Patented Jan. 28, 1947

2,415,002

UNITED STATES PATENT OFFICE

2,415,002

ORGANIC POLYSULFIDES

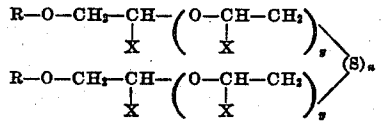
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No Drawing. Application January 16, 1945, Serial No. 573,141

7 Claims. (Cl. 260—608)

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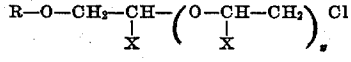
This invention relates to organic polysulfides having the formula:



wherein R is a carbocyclic nucleus, X is a member of the group consisting of hydrogen and lower alkyl groups, y is a number from zero to two, inclusive, and n is a number from two to four, inclusive.

An object of this invention is to provide a new group of organic polysulfides of the above formula, possessing a low degree of color, which can be added to lubricating oils to enhance their properties, more specifically for improving their resistance to oxidation, for reducing their corrosion of silver- or copper-containing bearings, and for improving their lubrication at increased or extreme pressures and high temperatures. These new polysulfides are remarkably free from skin irritation and can be used in cutting and boring oils on lathe and bench operations where the lubricants may come in contact with an operator's hands. They can also be used for preparing wire-drawing oils and gear oils where extremely high local pressures and temperatures are encountered.

The new compounds of this invention are obtainable by reacting a halide of the formula:



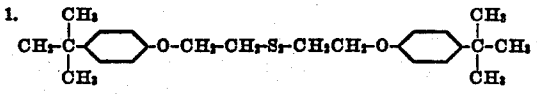
wherein R, X, and y have the significance mentioned above, with a solution of an alkali metal polysulfide, advantageously in a mutual solvent such as alcohol.

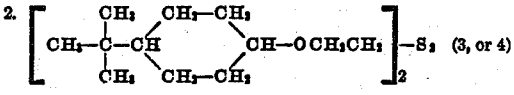
For use in petroleum oils, it is desirable that the above organic polysulfides be soluble in the oils to the extent of from about 0.5% to 10%, the optimum amount depending upon the character of the oil used, i. e., whether paraffinic or naphthenic, the percentage of sulfur present in the organic polysulfide, and the use to which the oil is to be subjected. In general, it has been found highly desirable to have present a hydrocarbon substituent, such as an alkyl or cycloalkyl group, attached to the carbocyclic nucleus, R, to enhance the oil solubility of the above polysulfides, particularly when R is, for example, an aromatic ring. In order to prevent separation of these organic polysulfides from petroleum oils at low temperatures, it is desirable that the substituent alkyl group of a benzenoid nucleus contain at least four carbon atoms, although when R is an

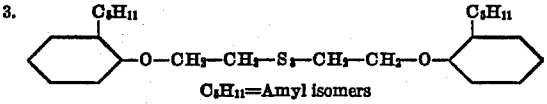
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alicyclic group, such as the dihydronorpolycyclopentadienyl, such hydrocarbon substituents are not required for low temperature oils.

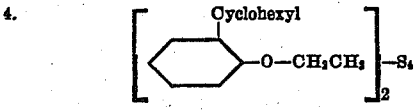
Typical highly desirable polysulfides obtainable according to this invention are the following:

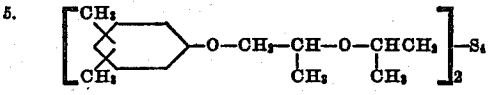
1. 

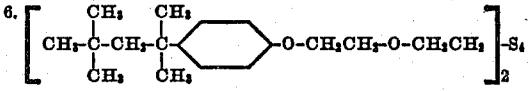
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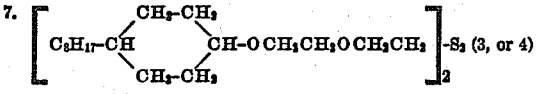
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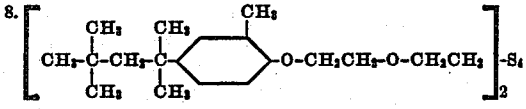
C_5H_{11}=Amyl isomers

