

Mixture of alkylaryl sulphonates of alkaline earth metals, its use as an additive for lubricating oils and preparation processes

5 The present invention relates to a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metals, its application as detergent-dispersant additives for lubricating oils, and processes for preparing said mixture.

10 In the prior art, processes are already known for preparing weakly or strongly superalkalinized sulphonates from sulphonic acids obtained by the sulphonation of different alkylaryl hydrocarbons and from an excess of alkaline earth base.

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

- 15 – 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.

20 However, while it is easy to obtain a good dispersion in the medium of the alkaline earth base not fixed in the form of a salt if the sulphonic acid is derived from a hydrocarbon obtained by alkylation of an aryl hydrocarbon with a branched olefin, this is not the case if said alkylation is carried out with a linear olefin, particularly containing at least 80 mol % of linear mono alpha olefin, due to the formation of a skin in the open air.

25 This poor dispersion is especially pronounced if the medium contains a high proportion of sulphonate, i.e. if it corresponds, according to Standard ASTM D-2.896, to a low base number BN (namely between 3 and 60), hence to a low content of free lime and the absence of carbon dioxide and carbonate.

30 In fact, during the alkylation reaction with benzene or another aromatic or aryl hydrocarbon, the molar proportion of the corresponding cyclic

hydrocarbon group in position 1 or 2 of the initial linear olefinic chain is about 25%.

Now, this high proportion of alkylaryl hydrocarbon having an aryl radical in position 1 or 2 of the linear alkyl chain results in a sulphonate which, when it is prepared by the process described, for example in French Patent No. 2,564,830 to the company Orogil, the former name of the Applicant, exhibits hygroscopic properties such that a superficial "skin" is formed, making this product unacceptable as an additive for lubricating oils.

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 deterioration of anti-rust performance, and an undesirable turbid appearance, or even sedimentation, when the sulphonate 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 analyses in order to identify each of the 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 alkylaryl sulphonates of alkaline earth metals obtained from these different isomers.

The Applicant has thus discovered that he could overcome the aforementioned drawbacks, inasmuch as the molar proportion of aryl hydrocarbon, other than benzene, fixed to the carbon atoms situated in position 1 or 2 of the linear alkyl chain was between 0 and 13%, preferably between 5 and 11%, and more particularly between 7 and 10%.

And this discovery was the subject of a French Patent Application filed on 8th March 1995 under No. 95 02709 by the Applicant.

Yet the Applicant had not succeeded in obtaining satisfactory results when the aryl hydrocarbon was benzene, because, heretofore, it had never been able to prevent the formation of the skin with the use of this aromatic hydrocarbon, even if said hydrocarbon was alkylated with a very long chain linear mono olefin on the carbon atom situated in position 1 or 2 of said

chain in a molar proportion of between 0 and 13%, and preferably between 5 and 11%, and more particularly between 7 and 10%.

As a result of more intensive studies, the Applicant has now discovered that the aforementioned drawbacks could be overcome by using a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metals comprising:

(a) at least 50% and not more than 85% by weight of a monoalkyl phenyl sulphonate in which the mono alkyl substituent is a linear chain, containing between 14 and 40 carbon atoms, and the phenyl sulphonate radical of the alkaline earth metal is fixed, in a molar proportion of between 0 and 13%, preferably between 5 and 11%, and more particularly between 7 and 10%, in position 1 or 2 of the linear alkyl chain, and

(b) at least 15% and not more than 50% by weight of a heavy alkylaryl sulphonate selected from:

(i) the dialkylaryl sulphonates wherein the aryl radical may be a phenyl radical substituted or not, such as in particular the phenyl, tolyl, xylyl, ethylphenyl and cumenyl radicals, and wherein the two alkyl substituents are both linear alkyl chains, of which the sum of the carbon atoms is between 16 and 40, and preferably between 18 and 40 carbon atoms, or

(ii) the mono- or poly-alkylaryl sulphonates wherein the aryl radical may be a phenyl radical substituted or not, such as in particular the phenyl, tolyl, xylyl, ethyl phenyl and cumenyl radicals, and wherein the alkyl substituent or substituents are branched chains, wherein the sum of the carbon atoms is on average between at least 15 and up to 48 carbon atoms.

said mixture of alkylaryl sulphonates having a maximum molar content of 10%, and preferably less than or equal to 8% of linear mono alkyl phenyl sulphonate, wherein the phenyl sulphonate radical is substituted in position 1 or 2 of the linear alkyl chain.

The mixtures of the invention preferably contain between 75 and 85% by weight of mono-alkyl phenyl sulphonate, as defined in (a) above and between 15 and 25% by weight of heavy alkylaryl sulphonate as defined in (b)

(i) or (b) (ii) above with, for the mixture, the same maximum content of mono-alkyl sulphonate substituted in position 1 or 2.

In fact, said mixtures exhibit a set of properties of solubility in the lubricating oil, filtration rate, viscosity, dispersion of impurities (carbonaceous particles), incorporation of alkaline earth metal in the medium, anti-rust properties, an absence of turbidity, and an absence or delay of the formation of a superficial skin, which makes them particularly attractive as detergent-dispersant additives in this type of oil.

This result is especially surprising since the use of a (linear) mono alkyl phenyl sulphonate, as defined in (a) above, i.e., obtained by alkylation of benzene with a linear olefin containing at least 80 mol % of linear mono-alpha olefin, having a low base number BN (i.e. between 3 and 60), had never heretofore been used to obtain the set of properties necessary for their use as detergent-dispersant additives for lubricating oils.

The first of the two ingredients in the composition of the mixtures which are the subject of the present invention, in a preponderant proportion with respect to the second, is a mono alkyl phenyl sulphonate, wherein the linear mono-alkyl substituent, derived from a linear olefin, as previously defined, must be substituted by the phenyl sulphonate radical in a certain proportion in position 1 or 2 of the linear alkyl chain.

The content of 13% is the threshold above which it is no longer possible to obtain an ingredient which can be used to obtain a mixture exhibiting a suitable improvement of the different properties listed hereinabove.

The content of 11% is the upper limit of the ingredient prepared on an industrial scale, and for which an attempt is made to obtain a mixture exhibiting all of the aforementioned properties.

And the content of 10% is the value desired for the industrial production of the additive used in the composition of the mixture which is the subject of the present invention.

Without wishing to be bound by any particular scientific explanation, it is assumed that the more the phenyl radical is fixed to a carbon

atom situated in a position far from the ends of the hydrocarbon chain of the linear olefin, the more pronounced is the hydrophobic character of the corresponding alkyl phenyl hydrocarbon, thereby bringing about the good properties of the mixtures of alkyl phenyl sulphonates according to the invention.

