert-butyl-phenol,
 2,6-di-tert- α -dimethylamino-p-cresol,
 2,6-di-tert-4-(N,N' dimethylaminomethylphenol),
 4,4'-thiobis(2-methyl-6-tert-butylphenol), 2,2'-thiobis(4-methyl-6-tert-butylphenol),
 10 bis(3-methyl-4-hydroxy-5-tert-butylbenzyl)-sulfide, and
 bis (3,5-di-tert-butyl-4-hydroxybenzyl).
 2) Diphenylamine type oxidation inhibitor: alkylated diphenylamine,
 phenyl- α -naphthylamine, and alkylated α -naphthylamine.
 3) Other types: metal dithiocarbamate (e.g., zinc dithiocarbamate),
 15 and methylenebis (dibutyldithiocarbamate).
 (4) **Rust inhibitors (Anti-rust agents):**
 1) Nonionic polyoxyethylene surface active agents: polyoxyethylene
 lauryl ether, polyoxyethylene higher alcohol ether, polyoxyethylene nonylphenyl
 ether, polyoxyethylene octylphenyl ether, polyoxyethylene octyl stearyl ether,
 20 polyoxyethylene oleyl ether, polyoxyethylene sorbitol monostearate,
 polyoxyethylene sorbitol mono-oleate, and polyethylene glycol monooleate.
 2) Other compounds: stearic acid and other fatty acids, dicarboxylic
 acids, metal soaps, fatty acid amine salts, metal salts of heavy sulfonic acid, partial
 carboxylic acid ester of polyhydric alcohol, and phosphoric ester.
 25 (5) **Demulsifiers:** addition product of alkylphenol and ethyleneoxide,
 polyoxyethylene alkyl ether, and polyoxyethylene sorbitane ester.
 (6) **Extreme pressure agents (EP agents):** zinc dialkyldithiophosphate
 (Zn-DTP, primary alkyl type & secondary alkyl type), sulfurized oils, diphenyl
 sulfide, methyl trichlorostearate, chlorinated naphthalene, benzyl iodide,
 30 fluoroalkylpolysiloxane, and lead naphthenate.
 (7) **Friction modifiers:** fatty alcohol, fatty acid, amine, borated ester, and
 other esters
 (8) **Multifunctional additives:** sulfurized oxymolybdenum
 dithiocarbamate, sulfurized oxymolybdenum organo phosphoro dithioate,
 35 oxymolybdenum monoglyceride, oxymolybdenum diethylate amide, amine-
 molybdenum complex compound, and sulfur-containing molybdenum complex
 compound

- (9) **Viscosity index improvers:** polymethacrylate type polymers, ethylene-propylene copolymers, styrene-isoprene copolymers, hydrated styrene-isoprene copolymers, polyisobutylene, and dispersant type viscosity index improvers.
- (10) **Pour point depressants:** polymethyl methacrylate.
- (11) **Foam Inhibitors:** alkyl methacrylate polymers and dimethyl silicone polymers.

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OIL OF LUBRICATING VISCOSITY

- The oil of lubricating viscosity used in such compositions may be mineral oil or synthetic oils of viscosity suitable for use in the crankcase of an internal combustion engine, such as gasoline engines and diesel engines, including passenger car, heavy duty on-road and off-road, railroad, natural gas and marine, such as trunk piston and in the cylinder for slow speed crosshead engines. Crankcase lubricating oils ordinarily have a viscosity of about 1300 cSt at 0°F (-18°C) to 24 cSt at 210°F (99°C). The lubricating oils may be derived from synthetic or natural sources. Mineral oil for use as the base oil in this invention includes paraffinic, naphthenic, and other oils that are ordinarily used in lubricating oil compositions. Synthetic oils include both hydrocarbon synthetic oils and synthetic esters. Useful synthetic hydrocarbon oils include liquid polymers of alpha olefins having the proper viscosity. Especially useful are the hydrogenated liquid oligomers of C₆ to C₁₂ alpha olefins, such as 1-decene trimer. Likewise, alkyl benzenes of proper viscosity, such as didodecyl benzene, can be used. Useful synthetic esters include the esters of both monocarboxylic acids and polycarboxylic acids, as well as monohydroxy alkanols and polyols. Typical examples are didodecyl adipate, pentaerythritol tetracaproate, di-2-ethylhexyl adipate, dilaurylsebacate, and the like. Complex esters prepared from mixtures of mono and dicarboxylic acids and mono and dihydroxy alkanols can also be used.

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Blends of mineral oils with synthetic oils are also useful. For example, blends of 10% to 25% hydrogenated 1-decene trimer with 75% to 90% 150 SUS (100°F) mineral oil gives an excellent lubricating oil base.

