OIL SOLUBLE ANIONIC SURFACE ACTIVE AGENT

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Related U.S. Application Data


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Field of Search ... 260/513 R, 429.9, 448, 260/501.21, 501.19

References Cited

UNITED STATES PATENTS

FOREIGN PATENTS OR APPLICATIONS
1,072,601 6/1967 United Kingdom ............ 260/513 R

OTHER PUBLICATIONS


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Attorney, Agent, or Firm—Woodhams, Blanchard and Flynn

ABSTRACT

An oil soluble anionic surface active agent consisting essentially of at least one member selected from the group consisting of a sulfonic acid, a sulfonate, and mixtures thereof, of an aliphatic monooolefin having a carbon atom number in the range of 32–40 and expressed by the general formula

\[
\begin{align*}
R & \quad C = C \quad R' \\
R'' & \quad R'''
\end{align*}
\]

(wherein, R is a saturated alkyl radical; R', R'', and R''' are each respectively a member selected from the group consisting of hydrogen and a saturated alkyl radical, providing that said R', R'', and R''' should not all be hydrogen and the total number of carbon atoms of said R, R', R'', and R''' is in the range of 30–38).

2 Claims, No Drawings
1. OIL SOLUBLE ANIONIC SURFACE ACTIVE AGENT
CROSS REFERENCE TO RELATED APPLICATION

This application is a continuation-in-part of Ser. No. 51 323, filed June 30, 1970, now abandoned.

BACKGROUND OF THE INVENTION

a. Field of the invention

The present invention relates to an oil soluble surface active agent which comprises substantially a sulfonic acid or sulfonate of a specific aliphatic monoolesin as an active component thereof.

b. Description of the prior art

As the oil soluble sulfonic-acid type surface active agents produced from petroleum material in the prior art, such substances as, for instance, the salt of mahogany acid, alkybenzene sulfonate, etc., are known, and these surface active agents have been widely used as a dry cleaning detergent, an emulsifier, a dispersant, a lubricant additive, a corrosion inhibitor and as a general cleaning agent.

Among the foregoing substances, the mahogany acid salt consists substantially of alkylaryl sulfonate and it can be obtained as a byproduct on the occasion of the preparation of the sulfonic acid refining of petroleum. But, because it is a substance originating from various hydrocarbons of unknown constitution and containing therein many impurities so as to render its color tone inferior, it must be refined by treatment with active clay or the like.

Accordingly, the qualities of the resultant product, per se, are variable, and particularly when said product is to be used as one constituent of a high quality emulsifier composition, dry cleaning detergent composition, etc., the mixing proportions of other compounding ingredients should be modified on account of the lack of uniformity of said mahogany acid salt produced.

Further, as a disadvantage ascribable to the substance from which it originates, said salt of mahogany acid contains so large a quantity of unsulfonated substances that an express treatment of deoiling by removing the unreacted oil must be carried out in order to increase the mahogany acid salt content thereof, thus increasing the production cost. The conventional commercial manufactures contain mahogany acid salt to the extent of 60–70 percent, and the existence of a relatively large quantity of non-sulfonic acid salt contained therein constitutes a cause of the lack of uniformity in the products of the prior art.

Moreover, the handling of this mahogany acid salt is quite troublesome because of its high viscosity, and, as a matter of fact, it has heretofore been customary to soften it by heating.

The alkylaryl sulfonate which has an alkyl radical of C₁₀₋₁₅, is free from such defects as discussed above, but its viscosity is as high as that of the foregoing mahogany acid salt so that the handling thereof is troublesome also.

And, in case of the long-chain alkylaryl sulfonate such as disclosed in the U.S. Pat. No. 3,410,925, the process of application is rather complicated because the preparation of the hydrocarbon to be employed as the material therefor requires further processing, namely, dimerization and alkylation of the alkyl radical.

From the viewpoint of efficiency, per se, these oil-soluble surface active agents in the prior art, because of the existence of cyclic aromatic compounds contained in molecules thereof, are considerably different from the olefin sulfonic acid or its salt constituting the principal component of the surface active agent of the present invention, not to mention the difference of their solubility in solvents. They are also inferior to the compounds of the present invention in their lubricative property, corrosion inhibiting property, emulsifying property, etc.