However, the hydrophobic character of this alkyl phenyl hydrocarbon is not sufficient to confer on the corresponding sulphonate properties making it suitable as a detergent-dispersant additive for lubricating oil.

To achieve this, it is in fact necessary to add to it, according to the invention, another heavy alkylaryl sulphonate in a minimum proportion of 15% and a maximum proportion of 50%, and preferably between 15 and 25% by weight, with respect to the mixture of sulphonates.

As described hereinabove, this heavy alkylaryl sulphonate can be of two types.

It can be a dialkylaryl sulphonate, wherein the aryl radical is a phenyl radical that is substituted or not, such as in particular the phenyl, tolyl, xylyl, ethylphenyl or cumenyl, and wherein each of the two alkyl groups is derived from a linear olefin which can contain at least 80 mol % of linear mono-alpha olefin and the sum of the carbon atoms in these two linear alkyl groups is between 16 and 40, and preferably between 18 and 40 carbon atoms.

These heavy dialkylaryl sulphonates can be obtained in several ways.

A first multi-stage process consists in first effecting the synthesis of the corresponding mono-alkylaryl hydrocarbon wherein the linear mono alkyl radical has the shortest chain length of carbon atoms, followed by the alkylation of this hydrocarbon by a linear olefin containing at least a number of carbon atoms which is sufficient to satisfy the ranges indicated hereinabove.

A second process consists of a direct alkylation of an aromatic carbide by a mixture of linear alpha olefins from C₈ to C₄₀ in an aromatic carbide/olefin mole ratio close to 0.5, in order to obtain a dialkylaryl

hydrocarbon wherein the sum of the carbon atoms of the two linear alkyl chains satisfies the aforementioned definition.

The heavy dialkyl phenyl sulphonates can also be products marketed under the name of 'LAB Bottoms': these are heavy by-products
5 obtained in the production of C₁₂ linear alkyl benzenes, routinely used in household detergents after sulphonation and caustic neutralization. During its production, the C₁₂ linear alkyl benzene is separated by distillation, and the heavy fraction, called 'LAB Bottoms', mainly consists of dialkyl benzenes substituted in the *para* and *meta* positions and, in a smaller proportion, of
10 certain heavy mono-alkyl benzenes, resulting from the oligo-polymerization of the initial linear olefin.

The other type of heavy alkylaryl sulphonate used in the mixtures according to the invention is a mono- or poly-alkylaryl sulphonate, wherein the alkyl substituent or substituents are no longer, as in the aforementioned
15 ingredients, a linear chain, i.e. derived from the oligo-polymerization of ethylene, but branched chains, i.e. derived from the oligo-polymerization of propylene, and wherein the sum of the carbon atoms is on average at least 15 and up to 48 carbon atoms.

These branched heavy mono- or poly-alkylaryl sulphonates can
20 be obtained by the alkylation of an aromatic hydrocarbon by a heavy hydrocarbon from propylene, on average C₁₅ to C₂₁, generally obtained as a by-product in the production of the propylene tetramer.

Such an alkylation reaction can be carried out in two ways:

- either in a single alkylation reactor, where a large molar excess
25 of aromatic carbide is used with respect to the olefin, routinely up to 10:1 and, after distillation of the aromatic carbide and the unreacted olefin and the alkylates whereof the alkyl portion comprises less than 13 carbon atoms or less, a heavy mono- or poly-alkylaryl product is obtained, which can be directly sulphonated and converted to the sulphonate,
30
- or in two reactors in series, where, in the first, a slight molar excess of aromatic carbide is used with respect to the olefin, at most 1.5, and,

in the second, a larger excess of at least 2, and preferably 5, with the aim of increasing the molecular weight of the alkylates, and which results in a complex mixture of heavy mono-alkyl aromatics and poly-alkyl aromatics, due to the fragmentation and oligo-polymerization of the branched olefin used in the
5 alkylation reaction.

The branched mono or poly alkyl benzenes can also be heavy by-products obtained in the production of dodecyl benzene, marketed under the name of BAB, which is an abbreviation corresponding to 'Branched Alkyl Benzene'. During the production of this product, a large molar excess of
10 benzene is alkylated by propylene tetramer and the heavy by-product is the one that remains at the bottom of the column during the distillation of dodecyl benzene at the top. This heavy by-product is essentially composed of a heavy mono-alkyl benzene wherein the number of carbon atoms in the branched alkyl chain is greater than or equal to 13, and of *para* and *meta* dialkyl benzenes.
15 By way of information, the molecular weight of dodecyl benzene is 242, whereas that of the heavy by-product, obtained during its production, can range between 300 and 390.

The different alkylation reactions described hereinabove are effected conventionally with Friedel and Craft catalysts, such as HF and $AlCl_3$,
20 for example.

The Applicant has discovered that mixtures of alkylaryl sulphonates according to the present invention were not subject to the formation of a superficial skin, during storage at ambient temperature, if their molar content of mono-alkylphenyl sulphonate wherein the phenyl sulphonate
25 substituent substituted in position 1 or 2 on the linear alkyl radical is lower than 10% and preferably equal to or less than 8%.

The limit of 10% is the threshold above which the formation of a skin appears within a period of less than 48 hours after storage, making the mixture difficult to use as an additive for lubricants.

30 By contrast, the maximum limit of 8% corresponds to mixtures for which the formation of a superficial skin only occurs after a storage time of

several days, indeed one or several weeks, making them suitable as detergents-dispersants for lubricating oils.

Without wishing to be bound by any specific scientific explanation, the Applicant assumes that the presence of a phenyl sulphonate substituent in position 1 or 2 of a linear alkyl group absorbs the water in particular, and this water absorption brings about the undesirable formation of a superficial skin during storage of the mixture containing it in the open air.

A further aim of the invention is processes for preparing such a mixture of alkylaryl sulphonates.

10 A first process according to the invention comprises the mixing of the corresponding alkylaryl hydrocarbons, the sulphonation of this mixture, and the reaction of the resulting sulphonic acids with excess of alkaline earth base.

A second process according to the invention comprises the separate preparation of each of the two alkylaryl sulphonic acids, their mixing and their reaction with an excess of alkaline earth base.

A third process according to the invention consists of separately preparing each of the alkylaryl sulphonates used in the composition of the mixtures and their mixing in the requisite proportions.

The first process is preferred because the sulphonates obtained exhibit better solubility in lubricating oils than the sulphonates obtained by the other two processes.

To prepare the first alkylphenyl sulphonate which is used in preponderant proportions in the mixtures according to the invention, benzene is first alkylated by a linear olefin according to the Friedel and Craft reaction.