LUBRICATING OIL COMPOSITIONS

The additives produced by the process of this invention are useful for imparting
5 detergency and dispersancy properties to the lubricating oil. When employed in
this manner, the amount of alkaline earth alkylaryl sulfonate ranges from about
0.5% to 40% of the total lubricant composition, preferably from about 1% to 25% of
the total lubricant composition. Such lubricating oil compositions are useful in the
crankcase of an internal combustion engine, such as gasoline engines and diesel
10 engines, including passenger car, heavy duty on-road and off-road, railroad,
natural gas and marine, such as trunk piston and in the cylinder for slow speed
crosshead engines. They are also useful in hydraulic applications.

The lubricating oil composition can be used in a method of decreasing black
15 sludge deposits, a method of decreasing piston deposits, or both.

Such lubricating oil compositions employ a finished lubricating oil, which may be
single or multigrade. Multigrade lubricating oils are prepared by adding viscosity
index (VI) improvers. Typical VI improvers are polyalkyl methacrylates, ethylene-
20 propylene copolymers, styrene-diene copolymers, and the like. So-called
dispersant VI improvers, which exhibit dispersant properties as well as VI
modifying properties, can also be used in such formulations.

In one embodiment, a lubricating oil composition would contain
25 (a) a major amount of an oil of lubricating viscosity;
(b) from 0.5% to 40% of a detergent comprising the alkaline earth alkylaryl
sulfonate of the present invention;
(c) from 0% to 20% of at least one ashless dispersant;
(d) from 0% to 5% of at least one zinc dithiophosphate;
30 (e) from 0% to 10% of at least one oxidation inhibitor;
(f) from 0% to 1% of at least one foam inhibitor; and
(g) from 0% to 20% of at least one viscosity index improver.

PROCESS FOR PRODUCING A LUBRICATING OIL COMPOSITION

- 5 In one embodiment, a lubricating oil composition is produced by blending a mixture of:
- (a) a major amount of an oil of lubricating viscosity;
 - (b) from 0.5% to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate of the present invention, preferably also comprising a sulfurized alkylaryl
 - 10 phenate;
 - (c) from 0% to 20% of at least one ashless dispersant;
 - (d) from 0% to 5% of at least one zinc dithiophosphate;
 - (e) from 0% to 10% of at least one oxidation inhibitor;
 - (f) from 0% to 1% of at least one foam inhibitor; and
 - 15 (g) from 0% to 20% of at least one viscosity index improver.

The lubricating oil composition produced by that method might have a slightly different composition than the initial mixture, because the components may interact. The components can be blended in any order and can be blended as

20 combinations of components.

ADDITIVE CONCENTRATES

Additive concentrates are also included within the scope of this invention. The

25 concentrates of this invention comprise the alkaline earth alkylaryl sulfonate of the present invention, with at least one of the additives disclosed above. Typically, the concentrates contain sufficient organic diluent to make them easy to handle during shipping and storage.

- 30 From 10% to 90% of the concentrate is organic diluent. From 0.5% to 90% of concentrate is the mixture of alkyl aryl sulfonates of alkaline earth metals of the present invention. The remainder of the concentrate consists of other additives.

Suitable organic diluents which can be used include for example, solvent refined

35 100N, i.e., Cit-Con 100N, and hydrotreated 100N, i.e., RLOP 100N, and the like. The organic diluent preferably has a viscosity of from about 1 to about 20 cSt at 100°C.

EXAMPLES OF ADDITIVE PACKAGES

Below are representative examples of additive packages that can be used in a variety of applications. These representative examples employ the novel dispersants of the present invention. The following percentages are based on the amount of active component, with neither process oil nor diluent oil. These examples are provided to illustrate the present invention, but they are not intended to limit it.

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The detergent cited below can be either the alkaline earth alkylaryl sulfonate of the present invention alone or in combination with another detergent.

I. MARINE DIESEL ENGINE OILS

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	1)	Detergent	65%
		Primary alkyl Zn-DTP	5%
		Oil of lubricating viscosity	30%
20	2)	Detergent	65%
		Alkenyl succinimide ashless dispersant	5%
		Oil of lubricating viscosity	30%
	3)	Detergent	60%
25		Primary alkyl Zn-DTP	5%
		Alkenyl succinimide ashless dispersant	5%
		Oil of lubricating viscosity	30%
	4)	Detergent	65%
30		Phenol type oxidation inhibitor	10%
		Oil of lubricating viscosity	25%
	5)	Detergent	55%
		Alkylated diphenylamine-type oxidation inhibitor	15%
35		Oil of lubricating viscosity	30%

