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LONG CHAIN ALKYL ACETOPHENONE-α-SULFONIC ACIDS AND SALTS

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4 Claims. (Cl. 260—511)

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My invention relates to new surface-active compounds useful as wetting, cleansing and dispersing agents.

My compounds are metal sulfo-derivatives of alkylated acetophenone and conform to the formula,

$$(RCOCH_2—SO_3—)_nM$$

in which R is an alkylated aryl group comprising an alkyl radical containing from 10 to 26 carbon atoms, *n* is 1 or 2, and M an alkali or alkaline earth metal. As exemplary of the compounds may be mentioned, the sodium, potassium, calcium, barium, and magnesium sulfonates of laurylacetophenone, tetradecylacetophenone, hexadecylacetophenone, heptadecylacetophenone, octadecylacetophenone, docosanylacetophenone, and the like.

The compounds are characterized, inter alia, in that they are soluble to a more than appreciable extent in mineral oils. It is my belief that this oil solubility obtains by reason of the sulfo group being positioned alpha with reference to the carbonyl group which allows of chelation between the metal and the carbonyl oxygen, but, of course, I am not to be held for the accuracy of this hypothesis. The oil solubility of the compounds is such as to permit of their use as detergents and dispersants in mineral lubricating oils. This is not true of most of the presently commercially available synthetic sulfonates of related chemical structure. Thus, whereas the alpha-sodium sulfonate of p-octadecylacetophenone, one of the preferred compounds of my invention, is soluble in mineral lubricating oils to the extent of 6% or more, the sodium sulfonates of methyl esters of high molecular weight fatty acids, the alpha-sodium sulfonate of methyl palmitate, for example, possess no appreciable solubility in such oils.

The compounds may be prepared by several different procedures. Generally, I prepare the sodium-containing compounds by reacting sodium sulphite, in the presence of a suitable solvent, with compounds of the formula $RCOCH_2X$, where R has the same significance as above and X represents halogen. The calcium or barium-containing compounds may be conveniently produced metathetically from the sodium-containing compounds by reacting the latter with salts of the alkaline earth metals, most suitably the chlorides or bromides.

The new compounds are particularly useful in mineral lubricating compositions, and this application represents a division of my copending application Serial No. 774,431, filed September 16,

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1947, now Patent Number 2,529,424, which discloses and claims such compositions. In preparing the lubricating composition I may add the metal sulfo-compound in any amount effective to impart a detergent property to the base oil, but the limit of solubility of the compound in the base oil, of course, should not be exceeded. Generally, the composition is prepared to contain from 0.25 to 2.0% on the weight of the oil of the metal sulfo-compound.

Addends other than the metal sulfo-compound may be present in the lubricating composition. Thus, there may be present a rust-inhibitor, for example, or a viscosity index improver or pour depressor, or an anti-oxidant, such as a phosphorus sulfide-turpentine reaction product.

My invention is illustrated by the following examples which are not to be taken as in any way restrictive of the scope of the invention:

EXAMPLE I

To about 0.14 mole of crude p-octadecylphenacyl bromide, produced by the bromination of acetylated octadecylbenzene, was added 53 grams (0.42 mole) of sodium sulphite in 400 cc. of an alcohol in water solution containing 30 volume percent alcohol. The mixture was refluxed with stirring for 9 hours, some of the solvent being allowed to distill off. The solvent was then evaporated to leave a brown solid which was taken up in benzol, filtered clear, and obtained again by evaporation of the benzol. Forty-two grams of product was obtained, analyzing 4.12% sodium as against 4.85% theoretical for the alpha-sodium sulfonate of p-octadecylacetophenone, a purity of about 85%.

EXAMPLE II

The alpha-sodium sulfonate of p-laurylacetophenone was prepared as follows: To a 1 gallon autoclave were charged 563 grams (1.52 mols.) of crude alpha-chloro-p-laurylacetophenone, 441 grams (3.5 mols.) of anhydrous sodium sulfite, 1500 cc. of water, 750 cc. of alcohol, and 1000 cc. of xylene. The reaction mixture was stirred and heated at 300° F. for 15 hours at a pressure of 100 p. s. i. gauge, and then removed from the autoclave and filtered. Some solid material at the bottom of the autoclave was discarded.

The organic layer of the filtrate was charged to a 3-liter, three-neck flask fitted with a water trap and a reflux condenser and refluxed until the water and alcohol were removed. The xylene solution was filtered and topped under plant vacuum to 360° F. bottom temperature giving 487

grams of a soft red-brown solid containing 7.25% sodium, 0.36% chlorine, and 6.50% sulfur.