SUMMARY OF THE INVENTION

The object of the present invention is to provide a novel high-molecular, oil-soluble surface active agent which can remedy the aforementioned shortcomings of the prior art, and more particularly, an oil-soluble anionic surface active agent consisting essentially of at least one member selected from the group consisting of a sulfonic acid, sulfonate (salt), and mixtures thereof, of an aliphatic monoolesin having a number of carbon atoms in the range of 32–40 and expressed by the general formula

\[ R \quad C = C \quad R' \]

\[ R'' \quad R''' \]

(wherin, \( R \) is a saturated alkyl radical having either a straight chain structure or a branched-chain structure; \( R', R'', \) and \( R''' \) are respectively either hydrogen or a saturated alkyl radical having either a straight chain structure or a branched-chain structure, providing that said \( R', R'', \) and \( R''' \) should not all be hydrogen and the total number of carbon atoms of said \( R, R', R'' \) and \( R''' \) is in the range of 30–38).

As the material for use in present invention, a monoolesin of \( C_{30–40} \) obtained by oligomerizing either monoolesins other than \( \alpha \)-olefin or equivalent low molecular monoolesins into dimers, trimers and so on are applicable.

As for the former monoolesin, either one with a branched-chain structure or one with a straight chain structure will do, but, preferably, a monoolesin of straight chain structure is particularly suitable.

In case of the latter monoolesin as the oligomerized material, in like fashion, either a branched-chain structure or a straight chain structure will do, but, more preferably, a straight-chain \( \alpha \)-olefin is applicable.

The latter material can be obtained at a high yield by, for instance, in case of dimerization, a reaction either between olefins of \( C_{10–20} \) or between a monoolesin of \( C_{10–15} \) and a monoolesin of \( C_{30} \) or more in the presence of a catalyst.

In addition, the oligomer of olefin of \( C_{10–15} \) and preferably olefin of \( C_{10–15} \) constitute important materials for the purpose of the present invention.

The former material, namely, monoolesin of \( C_{30–40} \) can be prepared by means such as paraffin cracking, ethylene polymerization, elimination of hydrogen chloride from chlorinated paraffin, dehydrogenation of paraffin, etc., and the latter material for oligomerized olefin can also be prepared by the foregoing method.

As the catalyst for use in said oligomerization, organic metal compounds such as organic aluminum compounds, metallic oxides, alkali metallic salts, boron fluoride, etc., are suitable.
Accordingly, the constitution of the oligomerized material varies with the composition, the properties or the conditions of polymerization (such as temperature, time, pressure, etc.) of the lower molecular weight straight-chain olefin employed therefor. For instance, when dimerization is effected by employing a straight-chain α-olefin of C₀₅₆-C₂₆₀, there are obtained high molecular monolefins mainly having the below-mentioned formulas or mixtures thereof.

(i) \[
\begin{array}{c}
R_1 \\
\text{CH}_2 \\
R_1 CH_2 CH_2 CH=CHR_2 \\
\end{array}
\]

(ii) \[
\begin{array}{c}
R_1 \\
\text{CH}_2 \\
R_1 CH_2 CH_2 CH=CHR_1 \\
\end{array}
\]

(iii) \[
\begin{array}{c}
R_1 CH_2 CH_2 CH_2 CH=CHR_1 \\
\text{CH}_3 \\
\end{array}
\]

(iv) \[
\begin{array}{c}
R_1 \\
\text{CH} \\
R_1 CH_2 CRCH_2 CH=CHR_1 \\
\end{array}
\]

(v) \[
\begin{array}{c}
R_1 \\
\text{C} = \text{CH}_2 \\
R_1 \\
\end{array}
\]

(vi) \[
\begin{array}{c}
R_1 CH = \text{CH}(CH_2)_n C \sim \text{CH}_3 \\
\end{array}
\text{(wherein, } n=0-21\text{)}
\]

(vii) \[
\begin{array}{c}
R_1 CH_2 CH = \text{C} \sim \text{CH}_3 \\
\end{array}
\]

(wherein, \( R_1 \) is an alkyl radical having a carbon-chain length such that the total number of carbon atoms of each molecule is in the range of 32-40.)

On this occasion, however, insomuch there occurs the isomerization of the material, per se, prior to the dimerization, according to the kind of the catalyst employed, it is presumed that these compounds of said formulas (i) and (ii) can be produced to a much greater extent than those of said formulas (iii) and (iv), and, moreover, further complicated formulas are feasible from the viewpoint of the transition point for the double bonding as well as the ways of combination of alkyl chain lengths. Further, as for the trimer or the tetramer, there can be obtained other various formulas in addition to those mentioned above. But, it boils down to this: it suffices if the high molecular monolefins applicable to the present invention possess a carbon atom number in the range of 32-40 as expressed by the foregoing general formula. Many of such monolefins, because of their having a branched chain or having a double bond inside thereof, even in case of a straight-chain mono-inner-olefin of the formula (iii) in the foregoing, show a low cloud point as well as pour point as compared with a straight-chain α-olefin having the same number of carbon atoms, and despite the high molecular weight thereof, display such an unexpected characteristic that they are usually in the state of a transparent liquid at room temperature. Hereunder shown are the properties of mixtures of typical monolefins of a high molecular weight.