6)	Detergent	65%
	Phenol-type oxidation inhibitor	5%
	Alkylated diphenylamine-type oxidation inhibitor	5%
5	Oil of lubricating viscosity	25%
7)	Detergent	60%
	Primary alkyl Zn-DTP	5%
	Phenol-type oxidation inhibitor	5%
10	Oil of lubricating viscosity	30%
8)	Detergent	60%
	Alkenyl succinimide ashless dispersant	5%
	Alkylated diphenylamine-type oxidation inhibitor	10%
15	Oil of lubricating viscosity	25%
9)	Detergent	55%
	Other additives	25%
	Primary alkyl Zn-DTP	
20	Alkenyl succinic ester ashless dispersant	
	Phenol-type oxidation inhibitor	
	Alkylated diphenylamine-type oxidation inhibitor	
	Oil of lubricating viscosity	30%
25	II. MOTOR CAR ENGINE OILS	
1)	Detergent	25%
	Alkenyl succinimide ashless dispersant	35%
	Primary alkyl Zn-DTP	10%
30	Oil of lubricating viscosity	30%
2)	Detergent	20%
	Alkenyl succinimide ashless dispersant	40%
	Secondary alkyl Zn-DTP	5%
35	Dithiocarbamate type oxidation inhibitor	5%
	Oil of lubricating viscosity	30%

3)	Detergent	20%
	Alkenyl succinimide ashless dispersant	35%
	Secondary alkyl Zn-DTP	5%
5	Phenol type oxidation inhibitor	5%
	Oil of lubricating viscosity	35%
4)	Detergent	20%
	Alkenyl succinimide ashless dispersant	30%
10	Secondary alkyl Zn-DTP	5%
	Dithiocarbamate type anti-wear agent	5%
	Oil of lubricating viscosity	40%
5)	Detergent	20%
15	Succinimide ashless dispersant	30%
	Secondary alkyl Zn-DTP	5%
	Molybdenum-containing anti-wear agent	5%
	Oil of lubricating viscosity	40%
20	6) Detergent	20%
	Alkenyl succinimide ashless dispersant	30%
	Other additives	10%
	Primary alkyl Zn-DTP	
	Secondary alkyl Zn-DTP	
25	Alkylated diphenylamine-type oxidation inhibitor	
	Dithiocarbamate type anti-wear agent	
	Oil of lubricating viscosity	40%
7)	Detergent	60%
30	Other additives 10%	
	Phenol type oxidation inhibitor	
	Alkylated diphenylamine-type oxidation inhibitor	
	Dithiocarbamate type anti-wear agent	
	Demulsifier	
35	Boron-containing friction modifier	
	Oil of lubricating viscosity	30%

III. HYDRAULIC OILS

1)	Detergent	20%
5	Primary alkyl Zn-DTP	50%
	Other additives	25%
	Phenol type oxidation inhibitor	
	Phosphorous-containing extreme pressure agent	
	Triazol type corrosion inhibitor	
10	Demulsifier	
	Nonionic anti-rust agent	
	Oil of lubricating viscosity	5%
2)	Detergent	10%
15	Primary alkyl Zn-DTP	40%
	Other additives	47%
	Phenol type oxidation inhibitor	
	Sulfur-containing extreme pressure agent	
	Triazol type corrosion inhibitor	
20	Demulsifier	
	Nonionic anti-rust agent	
	Oil of lubricating viscosity	3%
3)	Detergent	10%
25	Phosphorous-containing extreme pressure agent	40%
	Phenol type oxidation inhibitor	15%
	Other additives	25%
	Diphenylamine type oxidation inhibitor	
	Sulfur-containing extreme pressure agent	
30	Triazol type corrosion inhibitor	
	Demulsifier	
	Nonionic anti-rust agent	
	Oil of lubricating viscosity	10%

4)	Detergent	20%
	Phosphorous-containing extreme pressure agent	30%
	Other additives	45%
5	Diphenylamine type oxidation inhibitor	
	Sulfur-containing extreme pressure agent	
	Triazol type corrosion inhibitor	
	Demulsifier	
	Nonionic anti-rust agent	
10	Oil of lubricating viscosity	5%

IV. TRANSMISSION HYDRAULIC FLUIDS

1)	Detergent	35%
15	Primary alkyl Zn-DTP	20%
	Polyol type friction modifier	20%
	Sulfur-containing extreme pressure agent	5%
	Oil of lubricating viscosity	20%
20	2) Detergent	40%
	Primary alkyl Zn-DTP	15%
	Amide type friction modifier	15%
	Sulfur-containing extreme pressure agent	5%
	Oil of lubricating viscosity	25%
25	3) Detergent	30%
	Primary alkyl Zn-DTP	20%
	Other additives	30%
	Alkenyl succinimide ashless dispersant	
30	Amide type friction modifier	
	Ester type friction modifier	
	Phosphorous, sulfur-containing extreme pressure agent	
	Oil of lubricating viscosity	20%

4)	Detergent	35%
	Primary alkyl Zn-DTP	15%
	Other additives	25%
5	Polyol type friction modifier	
	Amide type friction modifier	
	Phosphorous, sulfur-containing extreme pressure agent	
	Oil of lubricating viscosity	25%

10

METHODS OF MEASUREMENTS

The examples contain test results obtained by the following methods of
15 measurements:

Viscosity at 100° C in cSt

The viscosity was measured at the temperature of 100° C after dilution of the
20 product sample to be measured in 600 N oil. The viscosity was measured following method ASTM D 445.

