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3,340,192

**LUBRICATING OIL COMPOSITIONS CONTAINING
AS A DETERGENT A BETA-(ALKYLAMINO)AL-
KYL ALKENYLPHENYL ETHER**

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9 Claims. (Cl. 252—51.5)

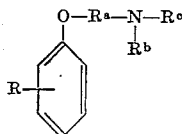
This invention relates to novel compositions of matter and to a method for preparing the same. More particularly, the present invention relates to lubricating oils containing these novel compositions.

It is recognized that lubricating oils tend to decompose under the temperature and pressure conditions encountered in the modern automotive engines. The typical products of this decomposition are acids which either permit the formation of or are themselves thick, cohesive sludges, lacquers which become baked onto the engine surfaces, or resinous materials which thicken the oil. In any case, the lubricating effect of the oil is drastically diminished and the deposition of solids upon the moving parts of the engine, particularly around the piston rings, can seriously hamper the efficient operation of the engine. In addition, the acids may corrode the cylinder walls, occasioning not only inefficient piston movement but also loss of fuel and the lubricants.

Ordinarily, agents must be added to lubricating oils to disperse the sludge and other sediment and also to neutralize the acids. Requirements for such dispersion agents, or detergents as they are also called, include both the ability to keep the impurities suspended in the oil in order to maintain the fluidity of the oil and to overcome the corrosiveness of these impurities. The agents must also be relatively stable so that the very additives themselves do not contribute to the harmful deposits. Certain metallic detergents, for example, deteriorate in the engine during normal operation and deposit ashy sediment there-within.

A major object of this invention therefore is to provide novel lubricating oil compositions containing agents which counteract the effects of oil decompositions. Another object is to provide novel non-metallic detergents for lubricating oils. A further object is to provide novel compounds which are useful in maintaining the lubricity of said oils.

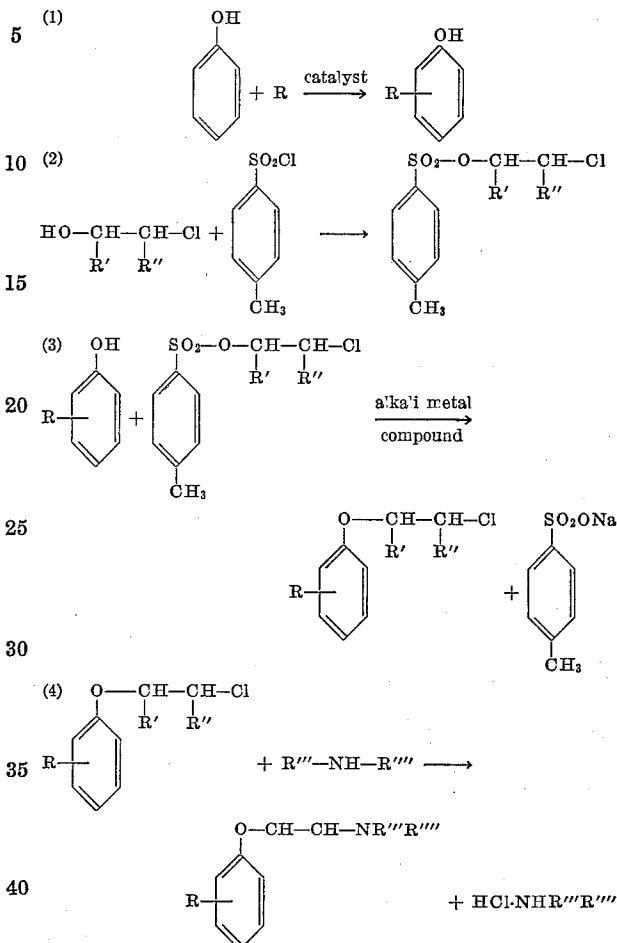
The aforementioned and other objects are accomplished, in accordance with the present invention, by incorporating in a lubricating oil a minor amount of a beta-(alkylamino)alkyl alkenylphenyl ether, wherein the said alkyl group contains from 2 to 4 carbons. A preferred class of ethers are beta-(alkylamino) ethyl alkenylphenyl ethers. The structure of the ether additives of this invention may be shown as follows:



wherein R is an alkenyl having a molecular weight of from about 600 to 3000, R^a is a lower alkylene group, R^b is selected from the group consisting of hydrogen and a lower alkyl and R^c is selected from the group consisting of hydrogen, alkyl, and (R^dNH)_xH where R^d is a lower alkyl and x is 1 to 4. The groups R^b, R^c, and R^d may have up to 6 carbon atoms per group.

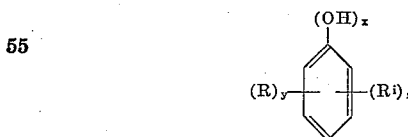
According to one aspect of this invention, the manner of preparing my ether compounds requires first reacting an alkenyl-phenol with a chloro (lower alkyl)

toluene p-sulfonate and thereafter reacting the phenyl ether so produced with an amine. This preparation is depicted by the equations below:



wherein R is an alkenyl, R' and R'' may be methyl or hydrogen, R''' may be alkyl or aminoalkyl and R'''' may be alkyl, aminoalkyl or hydrogen.

In a copending patent application filed herewith, in the name of F. P. Otto and A. Logothetis, U.S. Ser. No. 418,524, the alkenyl phenol is prepared from a phenol compound and a polyalkylene, including polypropylene, polybutene and polyamylene, having a molecular weight in the range of about 600 to 3000. The structure therein depicted is shown below



60 wherein R is a hydrocarbon or substituted hydrocarbon radical, R¹ is a polyalkylene or alkenyl radical where the repeating unit may be from C₃ to C₅, x is an integer from 1 to 2, y is an integer from 0 to 2, and z is an integer from 1 to 2. Polypropylene, for example, having a
65 molecular weight of 800 to 1100, is a particularly satisfactory substituent for preparing the novel dispersion agents of this invention. The reaction is catalytic, preferably using boron trifluoride phenolate or etherate complex. The reaction temperature for preparing this compound ranges from about 20° to over 200° C.
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The second precursor of the phenyl ether is the chloro (lower alkyl)toluene p-sulfonate. This compound is suit-

ably prepared by reaction of toluene p-sulfonyl chloride with an excess of a lower alkylene chlorohydrin, having from 2 to 4 methylene groups, preferably ethylene chlorohydrin and propylene chlorohydrin. The reaction proceeds comparatively readily under reflux conditions.

The alkenylphenol is then reacted with the chloro (lower alkyl)toluene p-sulfonate in the presence of an alkali metal hydroxide or carbonate. The reaction is preferably conducted at the reflux temperature of the reaction mass. Water and the alkali compound, such as sodium hydroxide, are added to the reactants and the temperature of reaction is preferably held at between about 90° and 100° C.

After the etherification, the reaction mixture is made alkaline and treated with a suitable organic solvent, such as benzene, for extracting the phenyl ether product. Excess alkali is washed out of the solvent solution and the solvent is distilled off.

The product remaining from the solvent distillation step is heated in the presence of an excess of an alkylamine, preferably in an inert atmosphere, at a temperature in the range of 170° to 210°. The product, which is recovered in substantially the same manner as that of the previous step, is the beta-(alkylamino)alkyl alkenylphenyl ether of this invention. The amine reactant is preferably present in excess of that required to yield the desired product and a portion of the amine is available as a hydrochloride acceptor. The amine hydrochloride side product may be washed away with water to yield a substantially pure final product.

The alkylamine may be any of the common, commercially available amino compounds, including diethylene triamine, dimethylamine, propylamine, and other primary and secondary mono- and polyamines. The preferred amines are short-chain amines having up to six carbon atoms per alkyl radical.

The following examples serve to illustrate this invention without limiting the same. Any references to parts and percents herein are deemed to refer to weights unless otherwise stated.