25 This alkylation reaction can be carried out either directly with a linear mono-olefin, already isomerized, containing a molar proportion between 0 and 13%, preferably between 5 and 11%, and more particularly between 7 and 10% of alpha olefin.

It can also be carried out, if one starts with a linear alpha-olefin which is not first isomerized, i.e. containing a conventional molar proportion of about 80% of alpha olefin, by splitting the alkylation reaction into two stages,

namely a first stage wherein the molar ratio between the benzene and the linear mono-olefin is a maximum of 1.5 and preferably 1, and a second stage, wherein said ratio is at least 2 and preferably 5.

In either of the alkylation processes according to the Friedel and Craft reaction, an alkylphenyl hydrocarbon is obtained, exhibiting the desired molar proportion of phenylated isomers in position 1 or 2 of the linear alkyl chain.

The catalyst used for the Friedel and Craft reaction is preferably selected from hydrofluoric acid, aluminium chloride, boron fluoride, a sulphonic ion exchange resin, and an acid-activated clay.

The conditions of this alkylation reaction depend on the type of Friedel and Craft catalyst used.

If the catalyst is hydrofluoric acid, the temperature is preferably between 20 and 70° C and the pressure between atmospheric pressure and 10×10^5 Pa.

If the catalyst is aluminium chloride or boron fluoride, these conditions are the ones described in the literature concerning this reaction.

Finally, if a solid Friedel and Craft catalyst is used, such as a sulphonic ion exchange resin or an acid-activated clay, the temperature of the alkylation reaction is between 40 and 250° C, and the pressure is between atmospheric pressure and 15×10^5 Pa.

Although the Applicant does not wish to be bound by any specific explanation, it would appear that the maintenance, at the onset of the alkylation reaction, of a molar ratio of benzene to linear mono-alpha olefin of a maximum of 1.5 and preferably 1, in the presence of a Friedel and Craft catalyst, causes the migration of the double bond of the linear olefin from the terminal alpha position to a more central position of the olefin, where the phenyl radical is fixed.

It is presumed that the alpha-olefin reacts with the Friedel and Craft catalyst to form an intermediate carbonium ion, which is isomerized, even more easily if the relative proportion of alpha olefin is higher.

The alkylation of this carbonium ion takes place by an aromatic electrophilic substitution reaction, wherein a hydrogen atom of the benzene is substituted by a carbon atom from the linear olefinic chain.

5 This isomerization reaction is unexpected because, heretofore, the alkylation reaction, which is highly exothermic, was always effected with a large molar excess of benzene with respect to the initial linear olefin.

However, it must be observed that this first isomerization stage must be followed by a second stage, during which the molar proportion of benzene is 2 and preferably 5 times greater than that of the initial linear olefin,
10 for the purpose of decreasing the proportion of unreacted olefin and accordingly increasing the conversion rate of the initial linear olefin to the alkylate up to a rate close to 100%.

Within the scope of the present description, the term radical or linear alkyl substituent or linear olefin means a radical or an olefin or a mixture
15 of radicals or straight-chain olefins, which can be obtained by oligo-polymerization of ethylene, and which contain between 14 and 40, preferably between 16 and 30, and more particularly between 20 and 24 carbon atoms, and wherein the molar proportion of mono-alpha olefin is at least 80%.

Specific examples of linear olefins corresponding to this definition
20 are provided by C₁₆ and C₁₈ olefins, C₁₄ to C₁₆, C₁₄ to C₁₈, C₁₆ to C₁₈ and C₂₀ to C₂₄ olefin cuts, or by combinations of several of these.

The C₁₄ to C₄₀ linear mono-alpha olefins which can be obtained by direct oligo-polymerization of ethylene, have an infrared absorption spectrum which exhibits an absorption peak at 908 cm⁻¹, characteristic of the presence of
25 an ethylene double bond at the end of the chain, on the carbon atoms occupying positions 1 and 2 of the olefin; also distinguished therein are two other absorption peaks at wavelengths of 991 and 1641 cm⁻¹.

By contrast, the isomerized C₁₄ to C₄₀ linear mono-olefins, i.e. wherein the molar proportion of alpha-olefin is between 0 and 13%, preferably
30 between 5 and 11%, and more particularly between 7 and 10%, have an infrared absorption spectrum which exhibits no significant peak in the regions

of 908, 991 and 1641 cm^{-1} , but which, on the contrary, display the appearance of an absorption peak at 966 cm^{-1} , characteristic of a *trans* internal ethylene double bond.

5 These isomerized mono olefins can be obtained by the heating, under atmospheric pressure and at a temperature of about 120° C for a period of 144 hours, of a cut of C_{20} to C_{24} linear mono-alpha-olefins, obtained directly by polymerization of ethylene, on a catalyst based on iron pentacarbonyl, for example as described in the Patent US-A-5,320,762.

10 Figures 1 and 2 appended illustrate this difference, by showing the infrared spectra of a cut of C_{20} to C_{24} linear mono-alpha-olefins, obtained directly by polymerization of ethylene, in Figure 1 (reference: none, solvent: none, concentration: 100%, thickness: 0.05, number of scans: 16), and, after the isomerization of this cut, by passage over an iron pentacarbonyl catalyst, to reduce its molar content of alpha-olefin to less than 10%, in Figure 2
15 (reference: none, solvent: none, concentration: 100%, thickness: 0.05, number of scans: 16).

The aromatic hydrocarbon with which these linear olefins are reacted is exclusively benzene, to the exclusion of any other benzene hydrocarbon, particularly to the exclusion of any alkyl derivative of benzene
20 wherein the aromatic ring is substituted by one or two C_1 to C_5 alkyl radicals.

The alkylation reaction according to the Friedel and Craft reaction to obtain the alkylphenyl hydrocarbon corresponding to the first sulphonate of the mixture according to the present invention can be effected in two stages, as described hereinabove, by a continuous reaction in two successive reactors in
25 the presence of the catalyst.

In the first reactor, the molar proportion of benzene with respect to the linear olefin is a maximum of 1.5, and preferably 1.2, and more particularly 1, to slow down the alkylation reaction and to promote the isomerization of the initial linear mono-alpha-olefin by migration of its double bond to the middle of
30 the hydrocarbon chain of the olefin.

In the second reactor, the molar proportion of benzene with

respect to the linear mono-alpha-olefin is increased to at least 2:1, and preferably 5:1 or more, to complete the alkylation reaction.

On completion of the successive passage through the two reactors, the Friedel and Craft catalyst is collected by phase separation, and
5 the excess benzene is recovered by distillation, as in the processes of the prior art.