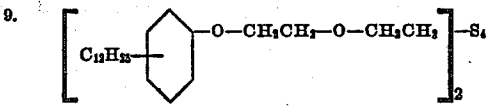
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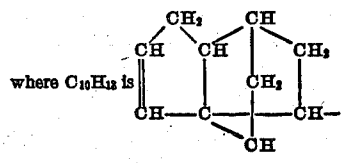
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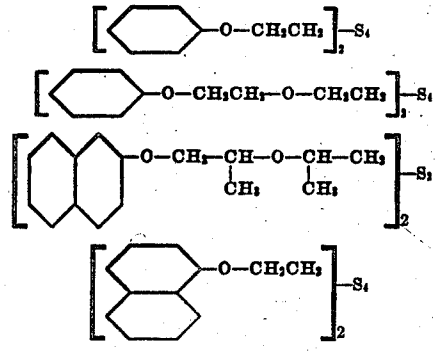
$C_{12}H_{25}$=Dodecyl isomers

10. $[C_{10}H_{13}—O—CH_2CH_2]_2—S_4$

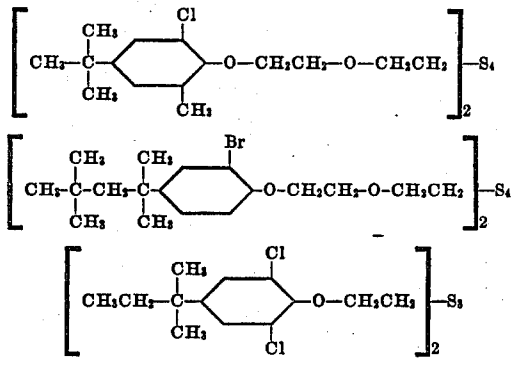
where $C_{10}H_{12}$ is 

For use in naphthenic type petroleum oils, the presence of an alkyl or cycloalkyl group is not as important for solubility and, consequently, compounds in which R is unalkylated can be used.

For this purpose, the following type compounds come within the purview of this invention:

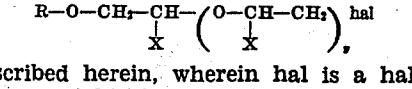


Furthermore, where extremely high pressures are encountered, as in the case of worm and gear oils, it is advantageous that one or more halogen atoms be present in the aromatic nucleus R. For this purpose, the following type compounds come within the purview of this invention:



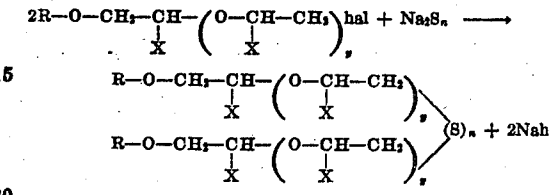
In practicing this invention, compounds in which R is a benzene or naphthalene ring which can be unsubstituted, or which can be nuclearly substituted with hydrocarbon groups (alkyl, aryl, cycloalkyl) or with halogen groups, are to be considered within its scope. Furthermore, X can be a short chain alkyl group other than methyl, such as ethyl, propyl, or butyl.

In preparing the organic polysulfides of this invention, a solution of an alkali polysulfide is prepared by dissolving flowers of sulfur in, for example, an aqueous sodium sulfide solution. The amount of sulfur dissolved is selected so that the solution of sodium polysulfide obtained contains one or more atoms of sulfur per atom of sodium. This solution is reacted in alcoholic solution at the boiling point thereof with two molecular equivalents of the halide having the formula:



as described herein, wherein hal is a halogen of atomic weight above nineteen. Such halides are conveniently obtained by reacting phenols or naphthols, the cyclic nucleus of which corresponds to group R, with alkylene dihalides or alkylene ether dihalides such as ethylene dichloride, β,β'-dichlorodiethyl ether, β,β'-dichlorodiisopropyl ether, β-chloroethoxy-β'-chlorodiethyl ether, and the like, in the presence of sodium hydroxide, as already known. Corresponding alicyclic ether halides may also be prepared. Certain of these are obtainable by reacting dicyclopentadiene in the presence of BF_3 with ethylene chlorohydrin or diethylene glycol chlorohydrin, or by reacting Diels-Alder type addition products of olefins and cyclopentadiene with ethylene chlorohydrin or diethylene chlorohydrin in the presence of sulfuric acid or phosphoric acid as catalysts.

