

# UNITED STATES PATENT OFFICE

2,659,694

## LUBRICATING OIL COMPOSITIONS CONTAINING ALKYL DIPHENYLALKANE MONOSULFONATES

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5 Claims. (Cl. 252—33)

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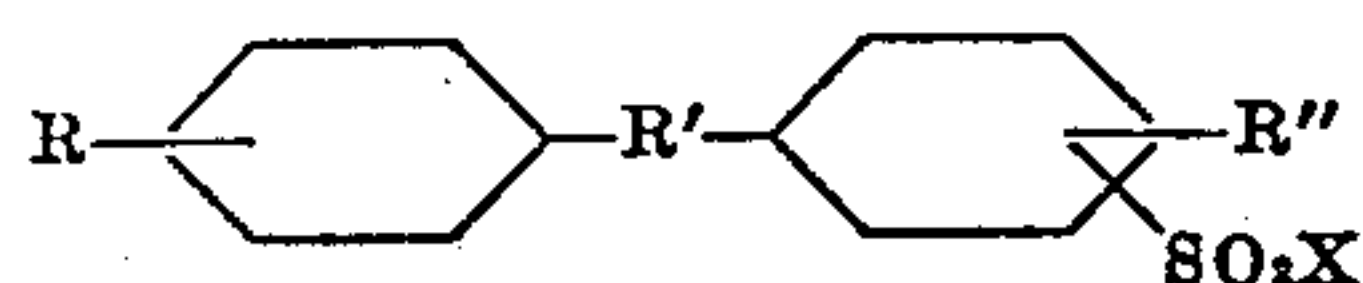
This invention relates to improved lubricating oil compositions containing certain oil-soluble sulfonic acids and their salts, especially the alkali metal and alkaline earth metal salts.

This application is a continuation-in-part application of Serial No. 193,547, filed November 1, 1950 now U. S. Patent No. 2,620,353.

It has now been found that certain monosulfonated, alkylated, aromatic condensation products are extremely effective lube oil detergents. These alkylated diphenylalkane monosulfonates in which the total aliphatic carbon atoms number between 16 and 42 are therefore valuable adjuncts to the ever-continuing search for synthetics of this nature.

The class of compounds of this invention function as lubricating oil additives when added in an amount between about 0.1% up to as much as 10% by weight of the oil. The resulting compositions exhibit improved lubricating properties, especially in heavy duty service such as encountered in diesel engines, aircraft engines, and the like. Oils containing the compounds of this invention have a detergent action on the parts of the engine that they lubricate and are capable of being used under increased loads and temperatures without causing seizure of bearings or sticking of piston rings by formation of varnish. Oils compounded with these sulfonates also act as rust preventatives in the engine during periods of quiescence.

Suitable typical compounds of the type of this invention which contain only one alkyl substituent on each of the phenyl groups are illustrated by Formula I below:



Formula I

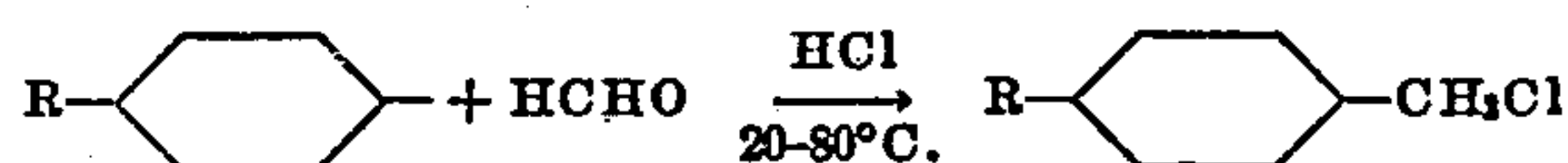
wherein R and R'' are alkyl radicals, which can be the same or different, R' is an alkylene radical and X is a radical selected from the group consisting of hydrogen, alkali metals, alkaline earth metals and the acyclic nitrogen base radicals such as guanidine, ammonia, etc. Those compounds wherein R' is an alkylene radical having from 1 to 10 carbon atoms, R and R'' are alkyl radicals, which can be the same or different, having a total carbon atom number of at least 15, the total carbon atom number of R, R' and R'' not exceeding 42, and X is sodium, calcium or barium, are especially effective. When additional alkyl substituents are attached to the phenyl groups it is desirable that the total num-