Example I.—Preparation of the alkenylphenol

Into a three-necked flask were added 4025 grams (4.57 moles) of polypropylene, having a molecular weight of about 880, and 537 grams (5.72 moles) of phenol, being 25 mole percent excess. The flask was fitted with a stirrer, a condenser, an addition funnel and a thermometer. The reaction mass was heated to 50° C. and 227 grams of boron trifluoride etherate was added portionwise over a ten minute period. At the end of this addition, the reaction mass was heated at 80° C. for 16 hours and thereafter quenched with 1,000 ml. of water.

The cooled reaction product was diluted with 1,000 ml. of toluene and washed with portions of hot distilled water until the washings were neutral to litmus paper. Solid residue was then filtered out, and the toluene and water were removed by stripping, first at 175° C. and 130 mm. Hg under a nitrogen blanket, and again at 175° C. and 5 mm. Hg.

The liquid product had an active hydrogen value of 0.90 millimoles of hydrogen per gram of material (H/g).

Example II.—Preparation of beta-chloroethyl toluene p-sulfonate

Into a reaction flask were charged 95 grams (0.5 mole) of toluene p-sulfonyl chloride and 100 grams (1.25 moles) of ethylene chlorohydrin. The mixture was heated at reflux for 3 hours. The excess ethylene chlorohydrin was distilled off at 250 mm. Hg. The residue liquid was treated with 100 grams of a 10% sodium hydroxide solution and taken up with benzene. The benzene solution was dried with anhydrous potassium carbonate and the benzene thereafter removed by distillation. The remaining liquid was fractionated through a Vigreux column at 21 mm.

Hg. The fraction boiling at 210° C. and 21 mm. Hg was beta-chloroethyl toluene p-sulfonate and weighed 60 grams which represented a yield of about 51% of theoretical.

Example III.—Preparation of beta-chloroethyl polypropylphenyl ether

One hundred and forty-two grams (0.128 mole using an active hydrogen ratio of 0.90 millimole of hydrogen per gram of product) of the polypropylphenol of Example I and 30 grams (0.128 mole) of the beta-chloroethyl toluene p-sulfonate of Example II were mixed together in a reaction flask with 5.1 grams of sodium hydroxide and 9.4 ml. of distilled water. The mixture was heated with agitation at 90° to 100° C. for 3 hours. The liquid mixture commenced to gel at about 100° C. necessitating the addition of 12 ml. of water to liquefy it.

After the heating, the reaction mixture was treated with 200 grams of 20% sodium hydroxide solution and extracted with benzene. The benzene solution was washed with 10% hydrochloric acid solution until the wash portions were neutral to litmus paper. The benzene was distilled off and the remaining product was topped at 200° C. and 21 mm. Hg. The active hydrogen ratio of the remaining product was 0.26 millimole of hydrogen per gram of product and the chlorine content was 1.58%.

Example IV.—Preparation of beta-tetra-ethylene pentamino-ethyl-polypropylphenyl ether

Into a reaction flask were added 112 grams (0.051 mole) of the beta-chloroethyl polypropylphenyl ether, the product of Example III, and 19.4 grams (0.102 mole) of tetra-ethylene pentamine. The mixture was heated under a nitrogen blanket at 180° C. for 19 hours, and at 200° C. for another 24 hours. Thereafter, the reaction mass was dissolved in xylene and washed with hot distilled water until the wash portions were neutral to litmus paper. The xylene was distilled off first at 175° C. and 130 mm. Hg, and again at 175° C. and 5 mm. Hg.

The oily product had the following analysis:

	Percent
Nitrogen	1.51
Basic nitrogen	1.08
Chlorine	0.06

EVALUATION OF PRODUCT

A product, prepared in the same manner as described in Example IV, having the following analysis:

	Percent
Nitrogen	1.78
Basic nitrogen	1.55
Chlorine	1.01

was blended into a refined mineral oil for the purpose of testing the product in an engine. The oil blend contained 3% of the product and 1% of a typical zinc dithiophosphate antioxidant.