Compatibility

25 Two methods were used to evaluate the appearance and the storage stability of the additives and the corresponding oils containing them. These methods are applicable to additives for lubricants.

Method No. 1 : Accelerated Stability Storage Test (ASST)

30

Procedure :

Form a blend of 100 grams in a beaker of 250 ml of the following products :

- A 250 BN phenate in a quantity such that the BN coming from the
35 phenate in blend of 100 grams is 35.

- A 400 BN sulfonate (or a 320 BN sulfonate) in a quantity such that the BN coming from the sulfonate in the blend of 100 grams is 35.

- 35 grams of diluent oil named 150 bright stock (from Idemitsu Kosan Company).
- Complete to 100 grams by adding a 500N diluent oil (from Idemitsu Kosan Company).

Blend during 30 minutes at 65°C, then put the oil obtained into a centrifuge tube. Keep it in an oven during 24 hours at 100°C then centrifuge during one hour at 4540 rpm.

10

Read the sediment content. If the sediment content is less than 0.05% the oil the results are a "pass", otherwise it is a "fail".

Method No. 2 : Compatibility /solubility in a severe base oil having the following composition :

15

- 20 % bright stock (from Idemitsu Kosan Company).
- 80 % 500 N (from Idemitsu Kosan Company).

Procedure :

20

Add to the severe base oil a quantity of 400 BN HOB Sulfonates in order to obtain a solution having 100 m moles calcium per liter.

Mix the base oil and sulfonates under agitation for thirty minutes at a temperature of 80°C.

25

Divide the oil into two bottles, one kept at room temperature and the other kept at a temperature of 80°C.

Evaluate the blend right after blending using a foam test (ASTM D 892).

30

Evaluate the appearance each week.

Method No. 3 : Compatibility /solubility in severe base oil :

35

A package formulated in severe base oils (Group II) and containing dispersant and detergent phenate (HOB sulfonate free) is completed at BN 70 with the audit sample of HOB sulfonate. Then this sample (100g) is stored in a centrifuge tube

(ASTM D 2273) for three weeks in a oven at 50°C and after that time it is centrifuged at 750 RCF for one hour and the sediment is reported.

- 5 To pass this test, the final sediment must be less than 0,05%

Color Test

A color test (ASTM D1500) was performed on the sulfonate prior to blending.

10

HYDROLYTIC STABILITY (ASTM D2619 MODIFIED)

This method is drawn from the modified ASTM D2619 method. Its purpose is to study the sensitivity to water of an oil and it is applicable to marine oils.

15

The method involves introducing a sample of oil to which demineralized water has been added into a bottle and agitating it in a thermostated oven. At the end of the test, the sample is dried, filtered and analyzed. The stability towards hydrolysis is expressed by the presence or absence of crystalline carbonate, characterized by IR spectroscopy. The results are classified as "Pass" in the absence of crystalline carbonate and "Fail" if crystalline carbonate is present.

20

PROCEDURES FOR PREPARATION

25 Synthesis of the Alkylate

The alkylate was synthesized in an alkylation pilot plant with hydrofluoric acid, which consists of two reactors in series of 1.150 liters each, and a 25 liter settler wherein the organic phase was separated from the phase containing the hydrofluoric acid, all of the equipment being maintained under a pressure of about 5×10^5 Pa.

30

The organic phase was then withdrawn via a valve, and expanded to atmospheric pressure, and the benzene was removed by topping, that means by heating to 160°C at atmospheric pressure.

35

After withdrawal, the mineral phase was neutralized by caustic potash.

The reaction was carried out in either one or two reactors:

If only one reactor was used, the benzene/olefin mole ratio was high, about 10:1,
5 and the second reactor was by-passed.

If two reactors were used, the benzene/olefin mole ratio was relatively low in the first reactor, about 1:1 to 1.5:1, and it was higher in the second reactor, about 2:1 to 10:1. Furthermore, the ratio of hydrofluoric acid to the olefin by volume was
10 about 1:1 in the first reactor and about 2:1 in the second reactor.

Distillation of the Alkylate

As benzene was alkylated by a C₂₀ to C₂₄ linear olefin, there was no formation of a
15 light fraction. Hence it was sufficient to effect a topping of the unreacted benzene and residual hydrofluoric acid to obtain the corresponding alkylate.

Sulfonation of the Alkylate

20 The molar proportion of the phenyl radical substituted on the carbon atoms in position 1 or 2 of the alkyl radical was determined on the alkylate, then the alkylate was subjected to the sulfonation reaction.

Sulfonation was conducted on the alkylate using sulfur trioxide (SO₃), produced by
25 the passage of a mixture of oxygen and sulfur dioxide (SO₂) through a catalytic furnace containing vanadium oxide (V₂O₅). The sulfur trioxide gas was introduced at the top of a sulfonation reactor (2 meter long and 1 cm in diameter) in a concurrent alkylate stream.