The same alkylphenyl hydrocarbon can also be obtained by separately effecting the isomerization of the initial alpha-olefin and then by adding the benzene to effect the catalytic alkylation reaction, using a Friedel
10 and Craft catalyst.

The alkylation reaction according to the Friedel and Craft reaction to obtain the heavy alkylaryl hydrocarbon corresponding to the second sulphonate of the mixture of the present invention is either a dialkylaryl obtained by the recovery at the bottom of the column of products of the reaction
15 of an aromatic hydrocarbon with a linear mono-alpha-olefin wherein the sum of the carbon atoms of the two mono-alkyl substituents is between 16 and 40, and preferably between 18 and 40 carbon atoms, or a mono- or poly-alkylaryl recovered at the bottom of the column, during the distillation of the alkylation reaction products of an aromatic hydrocarbon with a branched olefin wherein
20 the sum of the carbon atoms present in the different branched alkyl substituents is on average at least 15 carbon atoms.

The next stage of the sulphonation of each of the alkyl aromatic hydrocarbons or of the mixture of the different alkyl aromatic hydrocarbons corresponding to the mixture according to the invention is effected by
25 processes known per se, for example by reacting the product of the alkylation stage, with concentrated sulphuric acid, with an oleum, with sulphur trioxide diluted in nitrogen or air, or with sulphur trioxide dissolved in sulphur dioxide. This sulphonation reaction can also be effected by contacting the ingredients (alkylate and sulphur trioxide) in the form of a falling film in streams of the same
30 or opposite directions. After sulphonation, the acid or the different sulphonic acids obtained can be purified by conventional processes, such as washing

with water or by thermal treatment under agitation by nitrogen bubbling (see, for example, the technique described in the French Patent No. 93 11709 to the Applicant).

5 The next stage of the sulphonic acid or acids with an excess of alkaline earth base can be effected by the addition of an oxide or a hydroxide of alkaline earth metal, such as magnesium, calcium, barium, and particularly lime.

10 This neutralization stage is carried out in a dilution oil with an alcohol with a boiling point higher than 80° C and preferably with a carboxylic acid containing 1 to 4 carbon atoms, in the presence of water, as described in particular in aforementioned French Patent Application No. 2,564,830.

Among the alcohols with boiling points higher than 80° C, linear or branched aliphatic mono-alcohols are preferably selected, containing 4 to 10 carbon atoms, such as isobutanol, 2-ethyl hexanol and C₈ to C₁₀ oxo alcohols.

15 Among the carboxylic acids which can be used are preferably formic acid, acetic acid and their mixtures.

Among the dilution oils which are suitable for the neutralization stage, are the paraffinic oils such as 100 Neutral oil, as well as naphthenic or mixed oils.

20 After the water and alcohol are eliminated, the solid matter is removed by filtration, and the alkylaryl sulphonate or sulphonates of alkaline earth metal obtained are collected.

25 If the corresponding alkylaryl hydrocarbons or the corresponding sulphonic acids have not already been mixed, the alkylaryl sulphonates can be mixed at this stage to obtain the mixtures of the invention in the desired proportions.

30 The mixtures of alkylaryl sulphonates according to the invention are preferably weakly superalkalinized, i.e. their base number BN, measured according to Standard ASTM-D-2896, can range from 3 to 60, and they can be used in particular as detergent-dispersant agents for lubricating oils.

The mixtures of alkylaryl sulphonates of the invention are

particularly advantageous if their base number is low and corresponds to a range of BN between 10 and 40.

It should be noted that this is the first time that it is possible to use alkyl phenyl sulphonates having such a base number, namely between 3 and 60, and preferably between 10 and 40, and obtained exclusively by the alkylation of benzene, as detergent-dispersant additives for lubricating oil exhibiting satisfactory properties, and without the need to add calcium chloride or ammonium chloride to lower the viscosity.

In particular, the mixtures of alkylaryl sulphonates according to the present invention, wherein the proportion of (linear) mono-alkylphenyl sulphonate (constituent (a) defined hereinabove) is between 50 and 75% by weight, require no addition of chloride ions, particularly in the form of calcium chloride or ammonium chloride, to satisfy all the properties hereinabove listed, to serve as detergent-dispersant additives for lubricating oils.

This is not the case for the same mixtures containing 75 to 85% by weight of said (linear) mono-alkylphenyl sulphonate, for which it is preferable to add chlorine ions.

In fact, heretofore, only alkylaryl sulphonates derived from the alkylation of aryl hydrocarbons other than benzene or alkylaryl sulphonates derived from alkylation by branched olefins were considered as necessary to exhibit all the properties making them suitable as detergent-dispersant additives for lubricating oil.

The mixture of alkylaryl sulphonates according to the invention can be added to the lubricating oils in proportions ranging from 1 to 15% by weight depending on the nature of the lubricating oil.

For example, for a petrol engine oil, up to 1.7% by weight can be added; for a diesel engine oil or marine engine oil, up to 3.5% by weight can be added, and for a protection oil for a new car, up to 11.5% by weight can be added.

The lubricating oils to which the mixtures according to the present invention can be added can be lubricating oils with a naphthenic, paraffinic or

mixed base; they can consist of mineral oils or may be derived from coal distillation products, or they may consist of synthetic oils, such as polymers of alkylenes or esters of inorganic acids or carboxylic acids.

5 The present invention will now be described with the help of the following examples which are merely intended to illustrate the particular embodiments of the different aspects of the invention.

These examples contain a number of test results, obtained by the following processes of measurement.

Viscosity at 100° C in cSt

10 The viscosity is measured at the temperature of 100° C after dilution of the product sample to be measured in 100 N oil, until a solution is obtained having a total calcium content of 2.35% by weight. If the product to be measured has a total calcium content lower than 2.35% by weight, the viscosity is measured without dilution, following process ASTM D-445.

15 Compatibility

This process is aimed at evaluating the appearance and the storage stability of the additives and the corresponding oils containing them.

This process is applicable to additives for lubricants.

20 An additive is prepared based on monosuccinimide and zinc dithiophosphate, and containing about 75% by weight of the mixture of sulphonates to be tested, an additive which is placed in a 350 Neutral oil base stock. The appearance of the solution is examined after 30 days at ambient temperature.

25 The appearance of the product is evaluated before and after storage, and the results are qualified as 'GOOD' or 'POOR' according to whether or not a single phase is maintained without any deposition by sedimentation.

DISPERSION (SPOT TEST)

30 This process is aimed at evaluating the dispersive properties of an oil or of an additive, and to predict its performance level (deposits, sludge) in comparison with a reference oil.

It is generally applicable to land and marine engine oils.

According to this process, the dispersive power of the oil is obtained by carrying out a paper chromatography of a mixture of oil to be tested and of artificial sludge under the following conditions.