<table>
<thead>
<tr>
<th>No. of carbon atoms</th>
<th>Cloud point (°C)</th>
<th>Pour point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dimer olefin</td>
<td>32</td>
<td>1</td>
</tr>
<tr>
<td>dimer olefin</td>
<td>36</td>
<td>5</td>
</tr>
</tbody>
</table>

The product according to the present invention is prepared by sulfonating the above-mentioned materials. The sulfonated product thus obtained is serviceable as it is, but it is preferably neutralized once and then employed either in that condition without subjecting to hydrolysis or after subjecting it to hydrolysis. Also, a sulfone ring opening agent can be added to the sulfonation product. The methods of sulfonation, neutralization and cracking of sulfone to be applied on this occasion are the same as that for the conventional water-soluble olefin sulfone (for instance, the ones disclosed in British Pat. Nos. 1,072,601 and 1,139,158). In other words, the product of the present invention can be obtained through a process in which: the feed material olefin in the form of a thin film is contacted continuously with gaseous sulfur trioxide; then, the reaction product is further subjected to neutralization; subsequently, the sulfones contained therein are subjected to ring-opening either by means of hydrolysis or causing them to react with a sulfone cracking agent.

As to the sulfonation processing, insomuch as the feed material olefin has the form of a liquid at room temperature by nature, it can be fed at room temperature and independently as it is, without taking such troubles as an express heating or joint use of any solvent. As for the sulfonation equipment, a continuous falling film reactor is applicable, providing that it is so devised as to be capable of bringing a thin-film material into contact with SO₃ gas. In this context, as to the applicable size, length, etc. of said equipment, there is no particular limitation thereof, but it ranges from a laboratory-size one to an industrial-size one. In short, a reaction apparatus suitable for preparing the product according to the present invention is a continuous sulfonator capable of performing a high degree of sulfonation. The sulfonator of this sort is preferably provided with as large a heat exchangeable surface area as possible. In this connection, such a sulfonator which is provided therein with a thermal medium capable of controlling the inner temperature thereof is of course also applicable to the present invention. Further, it is also practicable to employ a sulfonator having annexed thereto a post-reactor for the purpose of completing the reaction.

As to the sulfonating agent to be employed in effecting the sulfonating reaction, either of sulfur trioxide prepared through the oxidation of sulfur dioxide and sulfuric anhydride stabilized liquid sulfur trioxide are applicable. The suitable concentration of SO₃ gas for
use in the reactor is in the range of 1–10 percent by volume with the balance being an inert gas. As for the inert gas, it is usual to employ air, but it will also do to use nitrogen, carbon dioxide, sulfur dioxide gas, etc. in lieu of air. The temperature of SO₂ gas being fed is in the range of 30°–100°C, and preferably in the range of 40°–50°C. The mole ratio of SO₂ gas to the feed material olefin is in the range of 0.5–1.5, and preferably in the range of 0.8–1.3. Furthermore, the preparation of mohagony acid salt according to the prior art is apt to be accompanied by the trouble that, should the rate of conversion of the petroleum fraction to sulfonate be raised too much, there will result an abrupt increase in viscosity to make the after-treatment rather complicated, but for the product of the present invention, even when said conversion rate exceeds 90 percent, there occurs no such increase in viscosity as to make the handling thereof difficult, and this also is an advantageous feature of the present invention. Next, as to the temperature for the sulfonation reaction, inasmuch as the feed material olefin has a low viscosity despite its high molecular weight as discussed in the foregoing, it can be sulfonated without applying a high temperature, and, for instance, even in case of a mixture of dimer olefin having 36 carbon atoms, it is well sulfonated at a temperature of 50°C or thereabout, and not only that, the resulting sulfonic acid mixture does not harden at a temperature above 40°C, either, and has a low viscosity, so that the sulfonation reaction can be easily effected. The suitable reaction temperature is to be higher than the solidifying point of the feed material olefin by 5°C or more, but not exceeding 100°C, and preferably in the range of 30°–70°C higher than said solidifying point.

