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GLYCOL ESTERS OF ALKYL-MERCAPTO-CARBOXYLIC ACIDS

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This invention relates to a new class of compounds which have been found to be particularly suitable for use as synthetic lubricants because of their low pour points, high viscosity indices and good load-carrying characteristics.

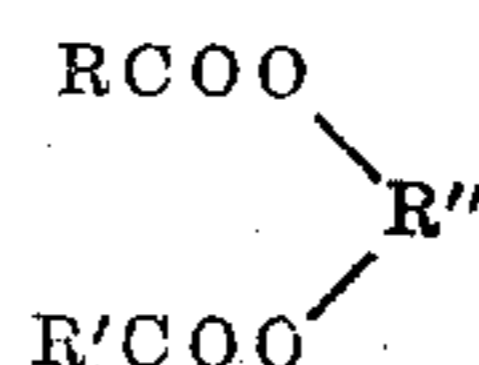
In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the second, addition agents capable of imparting particular properties to available lubricants. Thus, viscosity index improvers and pour depressants are added to automotive lubricants to render the lubricants more adaptable to wide changes in temperature conditions, while other agents are added to improve the load-carrying properties of a lubricant which is to be employed, for example, under extreme pressure conditions.

Recently, in an effort to obtain superior lubricants endowed with specific and superior characteristics, a new field has been explored, namely, the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. In general, they are characterized by higher viscosity indices and lower pour points than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit very low pour points, high viscosity indices, and in addition unusually good load-carrying properties. Lubricants possessing such properties are of special value in the lubrication of engines which are subjected to high temperatures such as combustion turbine engines, particularly those of the "prop-jet" type. Mineral oil lubricants containing added viscosity index improvers, thickeners or other highly non-volatile additives are undesirable for use in such engines because of the tendency to leave a residue which would accumulate and interfere with the operation of the engine. A synthetic lubricant of the type described in the present specification is especially adapted to use under such conditions, since the lubricant contains no additives and thus tends to leave no residue upon volatilization.

The new compounds of the present invention which have been found to be useful as synthetic lubricating oils are glycol esters of sulfur-containing monocarboxylic acids. The glycols may be the paraffin glycols or they may be glycols containing oxygen or sulfur in ether or thioether linkages.

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The new esters of the present invention may be defined more precisely by the general formula



where R and R' are open chain aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms, one or both of which contains a sulfur atom, and may be saturated or unsaturated and may consist of straight or branched chains. The sulfur atom is present as a thioether linkage and is separated from the carboxyl group by at least one carbon atom. The radicals R and R' may be alike or different. R'' of the formula may be a saturated aliphatic hydrocarbon group, straight chain or branched, containing 2 to 18 carbon atoms, or it may be a series of saturated aliphatic hydrocarbon radicals linked by oxygen or sulfur atoms, or by both oxygen and sulfur atoms, provided there are at least two carbon atoms between each carboxyl group and the nearest oxygen or sulfur atom and at least two carbon atoms between each oxygen or sulfur atom in the chain, and provided further that the total number of carbon and oxygen or sulfur atoms in the entire R'' radical is from 5 to 80 and that there are not more than two sulfur atoms in the chain. The compound should have a molecular weight of at least 300.

Many of the sulfur-containing acids employed in preparing the esters of the present invention may be conveniently prepared by reacting an olefin, e. g., diisobutylene, with hydrogen sulfide to form an alkyl mercaptan, after which the mercaptan is reacted with acrylonitrile to form the β -alkylmercaptpropionitrile, and the latter is in turn hydrolyzed to form the β -alkylmercaptpropionic acid. In general, mercaptans react very readily with acrylonitrile or acrylic acid esters to give acids containing sulfur atoms. The mercaptans may be formed from readily obtainable olefins and olefin polymers such as propylene, isobutylene, diisobutylene, triisobutylene, propylene polymers, and the like. Sulfur-containing acids may also be prepared by the reaction of halo-acids with mercaptans, by the addition of mercaptans to unsaturated acids, or by the addition of thioglycolic acid to olefins. It is not intended that this invention be limited to the β -alkylmercaptpropionic acids, although they are preferred from the standpoint of ease of preparation and cost. Acids suitable for use in accordance with the present invention are typified by compounds such as ethylmercaptoacetic acid, β -methylmercaptpropionic acid, β -ethylmercapto-