- 5 Spot No. 1: ambient temperature without water.
- Spot No. 2: 10 min at 200° C without water.
- Spot No. 3: 10 min at 250° C without water.
- Spot No. 4: ambient temperature with water.
- Spot No. 5: 1 min at 200° C with water.
- 10 Spot No. 6: 10 min at 200° C with water.

The spots are observed after 48 hours of rest, manually or using a CCD photometer.

- On each spot, a measurement is taken of the diameter (d) of diffusion of the mixture and the diameter (D) of diffusion of the oil alone and the
- 15 ratio $d/D \times 100$ is calculated.

The dispersive power of the oil is determined by comparing the sum of the six spots to the value found on one of the reference oils which must be tested in the same series of measurements.

- The addition of the ratios $d/D \times 100$ under the six conditions
- 20 hereinabove listed corresponds to a maximum dispersive power of 600, corresponding to an ideal dispersion of 100% under all conditions. In the results of this test, the higher the figure, the better the dispersant power of the oil.

EXAMPLES 1 to 10

- 25 (a) Synthesis of the alkylate

- The alkylate is synthesized in an alkylation pilot plant with hydrofluoric acid, which is constituted by two reactors in series of 1.126 litres each, and a 15 litre settler wherein the organic phase is separated from the phase containing the hydrofluoric acid, all of this equipment being maintained
- 30 under a pressure of about 4×10^5 Pa.

The organic phase is then withdrawn via a valve, and expanded to

atmospheric pressure, then the benzene is removed by topping, i.e. heating to 160° C at atmospheric pressure.

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

5 The variables of the alkylation reaction are as follows.

(i) reaction carried out in one or two reactors:

– if only one reactor is used, the benzene/olefin molar ratio is 10, which is very high, and the second reactor is by-passed,

– if two reactors are used, the benzene/olefin molar ratio is relatively low in the first reactor, about 1 to 1.5, and it is higher in the second reactor, about 2 to 10: furthermore, the ratio of hydrofluoric acid to the olefin by volume is 1 in the first reactor and 2 in the second.

(b) Distillation of the alkylate

15 If benzene is alkylated by a C₂₀ to C₂₄ linear olefin, there is no formation of a light fraction, i.e. of alkyl benzene, wherein the alkyl radical is lower than C₁₃; hence it is sufficient to effect a topping of the unreacted benzene in order to obtain the corresponding alkylate.

In all other cases, a light fraction is produced during the catalytic alkylation reaction, and this light fraction must be eliminated, just like the excess benzene, on a vacuum distillation column; light fraction means any alkyl benzene having an alkyl chain lower than C₁₃; to eliminate such a light fraction, the final distillation conditions are as follows:

- temperature at top of column: 262° C,
- temperature at bottom of column: 302° C,
- 25 – pressure: 187 x 10² Pa (187 mbar).

(c) Sulphonation of the alkylate

Sulphonation is effected directly on the mixture of the two alkylates of the present invention, wherein the molar proportion of the phenyl radical substituted on the carbon atoms in position 1 or 2 of the alkyl radical is determined with respect to the overall mixture of alkylates subjected to the sulphonation reaction.

This reaction is effected using sulphur trioxide SO_3 , produced by the passage of a mixture of oxygen and sulphur dioxide SO_2 through a catalytic furnace containing vanadium oxide V_2O_5 .

The gas thus produced is introduced at the top of a sulphonation
5 reactor 2 m long and 1 cm in diameter, in a cocurrent alkylate stream.

The resulting sulphonic acid is recovered at the bottom of the reactor. The sulphonation conditions are as follows:

- SO_3 flow rate set at 76 g/h,
- alkylate flow rate between 350 and 450 g/h, depending on the
10 desired SO_3 /alkylate molar ratio which varies from 0.8 to 1.2,
- sulphonation temperature between 50 and 60° C,
- and with nitrogen as vector gas to dilute the SO_3 to 4% by volume.

After the sulphonation reaction, the residual sulphuric acid is
15 removed by thermal treatment after dilution by 10% 100 N oil, nitrogen bubbling through at the rate of 10 l/h per kg of product, and agitation at 85° C, until a lower residual H_2SO_4 content is obtained (maximum 0.5% by weight).

The analyses given in the table below relative to the embodiments of the present invention correspond to the product obtained after thermal
20 treatment.

(d) Superalkalinization

In this stage, relative molar proportions of $\text{Ca}(\text{OH})_2$ and sulphonic acid obtained in the preceding stage are reacted, in order to obtain a proportion of 37% of lime non-neutralized by the sulphonic acid in the final
25 product. This proportion of 37% of non-neutralized lime makes it possible to obtain a BN of about 20 in the final sulphonate, according to Standard ASTM D-2.896.

To achieve this, a quantity of $\text{Ca}(\text{OH})_2$ is added which does not correspond to the stoichiometric neutralization of the quantity of sulphonic acid
30 reacted, i.e. 0.5 mol of $\text{Ca}(\text{OH})_2$ per mole of this sulphonic acid, but an excess of $\text{Ca}(\text{OH})_2$ is added with respect to this stoichiometric quantity, i.e. a

proportion of 0.73 mol of $\text{Ca}(\text{OH})_2$ per mole of sulphonic acid, to obtain a BN of about 20.

The conditions of the superalkalinization reaction used are those described in the aforementioned French Patent Application No. 2,564,830 of the company OROGIL, the former name of the Applicant, and published on 29 November 1985.

The performance obtained with the alkylaryl sulphonate mixtures according to the invention are summarized in the table given at the end of the present specification.

10 EXAMPLE 1

In this example, 80% by weight of a linear alkylate obtained by the alkylation of benzene by a C_{20} to C_{24} normal alpha-olefin, which is hereinafter called the reference linear product, is mixed with 20% by weight of a heavy branched alkylate, also called 'LAB Bottom', obtained by the alkylation of benzene by the tetramer of propylene, and the removal of the light aromatic fractions (with alkyl chains lower than C_{13}).

Sulphonation is effected on the aforementioned mixture of alkylates.

Example 2

20 80% by weight of reference linear alkylate is mixed with 20% of a heavy alkylate of the linear phenyl dialkyl type obtained as follows:

In a first alkylation reactor, benzene is reacted with a composition of C_8 linear alpha-olefins, in a benzene/olefin molar ratio of 1 and an HF/olefin volume ratio of 1, at a temperature of 45°C and a pressure of $4 \times 10^5 \text{ Pa}$. At the exit of this first reactor, a phenyl hydrocarbon substituted by a single C_8 alkyl radical is principally obtained, which serves as the aryl hydrocarbon to be alkylated in the next reactor.