The thus obtained sulfonated substance (acid) usually comprises at least 30 percent of monoalkene sulfonic acid having a high molecular weight, 0–50 percent of hydroxyalkylsulfonic acid, 0–30 percent of di- and poly-sulfonic acid, at least 10 percent of 1, 3- and 1, 4- sultones and the like, and 0–60 percent of unsulfonated substances.

The neutralization of these mixtures is effected by adding thereto an alkali metal hydroxide such as LiOH, NaOH, KOH, etc., carbonates such as Na₂CO₃, (NH₄)₂CO₃, etc., NH₄OH, organic amines (namely, primary, secondary and tertiary amines, alkanolamine, etc.) at the rate of 0.6–1.0 by equivalent per the introduced amount of SO₃ (in mol). And, the preparation of the metallic salt of olefin sulfonic acid according to the present invention can be also performed by subjecting the aforementioned mixture to hydrocracking by means of adding thereto an alkaline earth metal hydroxide and the like such as that of Ca, Mg, Ba, Zn, Al, or subjecting the same to hydrolysis by adding thereto alkali metal hydroxide and thereafter effecting double decomposition. The alkaline earth of other metal salt for use in the present invention, such as the salt of Ca, Mg, Ba, Zn, Al, etc., can thus be prepared as above.

Meanwhile, the sultonates contained in the foregoing mixture produce hydroxyalkane sulfonic by virtue of hydrolysis. But, inasmuch as the hydroxyl radical in this sulfonate is hydrophilic in nature, there are instances wherein said sulfonate is considered rather unnecessary for the purpose of obtaining a more useful oil-soluble surface active agent. In such a case, therefore, it suffices to check the formation of hydroxyl radical by first subjecting sulfonic acids contained in the products of sulfonation to neutralization with an alkali metal hydroxide and subsequently adding a sulfone cracking agent in such an amount as exceeding the equivalent subsequent to the ring-opening of the residual sulfone.

As for the sulfone ring opening agent to be employed for this purpose, such substances as alcohol, phenol, carboxylic acid, primary or secondary amines, inmines, the amide or imide of either carboxylic acid or sulfonic acid, active hydrogen-containing compounds such as mercaptan or thiourea or N-substitution products thereof, and those compounds not containing active hydrogen such as amine sulfonates, are suitable. Besides, the tertiary amine, thioether, t-phosphine, etc., are also applicable. Of these sulfone ring opening agents such a one as contains active hydrogen is to be employed in the presence of a salt or a radical capable of bonding onto the sulfonic acid radical, and can have as a substituent radical, an aliphatic radical, alicyclic radical, aromatic radical, etc., or a single or multi-functional radical. The salt for this purpose can be the salt of an inorganic acid, thiocycian acid, thiosulfuric acid or hydrogen sulfide. Meanwhile, such sulfone ring opening agent as does not contain active hydrogen does not necessarily require such salt or neutralizing agent.

What is especially noteworthy with respect to the neutralization process under the present invention is the fact that, notwithstanding the high molecular weight thereof, the viscosity of the olefin sulfonic acid according to the present invention is about 1000 cp at 50°C at the maximum, and therefore, even when the present olefin sulfonic acid is quickly added to a basic aqueous solution for neutralization and stirred, it never gives rise to the so-called solid matters, but it is readily neutralized usually without employing any solvent. This solidification is feasible in the process of neutralization on the occasion of preparing a water-soluble surface active agent even in case where an α-olefin sulfonate having the chain length in the range of C₅₋C₂₄ is employed. In this case, however, unless either the temperature is maintained as high as more than 80°C or an appropriate solvent is added, the neutralization will not progress. In case of the present invention, too, some quantity of solvent, if deemed necessary, can be employed in the process of neutralization.

A slurry thus obtained and containing the alkali or sulfone cracking agent is subsequently maintained at a fixed temperature for a fixed period of time while being stirred, thereby affecting hydrolysis or ring opening of the sulfone. The temperature and the time for such decomposition are closely related to each other; namely, the higher the temperature, the shorter the time required. The requirements for the decomposition of sulfone in terms of temperature and time are 100°–200°C and 7 hours-1 minutes, respectively. When these requirements are met, the ring opening of sulfone is readily effected.

In this connection, it goes without saying that it is necessary to maintain said slurry to be alkaline by controlling the amount of the alkali or sulfone ring opening agent.