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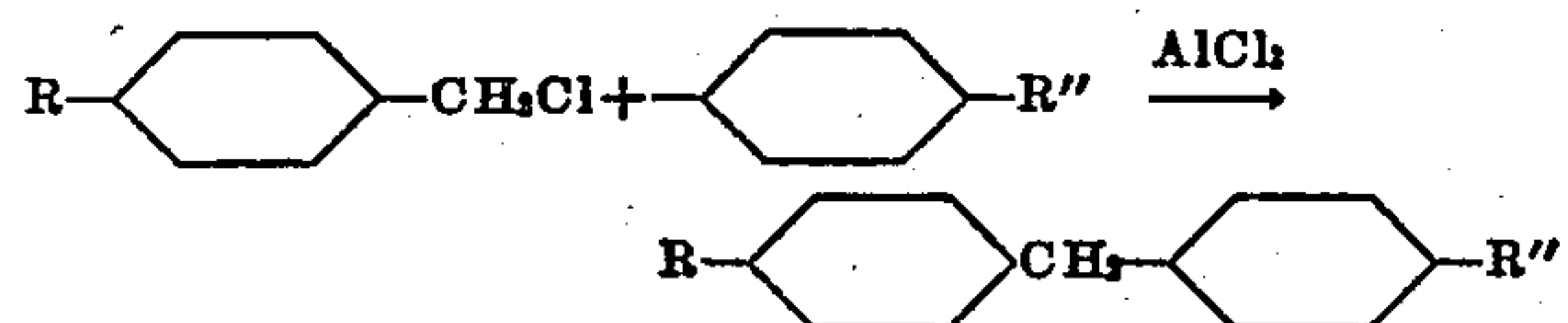
ber of aliphatic carbon atoms should be between 16 and 42. It is to be understood that the SO<sub>2</sub>X group can be attached to any of the vacant positions of either nucleus and the R and R'' radicals, while usually in the para position relative to the R' group, can also be in any vacant position of the particular benzene ring. Particularly effective and desirable compounds of the class of compounds of this invention are the bis(dodecylphenyl)methane, bis(nonylphenyl)methane, dodecylphenylmethylxylyldecane, and dodecylphenylmethylxyldecane sulfonic acids and their indicated salts such as the calcium sulfonates, etc.

Among other particular compounds that may be utilized for the purpose of this invention are the sulfonic acids of: bis(octadecylphenyl)methane, bis(octadecylphenyl)hexane, octylphenylmethylphenyloctadecane, octylphenylheptylphenylmethane and bis(decylphenyl)ethane.

The compounds of this invention can be prepared in general by condensing two moles of the indicated alkylated aromatic compounds such as kerylbenzene (from alkylating benzene with chlorinated kerosene), polypropyltoluene (from alkylating toluene with tripropylene, tetrapropylene, etc.), and octylnaphthalene (from alkylating naphthalene with diisobutylene) with a suitable aliphatic compound such as, for example, formaldehyde, acetaldehyde, etc., a chloromethyl ether such as chloromethyl ethyl ether or chloromethyl methyl ether, a dihalogenated aliphatic compound such as ethylene chloride, 1,3-dichloropropane, 1,4-dichlorobutane, 1,6-dichlorohexane, or other difunctional compound such as allyl chloride or by other conventional condensation reactions. The reaction itself is illustrated by Equations I and II below:



Equation I



Equation II

The bis(alkylated) compound is then sulfonated on an equimolar basis in the conventional manner. Sulfonating agents that may be employed include concentrated sulfuric acid, oleum, sulfonyl chloride, sulfur dioxide and chlorine gas, sulfur trioxide, sulfur trioxide and liquid SO<sub>2</sub>, brom- and chlor-sulfonic acids, etc., and their mixtures. In the sulfonation treatment the bis-



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(alkylaryl)alkane product is treated with the sulfonating agent such as concentrated sulfuric acid. The oil soluble sulfonic acids which are predominantly in the organic layer are subsequently neutralized with usually caustic soda. The sodium soaps are then extracted with aqueous alcohol solutions such as 50% aqueous isopropyl alcohol, 50% aqueous ethyl alcohol, etc. These sodium salts are then converted in oils by a double decomposition reaction to the corresponding alkaline earth salts when it is desired to use the latter in lubricating oils. The acids may also be neutralized directly with calcium hydroxide, barium hydroxide, nitrogen bases, etc.

The following examples are given to illustrate this invention, and include both the preparation of the compounds of this invention, their intermediates, and test results on their use as oil-soluble detergents.