Said C_8 -substituted mono-alkylphenyl hydrocarbon is transferred to a second alkylation reactor where the same quantity of HF is introduced as in the first reactor as well as C_{18} linear alpha-olefin in the molar proportion of 3 mol of said substituted phenyl hydrocarbon for 1 mol of C_{18} linear alpha-olefin.

After topping the unreacted benzene, all the alkylphenyl products are distilled, in which the sum of the atoms present in the alkyl chain or chains amounts to 18 carbon atoms inclusive. A product is collected at the column bottom, which is principally a linear phenyl dialkyl wherein one of the alkyl substituents is C₈ and the second is C₁₈.

Sulphonation is effected on the aforementioned mixture of alkylates.

EXAMPLE 3

80% by weight of reference linear alkylate is mixed with 20% by weight of a branched heavy alkylate obtained as follows:

In a first reactor, benzene is catalytically alkylated by propylene tetramer with a benzene/propylene tetramer molar ratio of 1.2 and an HF/propylene tetramer ratio of 1 by volume.

The product thus obtained is transferred to a second reactor to which hydrofluoric acid and benzene are added in the following proportions:

- aromatic/propylene tetramer: 5.8 in mol,
- HF/propylene tetramer: 1 in volume.

The benzene and alkylates wherein the length of the branched alkyl chain is lower than or equal to C₁₂ are removed by distillation.

Sulphonation is effected on the mixture of alkylates comprising, as hereinabove described, 80% of reference linear alkylate and 20% of said branched heavy alkylate thus prepared.

EXAMPLE 4

Sulphonation is effected on the following mixture of alkylates:

- 80% by weight of reference linear alkylate,
- and 20% by weight of branched alkylate derived from the catalytic alkylation reaction of benzene with an average C₁₅ to C₁₈ oleofinic composition, obtained in the production of propylene tetramer with a single reactor, after topping the benzene and removal by distillation of the light fractions corresponding to an alkyl chain lower than C₁₃.

EXAMPLE 5

Sulphonation is effected on the following mixture of alkylates:

- 80% by weight of reference linear alkylate,
- and 20% by weight of branched alkylate derived from the

5 catalytic alkylation reaction of benzene with an average C₁₇ to C₁₈ oleofinic composition, obtained in the production of propylene tetramer with two alkylation reactors in series, the alkylation conditions of which are given in the table below.

10 In comparison with Example 4, two differences exist, intended to promote the increase of the molecular weight: the first is a longer aliphatic chain, C₁₇ to C₁₈ instead of C₁₅ to C₁₈ of Example 4, and the second is a molar excess of benzene with respect to the branched olefin that is lower than in Example 4, namely close to stoichiometry 1.5, in a first reactor to promote, as much as possible, the dimerization of the olefin, either by the formation of two

15 alkyl substituents in the *meta* or *para* position, or by alkylation of the dimer on the benzene. This alkylation reaction in the first reactor is followed by a reaction in a second reactor with a very large molar excess of benzene with respect to the olefin, 10, to complete the alkylation of the aromatic carbide in question.

20

EXAMPLE 6

This example is identical to the preceding example except for the fact that the 20% by weight of branched alkylate with an average C₁₇ to C₁₈ olefin have been obtained with a single catalytic alkylation reactor and a molar

25 ratio of 10 of the benzene to this olefin.

EXAMPLE 7

This example of the invention is identical to Example 5, from which it differs in that the proportions of the alkylate mixture are 50%-50% instead of 80%-20%, as well as the absence of any addition of chloride ions to

30 the corresponding mixture of sulphonates.

EXAMPLE 8

In this example according to the invention, a mixture of 50% of reference linear alkylate and 50% of an alkylate obtained by the alkylation of benzene with a C₁₂ linear olefin is used, in a single reactor with topping of the benzene and elimination of the alkylphenyl hydrocarbons substituted by a single C₁₂ alkyl radical, and the corresponding mixture of sulphonates is analyzed without the addition of chloride ions.

EXAMPLE 9

This example only differs from Example 7 by the addition of chloride ions in the form of calcium chloride;

The results of the tests performed on the corresponding mixtures of sulphonates reveal a compatibility of this mixture in a lubricating oil at the limit of what is acceptable, because a slight turbidity appears during the mixing with the lubricating oil.

This Example 9 demonstrates the advantage of avoiding any addition of chloride ions to the mixtures of sulphonates according to the invention, comprising between 50 and 75% of linear mono-alkylphenyl sulphonate (a) and between 25 and 50% of a heavy alkylaryl sulphonate (b), as hereinbefore defined.

COMPARATIVE EXAMPLE 10

In this example, a single alkylate has been sulphonated, namely the heavy alkylate of the linear phenyl dialkyl type of Example 2.

The alkylation yield is found to be lower and the sulphonate rate has practically decreased by half, the H₂SO₃ content of the sulphonic acid obtained falls from 14.4% in Example 2 to 8.5% in Example 10.

COMPARATIVE EXAMPLE 11

In this example, the sulphonation is effected exclusively on the heavy branched alkylate corresponding to the one used in Example 5 according to the invention.

COMPARATIVE EXAMPLE 12

In this example outside the invention, sulphonation is effected

exclusively on the heavy branched alkylate described in Example 6 according to the invention.

COMPARATIVE EXAMPLE 13

In this example, alkylation is effected exclusively on the reference
5 linear alkylate, used at the rate of 80% by weight in the embodiments 1 to 6 of the present invention.

It may be recalled that, during the preparation of this alkylate, two catalytic alkylation reactions are used in succession:

- a first reactor wherein the molar ratio of benzene to C₂₀ to C₂₄
10 linear olefin is maintained at 1.2 to slow down the alkylation reaction in order to promote the migration of the double bond of the olefin from the ends to the interior of the chain before alkylation, and thereby to obtain a minimum 1- or 2-phenyl isomer content conforming to the present invention, and wherein the volume ratio of hydrofluoric acid to the olefin is 1, and
- 15 – a second reactor wherein a large excess of benzene is added with respect to the olefin, and wherein hydrofluoric acid is added to obtain a benzene/olefin molar ratio of 5.8 and an HF/olefin volume ratio of 2.

COMPARATIVE EXAMPLE 14

In this example, the sulphonation is effected exclusively on the C₁₅
20 to C₁₈ heavy branched alkylate used in Example 4, in order to determine the influence of the molecular weight.

It may be noted that, as in comparative Example 13, the corresponding sulphonate exhibits a superficial skin which makes it unfit for use as an additive for lubricating oils.