In case of a sulfone thus decomposed, it is next subjected to the after-treatment as set forth below: the product resulting from the decomposition of the sulfone usually contains mixed therein unreacted oil, water, some inorganic salt, alkali, etc., in addition to olefin sulfonate, so that this product is serviceable, in that condition, as an oil-soluble surface active agent, but
there are many instances where the effective components (inclusive of the unreacted oil) thereof are to be singled out for use, and accordingly, it is necessary to eliminate therefrom such impurities as inorganic salt, water, etc. As the means for separating said impurities from the effective components of the product from the decomposition, a petroleum based solvent or a chlorinated hydro-carbon based solvent is employed. That is, the effective components consisting substantially of olefin sulfonate are readily soluble in said solvents and can be thereby extracted, while the impurities remain as a residue. The petroleum based solvents suitable for this purpose include pentane, hexane, ligroin, octane, gasoline, kerosene, etc., while the chlorinated hydro-carbon based solvents suitable for the same include trichloroethylene, tetrachloroethylene, carbon tetrachloride, etc. Further, in case where simultaneous separation of polysulfonates is intended, a lower alcohol based solvent, such as ethanol, isopropanol, etc., may be additionally employed. Upon effecting the extraction, by evaporating the solvent under atmospheric pressure or at a reduced pressure, an olefin sulfonate having a high molecular weight and containing unreacted oil can be obtained. In this connection, said olefin sulfonate suffers no deterioration of its own efficiency because it contains the unreacted oil to a degree, and, accordingly, there is no necessity to go to the trouble of separating said unreacted oil by means of extraction employing an additional solvent, distribution, absorption, or the like; on the contrary, such unreacted oil can be rather positively made to be contained in the olefin sulfonate for the purpose of reducing its viscosity.

The oil-soluble surface active agent, which consists substantially of the olefin sulfonate according to the present invention, is rich in sulfonate and superior in color tone, antiscorrosive property, oil-solubility, etc., as compared with the conventional salt of mahogany acid and the like, and has such merits that it is very easy to work because of the low viscosity thereof and renders it possible to produce optionally products having almost uniform properties. And, from the viewpoint of the efficiency, the present surface active agent, when compared with conventional salt of mahogany acid and the like, has proved capable of demonstrating superior lubricating effect, anti-corrosive property, emulsifying effect, hydrating effect as required of a dry-cleaning detergent, and so forth.

Hereunder given is a further elucidation of the present invention by reference to specific examples.

**DESCRIPTION OF THE PREFERRED EMBODIMENTS**

**EXAMPLE 1**

3000g of α-olefin having 16 carbon atoms (composed of 93 percent of α-olefin, 6.6 percent of vinylidene type olefin and paraffin and 0.4 percent of inner olefin) prepared through ethylene polymerization and 600g of nickel oxide catalyst (composed of 6.2 percent of NiO, 84.4 percent of SiO₂ and 9.4 percent of Al₂O₃) were put in a 4 necked flask and caused to react for 8 hours at 35°C in the presence of N₂ current while being stirred vigorously. After filtering away the catalyst, the unreacted olefin (mostly isomerized inner olefin) was evaporated under a reduced pressure, whereby a dimerized olefin (including some higher polymerized olefin) was obtained at a 50 percent yield.

The result of analysis by spectra of infrared rays of thus obtained dimerized olefin showed almost no double bond at the end of 910~920 cm⁻¹, but there was observed, at 965~970 cm⁻¹, a peak ascribable to a trans-form inner double bond, and another peak—though weak and indistinct—at 800~900 cm⁻¹. This fact verifies that the present olefin contains a substantial amount of components having three substituents and double bond. This high-molecular olefin mixture was sulfonated by employing an apparatus for use in continuous thin-film sulfonation, sized for laboratory use.

This reaction apparatus is made of Pyrex glass, provided with a reactor 5mm in diameter and 120mm in length, and so devised as to make the olefin and SO₃ gas flow down in a parallel fashion to come into contact with each other. As for the conditions for reaction, the temperature of SO₃ gas was 50°C, the concentration of SO₃ was 2.8 percent by volume (as diluted with nitrogen gas), the time for contact was 30 seconds, the rate of olein feed was 6g/min, and the temperature of the olefin was 25°C. In this context, the mol ratio of SO₃/olefin and the reaction temperature employed were as shown in Table-1 appearing in the following.

A variety of sulfonic acids prepared as above were respectively neutralized with a 10 percent aqueous solution of NaOH in such an amount as to be equal in moles to the SO₃ introduced at the time of sulfonation, and then subjected to hydrolysis of the sulfone at 160°C for 20 minutes, thereby obtaining the sodium salt of the olefin sulfonic acid.