L-1 CATERPILLAR ENGINE TEST

The Caterpillar Engine test determines the ability of an oil to prevent deposits around important parts of the engine, including the piston and crankcase areas. A one-cylinder, 4-cycle Caterpillar engine is used. The operating conditions are as follows:

Oil temperature, ° F.	150
Jacket temperature, ° F.	180
Speed, r.p.m.	1000
Brake load, HP	19.8

The duration of the test was 240 hours. The diesel fuel for the engine contained 1% sulfur. The test results are reported in Table I.

Table I.—Caterpillar engine test results

Duration of run, hours	240
Engine rating	98.7
Lacquer demerits	0.3
Top groove packing, percent	5

The engine rating expresses the over-all condition of the engine at the end of the test run; a scale of 0 to 100 is used to indicate cleanliness, a 100 rating indicates a perfectly clean engine. The lacquer demerits indicate the amount of deposits coating the rings, the grooves and the lands, and the skirts of the piston; demerits are given for quantity of coating and the degree of lacquering as evidenced by color standards, the sticking tendencies of the piston rings; the scale is from 0 to 100, a rating of 0 indicating completely clean surfaces and no demerits of any kind. The top groove packing rating indicates in percent of groove volume the amount of carbon deposited in the top groove of the piston; the scale is from 0 to 100%, a rating of 0 indicating a completely clean groove.

The results of the above engine test show that the additive offers a high degree of detergency to the lubricating oil. Preferably, the detergent agents of this invention are utilized in conjunction with mineral oils, although synthetic oils may also be used, except with respect to the solubility of the additive in a specific oil. The presence of from about 0.05% to 25% by weight of the oil of these detergents, or dispersants, provides satisfactory results, the preferred amount being from about 1% to 5%.

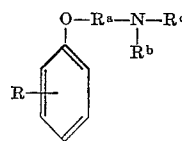
The agents of this invention are also compatible with other typical oil additives such as viscosity-index improvers, pour point depressants, antioxidants and the like.

Although the present invention has been described herein by means of certain specific embodiments and illustrative examples, it is not intended that the scope thereof be limited in any way thereby, but only as indicated in the following claims.

I claim:

1. A lubricating oil composition containing a minor amount sufficient to improve the detergency characteristics thereof of an alkenylphenyl ether having the structure

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wherein R is an alkenyl group having a molecular weight of from about 600 to about 3000, R^a is a lower alkylene group, R^b is selected from the group consisting of hydrogen and lower alkyl, and R^c is selected from the group consisting of hydrogen, lower alkyl and (R^dNH)_xH, where R^d is a lower alkyl and x is 1 to 4, and the alkyl groups in each of R^a, R^b, R^c, and R^d have up to 6 carbon atoms per group.

2. The lubricating oil composition of claim 1 wherein R is derived from polypropylene.

3. The lubricating oil composition of claim 1 wherein the alkenylphenyl ether is beta-(tetraethylenepentaminoethyl)alkenylphenyl ether, said alkenyl being polypropenyl.

4. The lubricating oil composition of claim 1, wherein the minor amount of the said ether is in the range of 0.05% to 25% by weight.

5. The lubricating oil composition of claim 1, wherein the minor amount of said ether is in the range of 1% to 5% by weight.

6. The lubricating oil composition of claim 1, wherein R^a is selected from the group consisting of ethylene and methyl substituted derivatives thereof.

7. The lubricating oil composition of claim 1, wherein the ether is a beta-(alkylamino)ethylene alkenylphenyl ether.

8. The lubricating oil composition of claim 1, wherein the alkylamino group is selected from the group consisting of dimethylamino, propylamino, diethylenetriamino, and tetraethylenepentamine.

9. The lubricating oil composition of claim 1, wherein R has a molecular weight in the range of 800 to 1100.

References Cited

UNITED STATES PATENTS

3,122,575	2/1964	Peterson et al.	252—51.5 X
3,219,666	11/1965	Norman et al.	252—51.5 X

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