EXAMPLE III

Four hundred and fifty-eight grams (1.45 mols. based on the sodium content) of alpha-sodium sulfonate of p-laurylacetophenone was dissolved in 1 liter of xylene and the solution heated to 190° F. Ninety-two and two-tenths grams of calcium chloride (155% of theoretical) in a 20% aqueous solution was added dropwise to the xylene solution, the temperature dropping to 170° F. The mixture was stirred at 170° F. for 2 hours before being allowed to settle overnight.

The aqueous layer was drawn off and 92.2 grams of calcium chloride in a 20% aqueous solution was added to the xylene layer at room temperature following which the mixture was heated, with stirring, to 220° F. in 2 hours. It was necessary to add more xylene from time to time as the mixture emulsified and became rather viscous. The emulsion was broken by heat and the water drawn off.

The xylene solution was heated to 150° F., 108 grams of calcium hydroxide and 75 cc. of water added, and the mixture stirred at 150–180° F. for 2 hours. It was then heated to 280° F. and held at that temperature for 15 minutes before it was filtered and topped under plant vacuum to 330° F. bottom temperature. A yield of 396 grams of product was obtained. The product, consisting chiefly of the desired alpha-calcium sulfonate of p-laurylacetophenone, contained 5.28% calcium, 5.38% sulfur, 0.68% chlorine, 0.08% sodium, and had an acid number of 9.5.

EXAMPLE IV

The product of Example III was blended with a lubricating oil fraction containing a pour depressor, corrosion inhibitor and an anti-foam agent and the blend subjected to a conventional test for determining the detergent-dispersant qualities of the product. The test used is that identified in the art as the "L–4 Chevrolet Engine Test." As indicated in the table below from which the results of the test are apparent, the blend contained 1.4% of the additive.

Table

	Base Oil Free of Metal Sulfo-compound	Alpha-Calcium Sulfonate of p-laurylacetophenone Blend
Composition, weight percent		
Base Oil	----------	97.10
Alpha-calcium sulfonate of p-laurylacetophenone	----------	1.40
Corrosion Inhibitor	----------	1.00
Pour Depressor	----------	0.50
Anti-foam Agent	0.0005	0.0005
Laboratory Tests		
Gravity	30.5	29.9
Flash	395	400
Fire	450	450
Vis. at 100	156	163.2
Vis. at 210	43.3	44.5
Viscosity Index	92.8	107
Pour	15	−15
Calcium, percent	----------	0.079
Sodium, percent	----------	----------
Phosphorus, percent	----------	0.032
Sulfur, percent	0.2	0.32

Table—Continued

	Base Oil Free of Metal Sulfo-compound	Alpha-Calcium Sulfonate of p-laurylacetophenone Blend
L–4 Ratings		
Varnish Rating:		
Piston Skirts	3.0	5.0
Rocker Arm Cover Plate	8.0	9.0
Push Rod Cover Plate	8.5	8.0
Cylinder Walls	3.0	5.0
Crankcase Oil Pan	6.0	9.0
Varnish Total	28.5	36.0
Sludge Rating:		
Rocker Arm Assembly	6.0	9.0
Rocker Arm Cover Plate	5.5	9.0
Push Rod Cover Plate	5.0	9.0
Oil Screen	7.0	9.5
Crankcase Oil Pan	7.5	9.0
Sludge Total	31.0	45.5
Total Varnish and Sludge Rating	59.5	81.5
Bearing Loss (Mg./Whole)	1,300	557
Used Oil Tests at 36 Hrs.:		
Vis. Rise at 100° F., percent	64.7	58.7
Acid No.	3.20	2.90

From this table it is to be particularly noted that the total varnish and sludge rating was materially higher in the case of the blend and that the bearing loss was more than halved. The high varnish-sludge rating, of course, demonstrates the detergent properties of the additive.

I claim:

1. A compound of the formula

$$(RCOCH_2—SO_3—)_nM$$

in which R is a substituted phenyl group having as the sole benzene ring substituent one alkyl radical containing from 10 to 26 carbon atoms, n is 1 or 2, and M an alkali or alkaline earth metal.

2. The alpha-sodium sulfonate of p-octadecylacetophenone.

3. The alpha-sodium sulfonate of p-laurylacetophenone.

4. The alpha-calcium sulfonate of p-laurylacetophenone.

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