This sodium salt of the olefin sulfonic acid, when mixed with ethanol and subjected to extraction processing by employing petroleum ether, divided into two layers: the upper layer, namely, the petroleum ether layer, was composed of the olefin sulfonate and unreacted olefin extracted thereby, while the lower layer consisted of water and ethanol. By removing the solvent from said petroleum ether layer, there was obtained the olefin sulfonate of the present invention. A single working of this extraction processing suffices to eliminate almost completely the surplus alkali and Glauber's salt, producing a product with a light color and low viscosity. The loss of the olefin sulfonate mixture in the course of refining work was always less than 2 percent.

**Table 1**

<table>
<thead>
<tr>
<th>No.</th>
<th>Mol ratio of SO₃/high molecular weight olefin (C₄₈₂)</th>
<th>Temperature for sulfonation reaction (°C)</th>
<th>Percent conversion of reaction 1 (%)</th>
<th>Color tone 2 (Klett value)</th>
<th>Solubility 3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>40</td>
<td>45</td>
<td>10</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>0.8</td>
<td>40</td>
<td>73</td>
<td>13</td>
<td>0</td>
</tr>
<tr>
<td>3</td>
<td>1.0</td>
<td>50</td>
<td>90</td>
<td>50</td>
<td>0</td>
</tr>
<tr>
<td>4</td>
<td>1.2</td>
<td>50</td>
<td>90</td>
<td>70</td>
<td>0</td>
</tr>
<tr>
<td>5</td>
<td>1.2</td>
<td>50</td>
<td>93</td>
<td>70</td>
<td>0</td>
</tr>
</tbody>
</table>
Table 1—Continued

<table>
<thead>
<tr>
<th>No.</th>
<th>Mol ratio of SO₃/ high molecular weight olefin</th>
<th>Temperature for sulfonation reaction (°C)</th>
<th>Percent conversion of reaction 1 (%)</th>
<th>Color tone 2) (Klett value)</th>
<th>CCl₄ petroleum based dry-cleaning solvent</th>
<th>Solubility 3)</th>
<th>spindle oil No. 1</th>
<th>T 110°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>6</td>
<td>1.5</td>
<td>90</td>
<td>92</td>
<td>90</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>7</td>
<td>50</td>
<td>50</td>
<td>95</td>
<td>110</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
</tbody>
</table>

Remarks:
1) Method of analysis: Estimated by sulfur content in the high molecular olefin sulfonate.
2) The Klett value in case of 5% iso-Octane solution.
3) In case of 30 Wxll solution at 25°C, the mark 0 denotes 'good'.

The sulfonate (Na salt) obtained through the sulfonation under the condition of the mol ratio of SO₃/high molecular olefin being 1.8 and the reaction temperature being 50°C as appearing in the foregoing Table 1, was employed as an anionic surface active agent of the active ingredient dry-cleaning detergent in lieu of conventional sodium salt of mahogany acid. The content of the olefin sulfonate (Na salt) within the dry-cleaning detergent in the present example was in the range of 5–30 percent. The present olefin sulfonates, both the one for use in petroleum-based solvent and that for use in tetrachloroethylene-based solvent, have proved to stand comparison with conventional products in every respect, such as cleansing efficiency, hydrating efficiency, finishing effect, softness of the finish, odor, influence on the fiber, etc., and therefore, was capable of serving equally well.

Especially, in the case of the olefin sulfonate employing mahogany acid Na according to the present invention, its hydrating property is by far superior to the conventional ones in that it can be solubilized with one and a half times as much water.

Further, the viscosity of the present sodium salt of olefin sulfonate was as shown in the following:

| No. 2 | 300 cp (25°C) |
| No. 3 | 450 cp (°C)  |
| No. 7 | 600 cp (°C)  |
| mahogany acid (sodium salt) | 3000 cp (°C) |

EXAMPLE 2

A material composed of 1 part by weight of α-olefin having a carbon atom number in the range of 15–18 which was obtained through wax-cracking and 1 part by weight of α-olefin having 18 carbon atoms which was obtained through ethylene polymerization was mixed with 5 percent of BF₃ etherate (BF₃ content=46 percent) and subjected to dimerization at 120°C for 6 hours, whereby an olefin having a carbon atom number in the range of 33–56 was obtained at a yield of 80 percent. Subsequently, the thus prepared material olefin was introduced into the industrial-size sulfonation apparatus disclosed in the Japanese Patent Gazette Sho-42-252, and subjected to sulfonation by applying sulfuric anhydride (mole ratio of SO₃/material olefin=1.15) diluted with dry air and at the reaction temperature of 60°C and 90°C respectively, whereby there were obtained two types of products from the sulfonation reaction at the rate of 100 kg/hr each. The contact time on this occasion was 25 seconds on the average.