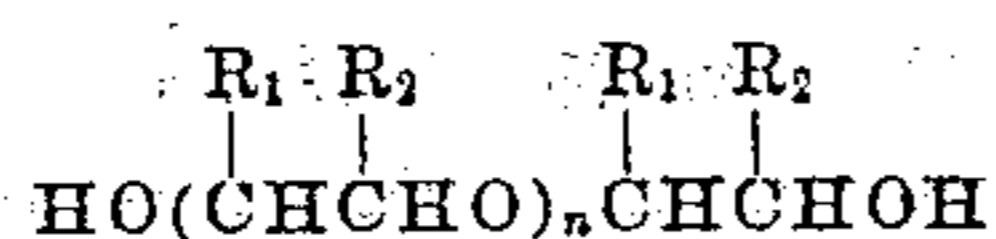
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propionic acid, β -sec.-butylmercaptopropionic acid, β -tert.-butylmercaptopropionic acid, β -tert.-octylmercaptopropionic acid, β -tert.-dodecylmercaptopropionic acid, β -cetylmercaptopropionic acid, β -allylmercaptopropionic acid, γ -octylmercaptobutyric acid, γ -dodecylmercaptobutyric acid, γ -hexadecylmercaptobutyric acid, ω -octylmercaptoundecanoic acid, ω -dodecylmercaptoundecanoic acid, ω -hexadecylmercaptoundecanoic acid, cyclopentylmercaptoacetic acid, pentenylmercaptoacetic acid, α -octylmercaptodimethylacetic acid, α -dodecylmercaptodimethylacetic acid, α -hexadecylmercaptodimethylacetic acid, and the like.

The glycols employed in preparing the esters of the present invention include ethylene glycol and any of the paraffinic homologues of the same containing up to 18 carbon atoms. These may include, for example, ethylene glycol, propylene glycol, butylene glycols, pinacone, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, and decamethylene glycol. Since the glycols may also contain oxygen or sulfur atoms, compounds such as diethylene glycol, triethylene glycol, tetraethylene glycol and the higher members of this series containing carbon and oxygen atoms to a combined total of 80 (exclusive of hydroxyl groups) may be employed. The polyethylene glycols of the formula



where n is 1 to 26, and the polypropylene glycols of the general formula



where either R_1 or R_2 is a methyl group and the other is hydrogen and where n is 1 to 20 are especially useful. Glycols containing sulfur atoms in thioether linkages may also be employed, and these include such compounds as thiodiglycol and 1,2-bis(2-hydroxyethylmercapto)ethane. There may also be used glycols containing both oxygen and sulfur in similar linkages. Such a compound is bis-[2-(2-hydroxy-ethoxy) ethyl] sulfide.

The esterification process may be carried out by known esterification means, preferably with

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dodecylmercaptopropionic acid with various glycols. The last two of the above-named acids were prepared as follows: To a mixture of 12 cc. of Triton B (benzyltrimethylammonium hydroxide) and 2 mols. of the mercaptan (prepared by reacting diisobutylene or triisobutylene with hydrogen sulfide) was added dropwise 3 mols of acrylonitrile at such a rate as to keep the temperature below 50° C. The mixture was then heated to 50° C.-60° C. for two hours, after which the product was poured into water, and an equal volume of ether added and a small quantity of hydrochloric acid to neutralize the Triton B. After stirring, the ether layer was isolated, washed with water, dried over sodium sulfate, and the ether removed on the steam bath. The residue was mixed with 2.1 mols of sodium hydroxide dissolved in 600 cc. of a 50% aqueous ethyl alcohol. This was heated on a steam bath for 40 hours, acidified with hydrochloric acid, extracted with ether, washed with water, dried over a desiccant, and distilled at about 5 mm. pressure.

The β -tert.-octylmercaptopropionic acid, prepared by the above method, was reacted with trimethylene glycol, hexamethylene glycol, triethylene glycol, tetraethylene glycol, and thiodiglycol, respectively, and the β -tert.-dodecylmercaptopropionic acid, also prepared by the above method, was reacted with trimethylene glycol, the following procedure being used as a general esterification procedure: Two mols of the acid and one mol of the glycol were mixed with 1/2% by weight of p-toluenesulfonic acid monohydrate and about 150 cc. of benzene or naphtha as an entraining fluid. The mixture was refluxed in an apparatus provided with a water trap until no more water distilled over, after which it was washed with sodium carbonate solution and with water, and then dried over a desiccant such as Drierite (anhydrous calcium sulfate). The material was stripped at 5 mm. to a bath temperature of 200°-220° C.