25 COMPARATIVE EXAMPLE 15

This is the same as comparative Example 13 except that a single alkylation reactor is used with a benzene/olefin ratio of 10, which results in an alkylate wherein the molar ratio of the phenyl substituents in positions 1 and 2 to the total phenyl substituents irrespective of position is 0.20 instead of 0.093.

30 The consequences on the corresponding sulphonate are a lower incorporation of lime (BN 14.5 instead of 19.4), a higher viscosity, a lower

filtration rate, and, above all, a quicker appearance of skin with gel formation and poor compatibility, making it unfit as an additive for lubricants.

COMPARATIVE EXAMPLE 16

An attempt was made to use the 80/20 mixture of alkylates containing 80%, not of the reference alkylate used in Examples 1 to 9 according to the invention, but an alkylate obtained with a single alkylation reactor, wherein the benzene/C₂₀ to C₂₄ linear olefin ratio is 10, first resulting in an alkylate having a molar content of 0.20 of substituent in positions 1 and 2. This content, which is lowered to 0.16 in the 80/20 mixture with 20% of a heavy alkylate, did not pass the tests satisfactorily, as shown in particular by the formation of a gel and a superficial skin after one day, and poor compatibility with the lubricating oil; whereas Example 5, starting from the same proportion in an 80/20 mixture but where the linear alkylate had 0.093 molar content in positions 1 and 2, had produced good results.

Dispersion tests, performed according to the spot test, as hereinabove defined, yielded the following results, which are also shown in Figure 3.

Dispersion				Foaming
	Alkylate composition		Spot test on corresponding sulphonates	ASTM D-892 Sequence 1
Example	Benzene/C ₂₀ to C ₂₄	Benzene/C ₁₇ to C ₁₈ propylene tetramer derivative		
13	100%	-	372	0/0
5	80%	20%	369	0/0
9	50%	50%	366	0/0
11	-	100%	337	270/60

It appears from these data that the dispersion is better with a chemical mixture of the sulphonates according to the invention than with a physical mixture of each of the individual sulphonates in the same proportions.

Foaming tests were also carried out following the standard process of ASTM D-892, Sequence 1, wherein the better the figure the better the product.

The results of these tests, which are given above concerning

Examples 5 and 9 according to the invention and the comparative Examples 11 and 13, confirm that, at excessively high contents of branched alkyl benzene (EXAMPLE 11), excessive foaming makes the sulphonate unacceptable as an additive for lubricants, and, on the contrary, at the contents according to the
5 invention (EXAMPLES 5 and 9) the sulphonates do not foam.

TABLE

TEST NO.	1		2		3		4		5		6	
ALKYLATION												
Aromatic	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene
Linear olefin	C20-24		C20-24	C8/C18	C20-24		C20-24		C20-24		C20-24	
Propylene tetramer derivative		C12				C12		C15-18		C17-18		C17-18
ALKYLATION CONDITIONS												
Catalyst	HF	HF	HF	HF	HF	HF	HF	HF	HF	HF	HF	HF
REACTOR 1												
Aromatic/olefin (mol)	1.2	10	1.2	1	1.2	1.2	1.2	10	1.2	1.5	1.2	10
REACTOR 2												
Total aromatic/olefin (mol)	5.8		5.8	3	5.8	5.8	5.8		5.8	10	5.8	
CONDITIONS FOR OBTAINING ALKYLATE	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal
ANALYSIS OF ALKYLATE												
<i>position 1 + 2(mol)</i>	0.093		0.093		0.093		0.093		0.093		0.093	
<i>∑ positions</i>												
Viscosity at 40° C (cSt)	17	35	17	25	17	16.5	17	17	17	49	17	27.5
% weight of alkylate	80	20	80	20	80	20	80	20	80	20	80	20
CHARACTERISTICS OF CORRESPONDING MIXTURE OF ALKYLATES, ACIDS AND SULPHONATES												
ANALYSIS OF ALKYLATE												
<i>position 1 + 2(mol)</i>	0.074		0.074		0.074		0.074		0.074		0.074	
<i>∑ positions for the 2 alkylates</i>												
ANALYSIS OF THE ACID												
% HSO ₃ (weight)	12.8		14.4		15.3		15.8		14.5		15.2	
% H ₂ SO ₄ (weight)	0.2		0.3		0.27		0.24		0.17		0.11	
ANALYSIS OF THE SULPHONATE												
With or without CaCl ₂	WITH		WITH		WITH		WITH		WITH		WITH	
% CaT (weight)	2.35		2.6		2.63		2.56		2.56		2.6	
% CaS (weight)	1.6		1.76		1.74		1.8		1.89		1.76	
BN (D2896)	17		19.8		19.7		17.7		17.9		20	
Viscosity at 100°C with 2.35 Ca (cSt)	30		18.4		21.8		80		36		35.5	
% crude sediment (vol)	0.6		0.4		0.6		0.6		0.6		1	
Filtration rate (kg/H/m ²)	1200		3350		240		480		790		1350	
Skin formation in open air	5 days		7 days		1 month		1 month		7 days		7 days	
Compatibility	GOOD		GOOD		GOOD		GOOD		GOOD		GOOD	

TABLE (cont. 1)

TEST NO.	7		8		9	
ALKYLATION						
Aromatic	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene
Linear olefin	C20-24		C20-24	C12	C20-24	
Propylene tetramer derivative		C17-18				C17-18
ALKYLATION CONDITIONS						
Catalyst	HF	HF	HF	HF	HF	HF
REACTOR 1						
Aromatic/olefin (mol)	1.2	1.5	1.2	10	1.2	1.5
REACTOR 2						
Total aromatic/olefin (mol)	5.8	10	5.8		5.8	10
CONDITIONS FOR OBTAINING ALKYLATE	Benzene topping	Bz + lights removal	Benzene topping	Bz + lights removal	Bz + lights removal	Bz + lights removal
ANALYSIS OF ALKYLATE						
$\frac{\text{position 1 + 2(mol)}}{\sum \text{positions}}$	0.093		0.093		0.093	
Viscosity at 40° C (cSt)	17	49	17		17	16.5
% weight of alkylate	50	50	50	50	50	50
CHARACTERISTICS OF CORRESPONDING MIXTURE OF ALKYLATES, ACIDS AND SULPHONATES						
ANALYSIS OF ALKYLATE						
$\frac{\text{position 1 + 2(mol)}}{\sum \text{positions for the 2 alkylates}}$	0.046		0.046		0.046	
ANALYSIS OF THE ACID						
% HSO ₃ (weight)	13.6		13.9		13.9	
% H ₂ SO ₄ (weight)	0.2		0.2		0.2	
ANALYSIS OF THE SULPHONATE						
With or without CaCl ₂	WITHOUT		WITHOUT		WITH	
% CaT (weight)	2.42		2.41		2.7	
% CaS (weight)	1.61		1.72		1.79	
BN (D2896)	18		17		19	
Viscosity at 100°C with 2.35 Ca (cSt)	27		50		22	
% crude sediment (vol)	0.7		0.6		0.4	
Filtration rate (kg/H/m ²)	600		300		600	
Skin formation in open air	over 1 month		2 months		1 month	
Compatibility	GOOD		GOOD		ACCEPTABLE	