The apparatus employed in the present example is provided with a 120 m-long main reaction zone, which is further equipped with a thermometer at 3 places, viz. the upper, middle and lower part thereof, respectively. The reaction products (acids) obtained as above were neutralized respectively with a 10 percent aqueous solution of NaOH in such an amount as equivalent to 95 percent of SO₃ introduced at the time of the sulfonation reaction, and then subjected to hydrolysis of the sulfate at the temperature of 150°C for 45 minutes.

Subsequently, by refining the above olefin sulfonates through the same process as in Example 1, high-molecular weight oil-soluble surface active agents were prepared. The properties of these agents are as shown in the following Table 3, which verifies that it is possible to provide, on an industrial basis, a sulfonate of the same quality as that prepared on the laboratory scale.

Table 2

<table>
<thead>
<tr>
<th>Sample</th>
<th>Properties of CAS-α-ol</th>
<th>Olefin Sulfonate Prepared on Industrial Scale</th>
<th>Solubility</th>
<th>spindle oil No. 1</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample</td>
<td>Temperature for sulfonation reaction (°C)</td>
<td>Percent conversion of reaction (%)</td>
<td>Color Tone (Klett value)</td>
<td>CCl₄ tetrachloroethylene petroleum based dry-cleaning solvent</td>
</tr>
<tr>
<td>-1</td>
<td>50</td>
<td>91.5</td>
<td>80</td>
<td>0</td>
</tr>
<tr>
<td>-2</td>
<td>50</td>
<td>91.3</td>
<td>100</td>
<td>0</td>
</tr>
</tbody>
</table>

The symbol "0" denotes good.
Sample-1 was subjected to double decomposition to reduce it to Ca salt and dissolve it in spindle oil No. 1. The efficiency of the thus prepared additive for lubricant was compared with that of Ca salt of mahogany acid. The result was as shown in the following Table-3.

Further, for the purpose of comparison, the solubility of various olefin sulfonates in the range of C_{15} to C_{24} for various solvents will be shown in the following Table-4. Besides, the comparative difficulty in preparation and the solubility for solvent of the product under present invention will be shown in the following Table-5 by means of comparing α-olefin having carbon atoms in the range of 32 to 40 with mahogany acid salt.

### Table 3

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wet strength* (non-rust period (hr))</th>
<th>Corrosion of** steel sheet</th>
<th>Coefficient*** of friction</th>
<th>Baking* Load (kg/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>spindle oil No. 1 only spindle oil No. 1 97% Ca salt of mahogany acid 3%</td>
<td>&lt;10</td>
<td>1</td>
<td>0.304</td>
<td>2.5</td>
</tr>
<tr>
<td>spindle oil No. 1 97% Ca salt of mahogany acid 3% spindle oil No. 1 97% Ca salt of mahogany sulfonate under Example 2 3%</td>
<td>48</td>
<td>2</td>
<td>0.223</td>
<td>3</td>
</tr>
<tr>
<td>Example 2 3%</td>
<td>72</td>
<td>1</td>
<td>0.198</td>
<td>4</td>
</tr>
</tbody>
</table>

Remarks:

* According to JIS-Z-0223, JIS-Z-2912.
** According to JIS-K-2513.
*** Result of test by means of Soda’s pendulum-type oiliness tester (25°C; 65% RH).

Further, the sulfonation of the foregoing olefins by means of SO₃ continuous processing is always readily performed except for the case of α-olefin having 20 carbon atoms, and the neutralization and hydrolysis are also easy to perform.

In the case of said α-olefin having 20 carbon atoms, the melting point is 29°C, and it is necessary to treat it by heating.

Moreover, it is apt to give rise to clots at the time of neutralization, and therefore, it is necessary either to heat it up to a high temperature or to use some solvent jointly.

### Table 4

<table>
<thead>
<tr>
<th>Olefin</th>
<th>No. of Carbon Atoms</th>
<th>Alkyl Radical</th>
<th>Water</th>
<th>EtOH</th>
<th>BuOH</th>
<th>Petroleum ether</th>
<th>Paraffin-based lubricant</th>
<th>Spindle oil No. 1</th>
<th>Petroleum-based dry-cleaning solvent</th>
<th>Tetrachloroethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>α-olefin</td>
<td>Straight</td>
<td>Chain C_{15}</td>
<td>0</td>
<td>0</td>
<td>Δ</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_{16}</td>
<td>Δ</td>
<td>o</td>
<td>o</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td>Vinyl-</td>
<td></td>
<td>C_{17}</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_{18}</td>
<td>Δ</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
</tr>
<tr>
<td>Dimer-</td>
<td></td>
<td>C_{19}</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_{20}</td>
<td>Δ</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
</tr>
<tr>
<td>Trime-</td>
<td></td>
<td>C_{21}</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
<td>x</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C_{22}</td>
<td>Δ</td>
<td>o</td>
<td>o</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
<td>Δ</td>
</tr>
</tbody>
</table>