## EXAMPLE I

*Preparation of dodecylphenylmethyl chloride*

A mixture of 492 (2 moles) grams of dodecylbenzene (from the alkylation of benzene with tetrapropylene) and 95 (1 mole) grams of chloromethyl ethyl ether at 40° C. was stirred while 10 ml. of anhydrous stannic chloride was added. The temperature of the reaction mixture rose spontaneously to 58° C., and was maintained at this temperature for a total of two hours, 1 ml. of stannic chloride being added every half hour. The reaction mixture was poured into cold water and was washed three times with water and then with dilute sodium carbonate. The oil layer was dried with sodium carbonate. The mixture was then stripped under vacuum to remove anything boiling below dodecylbenzene. The residue (496 g.) contained 3.46% chlorine. This indicated that the reaction mixture now consisted of one-half mole of dodecylphenylmethyl chloride and one and one-half moles of dodecylbenzene.

## EXAMPLE II

*Preparation of bis(dodecylphenyl) methane*

The reaction mixture from Example I was stirred at room temperature while 3 grams of aluminum chloride were added. The temperature rose from 26° C. to 32° C. spontaneously and then was heated to 40° C. for a total reaction time of two hours until the hydrogen chloride which was evolved rapidly at first was no longer liberated. The reaction mixture was washed with water several times and then with dilute potassium hydroxide. It was dried with anhydrous potassium hydroxide. The unreacted dodecylbenzene was stripped from the reaction mixture by distillation at reduced pressure, the pot temperature being raised to 200° at about 0.1 mm. Hg. pressure. The amount of unchanged dodecylbenzene recovered was 265 g. The bis(dodecylphenyl) methane which remained in the distillation flask as a rather viscous oil amounted to 190 g. The molecular weight determined cryoscopically was 502 as compared to a theoretical molecular weight of 504.

## EXAMPLE III

*Preparation of bis(dodecylphenyl) methane sodium sulfonate*

101 grams of the bis(dodecylphenyl) methane from Example II and about 200 ml. of liquid sulfur dioxide were placed in a flask under a Dry Ice cooled reflux condenser. The mixture was stirred while 16.8 g. of liquid sulfur trioxide and

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25 ml. of liquid sulfur dioxide were added dropwise over a period of about five minutes. Stirring was continued for one-half hour and the sulfur dioxide was then allowed to evaporate while the reaction mixture came to room temperature. The last of the sulfur dioxide was removed by applying partial vacuum. The residue was taken up in 50% aqueous isopropyl alcohol (400 ml.) and was neutralized with sodium carbonate. The unsulfonated oil was extracted from the resulting mixture by extraction with petroleum ether. The aqueous alcohol layer was saturated with sodium carbonate at about 50° C. and allowed to cool to room temperature. The alcoholic solution was separated from the aqueous layer and evaporated to dryness finishing in a vacuum oven at about 50° C. The dry product weighed 78 g. The sulfated ash was determined and found to be 16.1%.

## EXAMPLE IV

*Bis(dodecylphenyl) methane sodium sulfonate as an emulsifier*

A blend of 0.6 weight per cent of bis(dodecylphenyl) methane sodium sulfonate in a heavy duty motor lubricating mineral oil base was thoroughly mixed with 20 weight per cent of water and allowed to stand for 72 hours. There was no indication of separation of layers at the end of this period. This indicates that the material is an excellent emulsifier.

## EXAMPLE V

*Preparation of bis(dodecylphenyl) methane calcium sulfonate*

A blend of 454 g. of bis(dodecylphenyl) methane sodium sulfonate in 950 g. of a light lubricating oil was agitated in the presence of a solution of 300 g. of calcium chloride in 1500 ml. of water and heated to the boiling point. The mixture was kept hot while the layers were allowed to separate and the brine layer was drawn off. The oil was then heated to 150° C. with stirring in the presence of 20 g. calcium hydroxide until dry and was filtered while hot using a diatomaceous earth as a filter aid. The resulting blend was shown by analysis to be 26 weight per cent calcium sulfonate and possessed an alkalinity equivalent to 7.5 mg. KOH per g. of blend.