TABLE (cont. 2)

TEST NO.	10	11	12	13	14	15	16
ALKYLATION							
Aromatic	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene	Benzene
Linear olefin	C8/C18			C20-24		C20-24	C20-24
Propylene tetramer derivative		C17-18	C17-18		C15-18		C17-18
Catalyst	HF	HF	HF	HF	HF	HF	HF
REACTOR 1							
Aromatic/olefin (mol)	1	1.5	10	1.2	10	10	10
REACTOR 2							
Total aromatic/olefin (mol)	3	10		5.8			10
CONDITIONS FOR OBTAINING ALKYLATE	Bz + lights removal	Bz + lights removal	Bz + lights removal	Benzene topping	Bz + lights removal	Benzene topping	Benzene topping
ANALYSIS OF ALKYLATE							
<i>position 1 + 2(mol)</i> $\sum$ positions				0.093		0.20	0.2
Viscosity at 40° C (cSt)	25	49	27.5	17	17	18	18
% weight of alkylate	100	100	100	100	100	100	80
CHARACTERISTICS OF CORRESPONDING MIXTURE OF ALKYLATES, ACIDS AND SULPHONATES							
ANALYSIS OF ALKYLATE							
<i>position 1 + 2(mol)</i> $\sum$ positions for the 2 alkylates				0.093		0.20	0.16
ANALYSIS OF THE ACID							
% HSO ₃ (weight)	8.5	10.5	15	15.4	17.3	14.6	14.2
% H ₂ SO ₄ (weight)	0.3	0.35	0.1	0.18	0.1	0.2	0.2
ANALYSIS OF THE SULPHONATE							
With or without CaCl ₂	WITH	WITH	WITH	WITH	WITH	WITH	WITH
% CaT (weight)	2.67	2.66	2.4	2.64	2.59	2.35	2.45
% CaS (weight)	1.74	1.78	1.74	1.83	1.76	1.75	1.71
BN (D2896)	21.9	18	23	19.4	19	14.5	17.2
Viscosity at 100°C with 2.35 Ca (cSt)	22	30	103	46.4	97	100	52
% crude sediment (vol)	0.6	0.12	0.6	0.6	0.6	1.2	0.8
Filtration rate (kg/H/m ²)	15	500	250	710	545	30	208
Skin formation in open air	no skin	3 days	3 days	1 day gel	1 day	10 hours	gel 1 day
Compatibility	POOR	POOR	POOR	POOR	POOR	POOR	POOR



CLAIMS

1. Mixture of alkylaryl sulphonates of superalkalinized alkaline earth metals characterized in that it comprises

- 5 (a) at least 50% and not more than 85% by weight of a mono-alkylphenyl sulphonate in which the mono-alkyl substituent is a linear chain, containing between 14 and 40 carbon atoms, and the phenyl sulphonate radical of the alkaline earth metal is fixed, in a molar proportion of between 0 and 13%, preferably between 5 and 11%, and more particularly between 7 and 10 10%, in position 1 or 2 of the linear alkyl chain, and

(b) at least 15% and not more than 50% by weight of a heavy alkylaryl sulphonate selected from:

- (i) the dialkylaryl sulphonates wherein the aryl radical can be a phenyl radical substituted or not, such as in particular the phenyl, tolyl, xylyl, 15 ethyl phenyl and cumenyl radicals, and wherein the two alkyl substituents are both linear alkyl chains, of which the sum of the carbon atoms is between 16 and 40, and preferably between 18 and 40 carbon atoms, or

- (ii) the mono- or poly-alkylaryl sulphonates wherein the aryl radical can be a phenyl radical substituted or not, such as in particular the 20 phenyl, tolyl, xylyl, ethylphenyl and cumenyl radicals, and wherein the alkyl substituent or substituents are branched chains, wherein the sum of the carbon atoms is on average between at least 15 and up to 48 carbon atoms.

said mixture of alkylaryl sulphonates having a maximum molar content of 10%, and preferably not more than 8% of linear mono-alkylphenyl 25 sulphonate, wherein the phenyl sulphonate radical is substituted in position 1 or 2 of the linear alkyl chain.

2. Mixture according to claim 1 characterized in that it contains between 75 and 85% by weight of mono-alkyl phenyl sulphonates such as defined in (a), and between 15 and 25% by weight of the heavy alkylaryl 30 sulphonate as defined in (b) of said claim 1.

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3. Mixture according to claim 1 or claim 2, characterized in that the linear alkyl chain of the mono-alkyl phenyl sulphonate, as defined in (a) of claim 1, contains between 16 and 30, and more particularly between 20 and 24 carbon atoms.

5 4. Mixture according to claim 1, characterized in that it contains between 50 and 75% by weight of mono-alkyl phenyl sulphonate such as defined in (a), and between 25 and 50% by weight of the heavy alkylaryl sulphonate as defined in (b) of said claim 1, said mixture being free of chloride ions.

10 5. Mixture according to any of claims 1 to 4, characterized in that the base number BN of said mixture, as measured according to Standard ASTM-D-2896, is between 3 and 60, and preferably between 10 and 40.

6. Application of the mixture of alkylaryl sulphonates of superalkalinized alkaline earth metal according to any one of the preceding
15 claims as a detergent-dispersant additive for lubricating oils.

7. Lubricating oil containing a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metal according to any one of claims 1 to 5.

8. Process for preparing a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metal according to any one of claims 1 to 5,
20 characterized by the mixing of the corresponding mono-alkyl phenyl and heavy alkylaryl hydrocarbons, the sulphonation of the mixture of hydrocarbons, and the reaction of the resulting sulphonic acids with an excess of alkaline earth base.

9. Process for preparing a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metal according to any one of claims 1 to 5,
25 characterized by the separate preparation of each of the alkylaryl sulphonic acids, their mixing, and their reaction with an excess of base.

10. Process for preparing a mixture of alkylaryl sulphonates of superalkalinized alkaline earth metal according to any one of claims 1 to 5,
30 characterized by the separate preparation of each of the alkylaryl sulphonates

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entering into the composition of the mixtures and their mixing in the requisite proportions.

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