Upon heating carbocyclic oxyaliphatic halides of this type with sodium polysulfides having from one to two sulfur atoms per atom of sodium, the following reaction occurs:



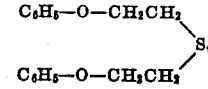
wherein n is equal to two to four, inclusive.

The new organic polysulfides obtained in this way are, after being washed and dried in vacuo, pale yellow to deep amber-colored thick oils. A few of them are waxy solids. They are practically non-volatile and almost inodorous when purified by warming with absorbent charcoal. They dissolve readily in aromatic hydrocarbons and also dissolve in other types of hydrocarbons, particularly if R is hydrocarbon substituted, and are not affected by steam, dilute acids, or alkalies. Furthermore, in contrast to monothioethers, they are not readily oxidized to form sulfoxides or sulfones and are, therefore, extremely stable in lubricating oils with which they may be mixed. It should be also noted that the mono-thioethers are lacking in those properties which render the polysulfides of this invention useful.

The following examples illustrate this invention:

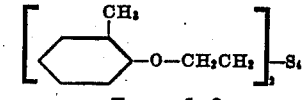
Example 1

To a stirred mixture of 72 grams of powdered sulfur and 180 grams of sodium sulfide crystals ($Na_2S.9H_2O$) at 90° C., there was gradually added a solution of 375 grams of ethanol and 156.5 grams of β-phonoxyethyl chloride. The mixture was then boiled under reflux for seven hours with constant stirring. The reaction product was poured into water and the oil layer separated and washed several times with warm water. The washed oil was dried in vacuo at 90°–95° C. The residue was an amber-colored oil which, on standing, become a waxy solid. Its composition corresponds to the formula:



Example 2

The procedure described in Example 1 was applied to 170.5 grams of β-(ortho-cresoxy)-ethyl chloride in place of the β-phenoxyethyl chloride. The product was a pale amber-colored oil corresponding to the formula:



Example 3

A mixture of 200 grams of β-(phenoxyethoxy)-ethyl chloride,

$C_6H_5—O—CH_2CH_2—O—CH_2CH_2Cl$

375 grams of ethanol was mixed with a solution

of Na_2S_4 prepared from 180 grams of $Na_2S.9H_2O$ and 72 grams of sulfur and boiled for seven hours under reflux with continuous stirring. The product was poured into water and the oil layer separated and washed several times with hot water. The residual oil, after being dried in vacuo, was an amber-colored liquid corresponding in composition to the formula:

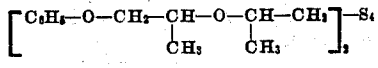
$$[C_6H_5—O—CH_2CH_2—O—CH_2CH_2]_2—S_4$$

Example 4

A mixture of 114 grams of β-(phenoxy-isopropoxy)-isopropyl chloride,

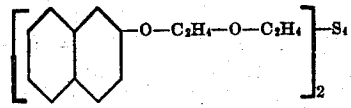
$$C_6H_5—O—CH_2—CH(CH_3)—O—CH(CH_3)CH_2Cl$$

and 190 grams of ethanol was boiled under reflux for six hours with a solution of Na_2S_4 prepared from 90 grams of $Na_2S.9H_2O$ and 36 grams of sulfur. The product was isolated by pouring it into water and washing and drying of the separated oil. It formed a pale yellow liquid having the formula:



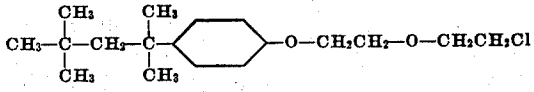
Example 5

A mixture of 90 grams of $Na_2S.9H_2O$, 36 grams of sulfur, 190 grams of ethanol, and 125 grams of β-naphthoxyethoxy ethyl chloride was boiled under reflux for six and one-half hours with rapid stirring. The product was poured into water, washed, and dried in vacuo. The product was a thick oil having the formula:

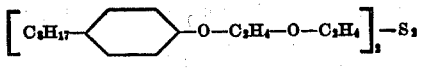


Example 6

A mixture of 144 grams of $Na_2S.9H_2O$ and 19.2 grams of flowers of sulfur was heated for fifteen minutes until a clear solution was obtained. To this was added 300 grams of ethanol and 250 grams of p-α,α,γ,γ-tetramethylbutylphenoxyethoxyethyl chloride:

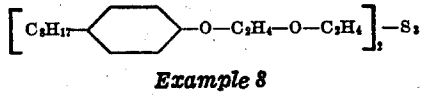


The mixture was stirred and boiled under reflux for seven hours. The product was poured into water and the oil layer separated, washed, and dried in vacuo at 95° C. The residual compound was a pale yellow oil having the formula:



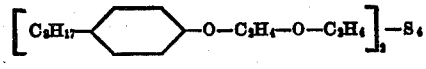
Example 7

The procedure of Example 6 was repeated except that 38.4 grams of flowers of sulfur was used instead of 19.2 grams. The product was a pale yellow oil having the formula:



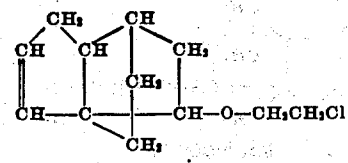
Example 8

The procedure of Example 6 was repeated except that 57.6 grams of flowers of sulfur was used instead of 19.2 grams. The product was a pale yellow viscous oil having the formula:



Example 9

(*a*) To a stirred mixture of 176 grams of dicyclopentadiene and 161 grams of ethylene chlorohydrin there was gradually added 28 grams of boron trifluoride-diethyl ether, $BF_3.O(C_2H_5)_2$, at 60° C. The mixture was stirred at 60° C. for four hours longer, then was washed with water and with soda solution and distilled in vacuo to give 250 grams of β-chloroethoxydihydronordicyclopentadiene:



as a colorless oil boiling at 132°–136° C./6 mm.

(*b*) A mixture of 216 grams of $Na_2S.9H_2O$ and 28.8 grams of sulfur was heated until the sulfur dissolved. To this solution was added 350 grams of ethanol and 250 grams of the chloroethyl ether from (*a*) above, and the mixture was stirred and boiled for seven hours under reflux. The product was poured into hot water and the oil layer was separated, washed, and dried. It was a pale amber-colored oil having the formula:

$$[C_{10}H_{13}—O—CH_2CH_2]_2—S_2$$

where $C_{10}H_{13}$ represents the dihydronordicyclopentadienyl nucleus as above.

(*c*) The procedure in (*b*) above was modified by using 57.6 grams of sulfur instead of 28.8 grams. The product obtained was a thick oil having the formula:

$$[C_{10}H_{13}—O—CH_2CH_2]_2—S_3$$

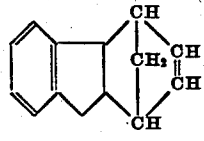
(*d*) The procedure in (*b*) above was modified by using 86.4 grams of sulfur instead of 28.8 grams. The product obtained was a thick oil having the formula:

$$[C_{10}H_{13}—O—CH_2CH_2]_2—S_4$$

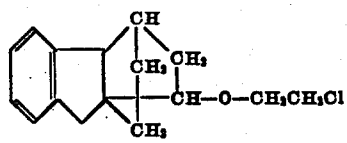
These polysulfides are extremely soluble in refined Pennsylvania lubricating oils and can be used in amounts up to 10% on the weight of such oils to improve their lubricating properties for wire-drawing and lathe-cutting operations.

Example 10

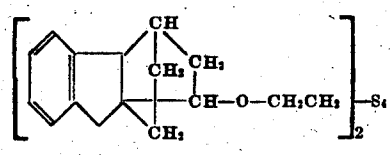
To a stirred solution of 60 grams of ethylene chlorohydrin and five grams of $BF_3.O(C_2H_5)_2$ heated to 70° C., there was gradually added 91 grams of the Diels-Alder addition product of indene and cyclopentadiene, namely, 1,4-endomethylene tetrahydrofluorene, having the formula:



The reaction was exothermic, the temperature rising to about 85°–90° C. The mixture was then heated further at 95° C. for five hours with constant stirring. The dark oil obtained was washed with water and with dilute caustic soda solution, dried, and distilled in vacuo to yield 102 grams of a colorless oil boiling at 155°–157° C. at 1 mm., having the formula:



Two molecular equivalents of the above ether chloride dissolved in an equal volume of ethanol was boiled for seven hours on a steam bath, with stirring, with a product obtained from one molecular equivalent of $Na_2S.9H_2O$ and three atomic equivalents of sulfur. The reaction mixture was poured into water and the oil layer was separated, washed with hot water, and dried in vacuo. The final product was an amber-colored thick oil having the formula:



Example 11

In substantially the same manner, the following ether chlorides were reacted with alcoholic aqueous solutions of Na_2S_2, Na_2S_3, and Na_2S_4 to yield the corresponding organic polysulfides:

(*a*) p-Tert.-butyl-phenoxyethoxy ethyl chloride
(*b*) p-Tert.-amyl-phenoxyethoxy ethyl chloride
(*c*) o-Cyclohexyl-phenoxyethoxy ethyl chloride
(*d*) o-Dodecyl-phenoxyethoxy ethyl chloride
(*e*) 3,5-dimethyl-phenoxyethoxy ethyl chloride
(*f*) 2,6-dichloro-4-p-tert.-amylphenoxyethoxy ethyl chloride
(*g*) 2-bromo-4-p-tert.-octylphenoxyethyl chloride
(*h*) 2-tert.-butyl-1-naphthoxyethoxy ethyl chloride
(*i*) p-Tert.-octylphenoxy ethoxy ethoxy ethyl chloride
(*j*) p-Tert.-octylphenoxy isopropoxy-isopropyl chloride

The products obtained were in each case thick oils which were soluble in petroleum products and effective therein as additives for improving properties, as described above. They may be used as the sole additive or they may be used in conjunction with other additives, including other antioxidants, pourpoint depressors, viscosity-index improvers (typified by lauryl or cetyl polymethacrylates), etc., or with metal soaps in the preparation of greases.

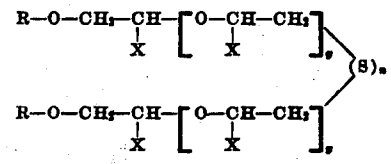
The preferred sub-class of compounds of this invention may be represented by the formula:

$$[R(OCH_2CH_2)_{y'}]_2-S_n$$

wherein R is an aromatic nucleus, y' is a number from one to three, inclusive, and n is a number from two to four, inclusive. R may be a phenyl nucleus, particularly one having a hydrocarbon substituent.

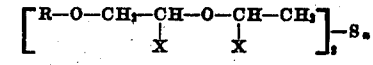
I claim:

1. As a new compound, an organic polysulfide having the formula:



wherein R is a carbocyclic hydrocarbon group having five to six carbon atoms in any single cycle, X is a member of the group consisting of hydrogen and lower alkyl groups, y is a number from zero to two, inclusive, and n is a number from two to four, inclusive.

2. As a new compound, an organic polysulfide having the formula:



wherein R is an aromatic ring of the benzene series, X is a member of the group consisting of hydrogen and lower alkyl groups, and n is a number from two to four, inclusive.

3. As a new compound, an organic polysulfide having the formula:

$$[R(OCH_2CH_2)_{y'}]_2-S_n$$

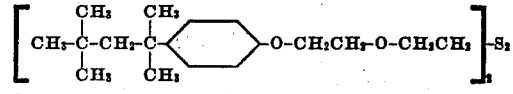
wherein R is an alkylated phenyl group, y' is a number from one to three, inclusive, and n is an integer from two to four, inclusive.

4. As a new compound, an organic polysulfide having the formula:

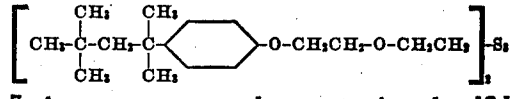
$$(R-O-CH_2CH_2-O-CH_2CH_2)_2\,S_n$$

wherein R is an alkylated benzene ring and n is a number from two to four, inclusive.

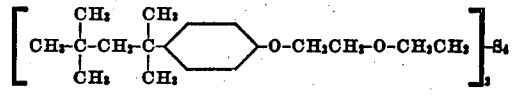
5. As a new compound, an organic polysulfide having the formula:



6. As a new compound, an organic polysulfide having the formula:



7. As a new compound, an organic polysulfide having the formula:



HERMAN A. BRUSON.