## EXAMPLE VI

*Behavior of bis(dodecylphenyl) methane calcium sulfonate in the carbon dispersion test*

The bis(dodecylphenyl) methane calcium sulfonate was tested for colloidal dispersing effect in the Carbon Dispersion Test, and was shown to be equivalent in this respect to commercially available oil-soluble calcium sulfonates, as may be seen in the following table:

CARBON DISPERSION TEST

	24 Hour Readings	
	Dispersed Layer, Percent	Upper Layer, Percent
Bis(dodecylphenyl) methane Calcium Sulfonate.....	100	0
Product A.....	100	0
Product B.....	100	0
Blank.....	54	46

The test is conducted as follows:

0.3 weight per cent of product under test is mixed with HD 30 base mineral oil and heated to 240° F. with stirring. The blend is cooled to



225° F. and 6 weight per cent carbon black added with stirring in small portions. Stirring is continued for 5 minutes at 225° F., after which sample is placed in a graduate and allowed to stand for 24 hours in an oven at 200° F.

#### EXAMPLE VII

##### Behavior of bis(dodecylphenyl)methane calcium sulfonate in engine tests

Lauson engine tests were made on a series of lubricating oils. The first, the control, was a mineral lubricating oil containing some additives but no detergent additive. The second test was made with an oil of the same composition to which had been added 3 weight per cent of bis(dodecylphenyl)methane calcium sulfonate. Two other oil compositions were tested, being the same in every respect except that commercially available oil-soluble calcium sulfonates (products A and B) were added in place of bis(dodecylphenyl)methane calcium sulfate. The results of these tests are tabulated below, and it is clear from these data that the product of this invention is a superior detergent additive for lubricating oils.

LAUSON ENGINE TEST

Detergent Additive	Sulfonate		Engine Demerits	
	Neut. #, Mg. KOH/g.	Mol. Wt.	Var- nish	Bearing Wt. Loss
Oil I, None			6.00	0.096
Oil I+Bis(dodecylphenyl)- methane calcium sulfonate. <sup>1</sup>	7.5 alk	800	0.88	0.030
Oil I+Product A <sup>1</sup>	7.6 alk	1,020	1.10	0.035
Oil I+Product B <sup>1</sup>	7.6 alk	905	1.00	0.039

<sup>1</sup> 3 weight percent.

These results clearly indicate how the compounds of this invention minimize undesirable varnish and prevent bearing wear.

The lubricating oil base stocks used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. Hydrogenated oils or white oils may be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides or carbon with hydrogen or by the hydrogenation of coal or its products. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils, or their hydrogenated or volatilized products, may be employed, either alone or in admixture with mineral oils.

Other synthetic lubricants useful as a base for the improved compositions of this invention include long chain esters of monobasic acids, polybasic acids mono and polyhydroxy alcohols, polymerized esters, ethers, ether esters, ester ethers, and the like. Of these various types of synthetic lubricants, the synthetic esters, either simple or complex, are usually preferred.

The lubricating oils, however, they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubrication of certain low and medium speed diesel engines the

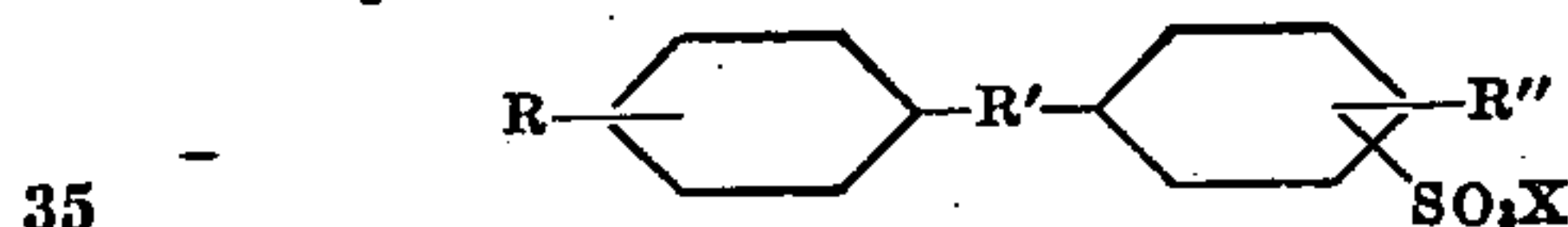
general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel service, particularly with high speed diesel engines, and in aviation engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the materials to be added according to the present invention, other agents may also be used in the lubricants such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resin, rubber, olefin polymers, volatilized fatty oils or fats, volatilized mineral oils, and/or volatilized waxes and colloidal solids such as graphite or zinc oxide, etc.

It is to be understood that the invention is not limited to the specific examples which have been offered merely as illustrations, since modifications may be made without departing from the spirit of this invention.