30 The resulting sulfonic acid was recovered at the bottom of the reactor. The sulfonation conditions are as follows :

The SO₃ flow rate was set at 76 grams/hour.

35 The alkylates flow rate was between 300 and 450 grams/hour, depending on the desired SO₃:alkylate mole ratio, which varied from 0.8:1 to 1.2:1.

The sulfonation temperature was between 50° and 60° C.

Nitrogen was used as vector gas to dilute the SO_3 to 4% by volume.

After the sulfonation reaction, the residual sulfuric acid was removed by thermal treatment after dilution by 10% 100 N oil, nitrogen bubbling at the rate of 10 liter/hour per Kg of product, and stirring at 85°C , until a lower residual H_2SO_4 content was obtained (maximum 0.5 % by weight).

Superalkalinization

10

In this step, hydrated lime $\text{Ca}(\text{OH})_2$ was added to the reaction product at a very high molar ratio of hydrated lime versus sulfonic acid, and the product was reacted in order to obtain a final product having a BN higher than 250 according to standard ASTM D 2896.

15

To obtain this, a quantity of $\text{Ca}(\text{OH})_2$ was added in large excess to the stoichiometric neutralization of the quantity of sulfonic acid reacted (0.5 mole of $\text{Ca}(\text{OH})_2$ per mole of this sulfonic acid).

20 The lime reagent was methanol and the solvent was xylene. The carbonation was carried out by CO_2 at a temperature between 20° and 55°C . Before elimination of the solvent, the sediment was eliminated by centrifugation.

25 The performance obtained by the alkyl aryl sulfonate mixtures of the invention are summarized in the table given at the end of the present specification.

EXAMPLES

EXAMPLE 1

30

The product of the present invention is produced in one continuous reactor with hydrofluoric acid. The molar ratio benzene/olefin is 10:1 and alkylation temperature is 60°C . A high level 0.29 (or 29%) of the arylsulfonate fixed on position 1 or 2 of the linear alkyl chain is obtained. This high overbased

35

alkylarylsulfonate performs very well in compatibility/solubility. A 426 BN high overbased alkylarylsulfonate is obtained. Molecular weight of the starting sulfonic acid is 470 (determined by ASTM D3712 method).

5

EXAMPLE 2

Similar to Example 1 but at the alkylation step benzene is substituted by toluene. 0.22 (or 22%) of the arylsulfonate is fixed on position 1 or 2 of the linear alkyl

10 chain. A 423 BN high overbased alkylarylsulfonate is obtained.

EXAMPLE 3

Similar to Example 1, but a higher BN is targeted (502 instead of 426). The

15 process used for superalkalinization is identical to Example 1 but 1) quantity of lime, methanol, xylene and CO₂ are different because the target is a higher BN 2) some water is introduced at 79°C during elimination step of methanol/water before centrifugation. This high overbased arylsulfonate performs very well in compatibility/solubility and hydrolytic stability and no significant deterioration is

20 observed, even though the increase of BN is important. Moreover, the compatibility/solubility are better than the Comparative Example A (BN 418 where only 0,10 (10%) of the arylsulfonate is fixed on position 1 + 2).

EXAMPLE 4

25

Similar as Example 1 but a normal alpha olefin is preisomerized on a fixed bed of zeolite Y before alkylation.

The conditions of preisomerization of the olefin are such the level of branching

30 olefin is very low. About 10% of the total double bonds are between carbon 1 and carbon 2 (alpha position). Molar ratio benzene/olefin is 12:1 and the alkylation temperature is 60°C (continuous reactor with hydrofluoric acid).

Solubility/compatibility are much better than in Comparative Example A where two reactors were used and molar ratio benzene/olefin was low 1,2 : 1 in the first

35 reactor and even though in Comparative Example A the starting material is NAO C₂₀₋₂₄ (90% alpha and almost no branching). This example demonstrates that the molar ratio benzene : olefin used in the first (or single reactor) should be high.

EXAMPLE 5

Similar to Example 2, a normal alpha olefin C₂₀₋₂₄ and toluene are used, but the
5 alkylation instead of using hydrofluoric acid as catalyst is done continuously on a
fixed bed of zeolite Y. This high overbased alkylarylsulfonate performs very well in
compatibility/solubility.

EXAMPLE 6

10

The sulfonation step is conducted on the following mixture of alkylates : 80 weight
percent of alkylates of Example 1 and 20% of a dialkyl benzene having a
molecular weight of about 430. The other steps are similar to Example 1.

Compatibility/solubility performances of Example 6 are almost as good as Example
15 1.