Remarks:
mark x denotes insoluble
mark Δ denotes partially soluble
mark o denotes transparent and soluble.
Table 5

<table>
<thead>
<tr>
<th>Material of Carbon Atoms</th>
<th>Alkyl Radical No.</th>
<th>Salt</th>
<th>Heating of material or dilution of solvent is required</th>
<th>Neutalization is rather difficult; heating up to high temperature and dilution of solvent is required</th>
</tr>
</thead>
<tbody>
<tr>
<td>C_22</td>
<td>Na</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C_24</td>
<td>Ca</td>
<td></td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>α-olefin</td>
<td>C_22</td>
<td>Na</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C_26</td>
<td>Na</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C_28</td>
<td>Na</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
<tr>
<td>C_30</td>
<td>Na</td>
<td>&quot;</td>
<td>&quot;</td>
<td>&quot;</td>
</tr>
</tbody>
</table>

Example 1: C_22 SO_3 Na mole ratio 1.00, Reaction temperature 50°C

<table>
<thead>
<tr>
<th>Examples of Present Invention</th>
<th>Example 2 C_24-60 Olefin SO_3 mole ratio 1.15 Reaction Temperature 50°C, 80°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mahogany Acid Salt C_24H_4SO_3Na</td>
<td>Ca Na</td>
</tr>
<tr>
<td></td>
<td>good good</td>
</tr>
</tbody>
</table>

Extraction and refining is required

Solubility for various solvents (in case of 30% solution at 25°C)

<table>
<thead>
<tr>
<th>Water</th>
<th>BuOH</th>
<th>Petroleum ether</th>
<th>Spindle oil No. 1</th>
<th>Paraffine-based lubricant</th>
<th>CCI_4</th>
<th>Tetrachloroethylene</th>
</tr>
</thead>
<tbody>
<tr>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>x</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>x</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>x</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
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<td>δ</td>
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</tr>
<tr>
<td>x</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>x</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
<td>δ</td>
</tr>
<tr>
<td>x</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
<tr>
<td>x</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
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<td>o</td>
</tr>
<tr>
<td>x</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
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<td>o</td>
</tr>
<tr>
<td>x</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
<td>o</td>
</tr>
</tbody>
</table>

Remark:
Mark x denotes "insoluble"
Mark δ denotes "partially soluble" and
Mark o denotes "transparent and soluble".

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A low viscosity, oil-soluble surface active agent prepared by sulfonating monoolefin of the formula

\[
\begin{align*}
R & \quad C = C \quad R' \\
R'' & \quad R''' 
\end{align*}
\]

wherein R is alkyl, R', R'', and R''' each is hydrogen or alkyl, with the proviso that not all of R', R'', and R''' are hydrogen and with the further proviso that the total number of carbon atoms of R, R', R'', and R''' is 30 to 38, by contacting a thin film of said olefin with a gas having a temperature of 30°C to 100°C and containing 1 to 10 vol. percent of SO_3 and the balance is inert gas, at a molar ratio of SO_3/olefin in the range of 0.5 to 4.5/1.0, at a reaction temperature from 5°C to 100°C above the solidifying point of said olefin, to form a sulfonated reaction product, containing alkenesulfonic acids and sulfones, and neutralizing said reaction product by adding to said reaction product from 0.6 to 1.0 equivalents, based on the SO_3 reacted, of an alkali metal, ammonium or alkaline earth metal hydroxide or carbonate, the amount added being sufficient to render the reaction mixture alkaline and then maintaining said reaction mixture at a temperature of 100°C to 200°C for a period of 1 minute to 7 hours to hydrolyze the sulfones.

2. A surface active agent as claimed in claim 1, in which said monoolefin is a dimerized monoolefin prepared by dimerizing a straight-chain α-olefin having 16 to 20 carbon atoms.

* * * *
UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3 883 583 Dated May 13, 1975

Inventor(s) Masuzo Nagayama and Hiroshi Okada

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

On the first page insert the following:

---Foreign Application Priority Data
July 1, 1969 Japan ........... 44-51 929 ---.

Signed and Sealed this twenty-sixth Day of August 1975

[SEAL]

Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents and Trademarks