What is claimed is:

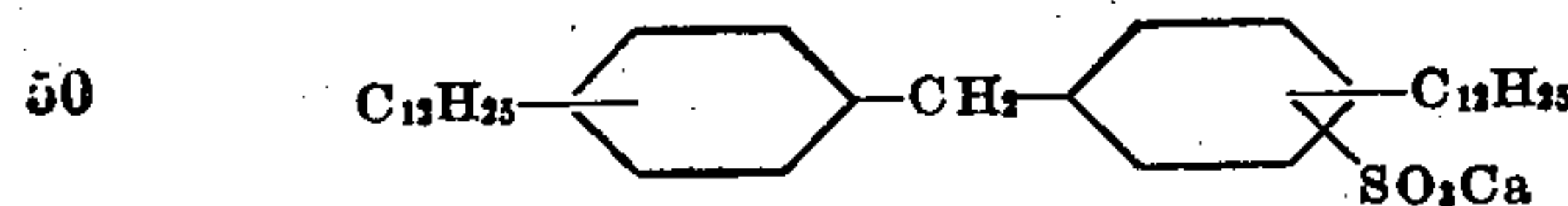
1. An improved lubricating composition which comprises a major proportion of a lubricating oil and a minor proportion sufficient to improve the detergency of said lubricating oil of a sulfonate corresponding to the following general formula:



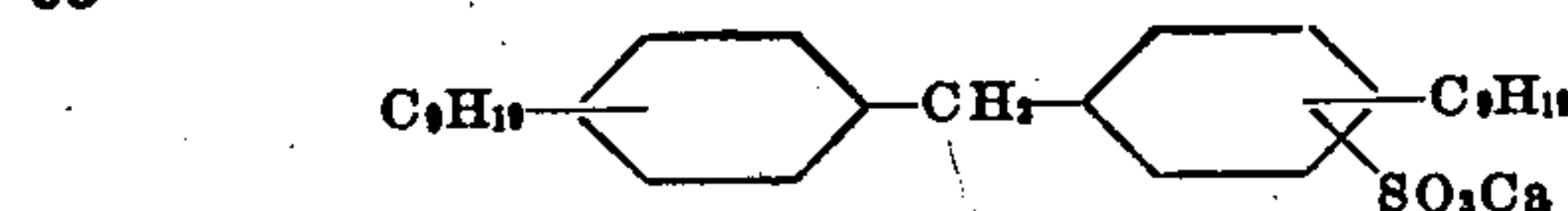
wherein R' is an alkylene radical having from 1 to 10 carbon atoms, R and R'' are alkyl radicals, which can be the same or different, having a total carbon atom number of at least 15, the total carbon atom number of R, R' and R'' not exceeding 42, and X is a radical selected from the group consisting of alkali metal, alkaline earth metal and nitrogen base radicals.

2. The composition of claim 1 in which the lubricating oil is a mineral lubricating oil.

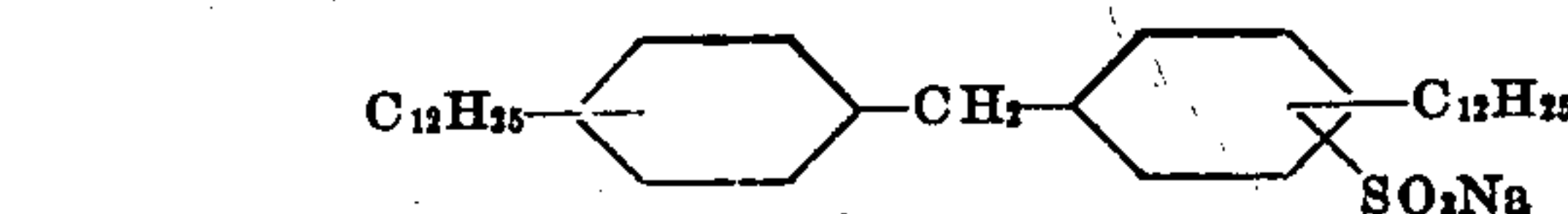
3. A composition as in claim 1 in which the sulfonate is bis(dodecylphenyl)methane calcium sulfonate corresponding to the formula



4. A composition as in claim 1 in which the sulfonate is bis(nonylphenyl)methane calcium sulfonate corresponding to the formula



5. A composition as in claim 1 in which the sulfonate is bis(dodecylphenyl)methane sodium sulfonate corresponding to the formula



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FREDERICK NEIL BAUMGARTNER.  
HOWARD L. YOWELL.

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