EXAMPLE 7

Similar to Example 1 but instead of a C₂₀₋₂₄ a NAO C₂₀₋₂₈ is used. The molecular
20 weight of the sulfonic acid is 510 instead of 470 in Example 1 (ASTMD 3712). A
419 BN high overbased arylsulfonate is obtained, and performs very well in
compatibility/solubility.

COMPARATIVE EXAMPLE A

25

Similar to Example 1 but two continuous reactors were used instead of one. The
benzene/olefin mole ratio was relatively low in the first (1.2:1, so a lot of
30 isomerization and branching occur) and higher in the second reactor (5.8:1).

Furthermore, the ratio of hydrofluoric acid to the olefin by volume was about 1:1 in
the first reactor and about 2:1 in the second reactor. The compatibility/solubility
was much poorer than Example 1 (for example in Method 3, percentage sediment
35 is 0.80% versus 0.02% for example 1). By adding 2% dispersant to the formulation
containing Comparative Example A used for compatibility/solubility test of Example

3, the level of sediment is decreased down to 0.02%. That means the alkylates of the invention have the advantage to allow less dispersant in Marine cylinder lubricant.

5

COMPARATIVE EXAMPLES B and C

- 10 NAO C₂₀₋₂₄ is preisomerized in the first step on a fixed bed in such conditions that the level of branching is high, then alkylation is done continuously in conditions described in Example 1 (hydrofluoric acid, one reactor). Even though the molar excess benzene/olefin is high (10:1), the compatibility/solubility performances are deteriorated due to too high a level of branching, and the higher the level of
- 15 branching, the poorer the compatibility/solubility.

Data and results for the above Examples are shown in the table below.

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EXAMPLES	1	2	3	4	5	6	7	Compara tive Example A	Compara tive Example B	Compara tive Example C
Starting olefin	NAO C20-24	NAO C20- 24	NAO C20- 24	ISO NAO C20-24	ISO NAO C20-25	80% NAO C20- 24 (example 1) + 20% dialkyl	NAO C20-28	NAO C20-24	NAO C20-24	ISO NAO C20-24
% alpha content (Mole)	90%	90%	90%	10%	90%	90%	90%	90%	3,5%	2%
% branched	NIL	NIL	NIL	20%	NIL	NIL	NIL	NIL	42,6%	50%
Aromatic	Benzene	Toluene	Benzene	Benzene	Toluene	Benzene	Benzene	Benzene	Benzene	Benzene
Alkylation catalyst	HF	HF	HF	HF	Fixed bed zeolite Y	HF	HF	HF	HF	HF
Position 1 + 2 Σ positions	0,29	0,22	0,29	0,16	0,17	0,23	0,29	0,10	0,11	0,07
Viscosity at 40°C (cst)	18,2	20,9	18,2	19,4	21,8		20	17,8	20,2	20,6
Iodine index grams / (100 grams)	0,6	0,65	0,55	0,8	0,9	0,55	1	1,1	1,2	1,3
ANALYSES OF THE ACID										
% HSO ₃ - weight	15,8	15,6	15,8	15,5	15,5	15,2	14,9	15,1	15,1	15,0
% H ₂ SO ₄ % weight	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,2	0,3	0,3
ANALYSES OF THE SULFONATE										
% Ca (total)	16,1	16	18,8	16,1	16,4	16,05	15,8	15,8	16,1	16,2
BN ASTM D2896	426	423	502	426	435	425	419	418	427	428
Viscosity at 100°C (cst)	119	127	172	149	135	118	112	92	121	116

<u>Comnatibility</u>	1	2	3	4	5	6	7	Compara tive Example A	Comparti ve Example B	Compara tive Example C
Method 1	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail	Fail
Method 2 1 week	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Pass
2 weeks	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail	Fail
3 weeks	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail	Fail
4 weeks	Pass	Pass	Pass	Pass	Pass	Pass	Pass	Fail	Fail	Fail
Method 3	0,02	0,03	0,03	0,04	0,02	0,04	0,02	0.8	0,4	1%
% sed (after 30 days)										
Foaming (sequence 1) ASTM D892	0/0	0/0	0/0	0/0	0/0	0/0	0/0	20/0	20/0	40/0
Color ASTM D 1500	4,8D	4,9D	4,7D	5,8D	5,9D	4,7D	6,1D	6,2D	6,3D	6,5D
Hydrolytic stability ASTM D2619 modified	Pass		Pass							



What is claimed is:

- 5 1. An alkaline earth alkylarylsulfonate having a BN of at least 250, where the aryl radical is other than phenol, wherein the alkyl chain is a linear chain that contains between 14 and 40 carbon atoms, and wherein the mole percentage of the alkaline earth alkylaryl sulfonates having the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl is higher than 13 mole percent.
- 10 2. An alkaline earth alkylarylsulfonate of claim 1 wherein the mole percentage of the alkaline earth alkylaryl sulfonates having the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl is higher than 20 mole percent.
- 15 3. An alkaline earth alkylarylsulfonate of claim 1 wherein the alkyl chain is derived from a C₁₄₋₄₀ normal alpha olefin.
4. An alkaline earth alkylarylsulfonate of claim 1 wherein the alkyl chain is derived from a C₂₀₋₂₈ normal alpha olefin.
- 20 5. An alkaline earth alkylarylsulfonate of claim 1 wherein the alkyl chain is derived from a C₂₀₋₂₄ normal alpha olefin.
6. An alkaline earth alkylarylsulfonate of claim 1 wherein the alkyl chain is derived from a C₁₄₋₄₀ normal alpha olefin and the aryl group is benzyl.
- 25 7. An alkaline earth alkylarylsulfonate of claim 1 wherein the alkyl chain is derived from a C₂₀₋₂₈ normal alpha olefin and the aryl group is benzyl.
8. An alkaline earth alkylarylsulfonate as claimed in claim 1 wherein the alkyl chain is derived from a C₂₀₋₂₄ normal alpha olefin and the aryl group is benzyl.
- 30 9. An alkaline earth alkylarylsulfonate of claims 1 to 8 wherein the alkaline earth alkylaryl sulfonate is derived from an alkylate formed by the reaction of benzene and a C₁₄₋₄₀ normal alpha olefin in the presence of hydrogen fluoride.
- 35 10. An alkaline earth alkylarylsulfonate according to claims 1 to 8 wherein the alkaline earth alkylarylsulfonate is derived from an alkylate formed by the reaction of benzene and a C₁₄₋₄₀ normal olefin on a fixed bed reactor using a



solid acidic alkylation catalyst.

11. An alkaline earth alkylarylsulfonate of claim 9 wherein the alkylate is formed in a one-stage reactor.
- 5
12. An alkaline earth alkylaryl sulfonate claims 1 to 8 wherein the alkaline earth alkylaryl sulfonate is derived from an alkylate formed by the reaction of toluene and a C₁₄₋₄₀ normal alpha olefin in the presence of hydrogen fluoride.
- 10
13. An alkaline earth alkylarylsulfonate of claim 12 wherein the alkylate is formed in a one-stage reactor.
14. An alkaline earth alkylaryl sulfonate claims 1 to 8 wherein the alkaline earth alkylaryl sulfonate is derived from an alkylate formed by the reaction of ortho-xylene and a C₁₄₋₄₀ normal alpha olefin in the presence of hydrogen fluoride.
- 15
15. An alkaline earth alkylarylsulfonate of claim 14 wherein the alkylate is formed in a one-stage reactor.
- 20
16. An alkaline earth alkylarylsulfonate of claim 1 having a BN of at least 350.
17. An alkaline earth alkylarylsulfonate of claim 3 having a BN of at least 350.
18. An alkaline earth alkylarylsulfonate of claim 4 having a BN of at least 350.
- 25
19. An alkaline earth alkylarylsulfonate of claim 5 having a BN of at least 350.
20. An alkaline earth alkylarylsulfonate of claim 1 having a BN of at least 450.
- 30
21. An alkaline earth alkylarylsulfonate of claim 3 having a BN of at least 450.
22. An alkaline earth alkylarylsulfonate of claim 4 having a BN of at least 450.
23. An alkaline earth alkylarylsulfonate of claim 5 having a BN of at least 450.
- 35
24. An alkaline earth alkylarylsulfonate of claim 1 having a BN of at least 500.
25. An alkaline earth alkylarylsulfonate of claim 3 having a BN of at least 500.



26. An alkaline earth alkylarylsulfonate of claim 4 having a BN of at least 500.
27. An alkaline earth alkylarylsulfonate of claim 5 having a BN of at least 500.
- 5 28. An alkaline earth alkylarylsulfonate of claim 1 wherein the sulfonic acid portion of the molecule has a molecular weight that is lower than 500.
- 10 29. A composition comprising a mixture of (1) a first component comprising an alkaline earth alkylarylsulfonate having a BN of at least 250, where the aryl radical is other than phenol, wherein the alkyl chain is a linear chain that contains between 14 and 40 carbon atoms, and wherein the mole percentage of the alkaline earth alkylaryl sulfonates having the arylsulfonate radical fixed on position 1 or 2 of the linear alkyl is higher than 13 mole percent and (2) a second component selected from the group consisting of an alkaline earth sulfonate prepared from dialkyl benzene where the number of carbon atoms on both alkyl chains is between 14 and 60; a mono- or polyalkylaryl sulfonate in which the aryl radical may be a substituted or unsubstituted phenyl, tolyl, xylyl, ethyl phenyl or cumenyl in which the alkyl groups are branched or linear chain having a total number of carbons of at least on average 15 and up to 48; and an alkyl naphthalene, a petroleum fraction or polyisobutene having a molecular weight between 400 and 2300.
- 15
- 20
30. A lubricating oil formulation containing the composition of claim 29.
- 25 31. An alkaline earth alkylarylsulfonate as claimed in any of claims 1 to 8 wherein the alkyl chain is derived from an olefin that has been preisomerized on a fixed bed before alkylation.
32. An alkaline earth alkylarylsulfonate of claim 9 wherein the alkyl chain is derived from an olefin that has been preisomerized on a fixed bed before alkylation.
- 30
33. An alkaline earth alkylarylsulfonate of claim 9 wherein the alkyl chain is derived from an olefin that has been preisomerized on a fixed bed before alkylation.
- 35 34. An alkaline earth alkylarylsulfonate of claim 12 wherein the alkyl chain is derived from an olefin that has been preisomerized on a fixed bed before alkylation.
35. An alkaline earth alkylarylsulfonate of claim 14 wherein the alkyl chain is derived



from an olefin that has been preisomerized on a fixed bed before alkylation.

- 5 36. An alkaline earth alkylarylsulfonate as claimed in any of claims 16 to 28 wherein the alkyl chain is derived from an olefin that has been preisomerized on a fixed bed before alkylation.
37. A lubricating oil formulation containing the alkaline earth alkylaryl sulfonate as claimed in any of claims 1 to 8.
- 10 38. A lubricating oil formulation containing the alkaline earth alkylaryl sulfonate of claim 9.
39. A lubricating oil formulation containing the alkaline earth alkylaryl sulfonate of claim 12.
- 15 40. A lubricating oil formulation containing the alkaline earth alkylaryl sulfonate of claim 14.
41. A lubricating oil formulation containing the alkaline earth alkylaryl sulfonate as claimed in any of claims 16 to 28.
- 20 42. A lubricating oil composition comprising the product produced by blending:
- (a) a major amount of a base oil of lubricating viscosity;
 - (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate as claimed in any of claims 1 to 8;
 - (c) from 0 to 20% of at least one ashless dispersant;
 - (d) from 0 to 5% of at least one zinc dithiophosphate;
 - (e) from 0 to 10% of at least one oxidation inhibitor;
 - (f) from 0 to 1% of at least one foam inhibitor; and
 - (g) from 0 to 20% of at least one viscosity index improver.
- 25 43. A lubricating oil composition comprising the product produced by blending:
- (a) a major amount of a base oil of lubricating viscosity;
 - (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate of claim 9;
 - (c) from 0 to 20% of at least one ashless dispersant;
 - (d) from 0 to 5% of at least one zinc dithiophosphate;
- 35



- (e) from 0 to 10% of at least one oxidation inhibitor;
 - (f) from 0 to 1% of at least one foam inhibitor; and
 - (g) from 0 to 20% of at least one viscosity index improver.
- 5 44. A lubricating oil composition comprising the product produced by blending:
- (a) a major amount of a base oil of lubricating viscosity;
 - (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate of claim 12;
 - (c) from 0 to 20% of at least one ashless dispersant;
 - 10 (d) from 0 to 5% of at least one zinc dithiophosphate;
 - (e) from 0 to 10% of at least one oxidation inhibitor;
 - (f) from 0 to 1% of at least one foam inhibitor; and
 - (g) from 0 to 20% of at least one viscosity index improver.
- 15 45. A lubricating oil composition comprising the product produced by blending:
- (a) a major amount of a base oil of lubricating viscosity;
 - (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate of claim 14;
 - (c) from 0 to 20% of at least one ashless dispersant;
 - 20 (d) from 0 to 5% of at least one zinc dithiophosphate;
 - (e) from 0 to 10% of at least one oxidation inhibitor;
 - (f) from 0 to 1% of at least one foam inhibitor; and
 - (g) from 0 to 20% of at least one viscosity index improver.
- 25 46. A lubricating oil composition comprising the product produced by blending:
- (a) a major amount of a base oil of lubricating viscosity;
 - (b) from 0.5 to 40% of a detergent comprising the alkaline earth alkylaryl sulfonate as claimed in any of claims 16 to 28;
 - (c) from 0 to 20% of at least one ashless dispersant;
 - 30 (d) from 0 to 5% of at least one zinc dithiophosphate;
 - (e) from 0 to 10% of at least one oxidation inhibitor;
 - (f) from 0 to 1% of at least one foam inhibitor; and
 - (g) from 0 to 20% of at least one viscosity index improver.
- 35 47. A concentrate comprising from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate as claimed in any of claims 1 to 8 and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said



sulfonate.

5 48. A concentrate comprising from about from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate of claim 9 and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said sulfonate.

10 49. A concentrate comprising from about from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate of claim 12 and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said sulfonate.

50. A concentrate comprising from about from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate of claim 14 and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said sulfonate.

15 51. A concentrate comprising from about from about 0.5 weight % to 90 weight % of the alkaline earth alkylaryl sulfonate of any of claims 16 to 28 and from about 10 weight % to 90 weight % of a organic liquid diluent compatible with said sulfonate.

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