The esters prepared by the above method were tested with respect to various properties which are of interest in connection with their proposed use as synthetic lubricating oils, the results being shown below in the table of data.

| Acid | Glycol | Kinematic Viscosity | | ASTM Slope | Viscosity Index | ASTM Pour Point (°F.) | Almen Machine Weights Carried (Gradual Loading) | |
|---|-----------------------------------|---------------------|---------|------------|-----------------|-----------------------|---|--------------------------------|
| | | 100° F. | 210° F. | | | | Alone | 6% in Mineral Oil ¹ |
| β -tert.-Octylmercaptopropionic | Polypropylene glycol ² | 43.970 | 7.865 | 0.634 | 142 | -40 | 15 | 7 |
| | Trimethylene glycol | 43.590 | 6.508 | 0.725 | 110 | <-35 | 6 | |
| Do | Hexamethylene glycol | 54.048 | 8.005 | 0.682 | 122 | <-35 | 15 | 5 |
| | Triethylene glycol | 47.470 | 7.101 | 0.707 | 131 | <-35 | 15 | 9 |
| Do | Petraethylene glycol | 50.745 | 7.764 | 0.680 | 124 | <-35 | 15 | 11 |
| | Thiodiglycol | 145.6 | 15.852 | 0.635 | 116 | -5 | 15 | 7 |
| β -tert.-Dodecylmercaptopropionic | Trimethylene glycol | 163.6 | 12.207 | 0.764 | 60 | -10 | 8 | |

¹ Conventionally refined Coastal naphthenic oil of 40 seconds Saybolt viscosity at 210° F. The unblended mineral oil carries not more than two weights on the Almen machine.

² Molecular weight = 400.

the use of a catalyst such as p-toluenesulfonic acid. If an ester containing two different acid radicals is desired, the glycol is reacted with a mixture of acids.

Data will be given below showing the properties of seven examples of esters which illustrate the present invention, these esters having been prepared by esterifying ethylmercaptoacetic acid, β -tert.-octylmercaptopropionic acid, and β -tert.-

The above data indicate that the esters possess characteristics which render them suitable for general use as lubricating oils. The esters of the present invention may also be blended with mineral lubricating oils to give lubricants of improved viscosity index, pour point, and load-carrying capacity.

For the purpose of increasing the film strength and load-carrying capacity of mineral oils, the

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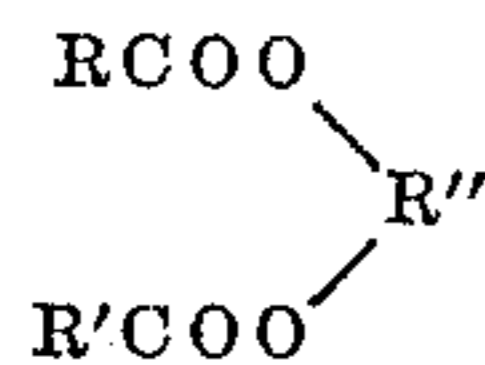
esters are preferably blended in proportions ranging from 1% to 10% by weight of the mineral oil. The data in the last column of the table of data show the usefulness of these compounds when blended with a mineral oil. The unblended mineral oil employed in these tests was capable of carrying only one or two weights on the Almen machine under similar conditions of test.

The mineral lubricating oil base stocks which may be improved in load-carrying capacity by the addition of the new compounds of the present invention may be derived from various types of crude petroleum or may consist of distillates or blends of various kinds which have been refined by any of the conventional methods. Synthetic oils may also be used such as those obtained by the polymerization of olefins or the hydrogenation of coal or its products. The base oils may vary considerably in viscosity and other properties depending upon the particular uses for which they are desired.

If desired, other known addition agents, such as thickeners, pour depressants, antioxidants, dyes, etc., may be added to the mineral oil composition prepared in accordance with this invention.

What is claimed is:

1. As a new composition of matter a compound of the formula



where R and R' are open chain aliphatic hydrocarbon radicals containing 2 to 22 carbon atoms, at least one of the radicals containing a sulfur atom as a thioether linkage, the sulfur atom being separated from the COO group by at least one carbon atom, and where R'' is an organic radical selected from the group consisting of (1) saturated aliphatic hydrocarbon radicals of 2 to 18 carbon atoms and (2) radicals consisting of series of saturated aliphatic hydrocarbon radicals linked through at least one non-carbon atom of the group consisting of oxygen and sulfur, not more than two sulfur atoms being in the radical, each hydrocarbon radical so linked by a non-carbon atom containing at least two carbon atoms, the sum of the carbon atoms and said non-carbon atoms in the entire radical being from 5 to 80, and the molecular weight of the entire compound being at least 300.

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2. A composition according to claim 1 in which R and R' are β -tertiary-octylmercaptoethyl groups and R'' is a saturated hydrocarbon group.

3. A composition according to claim 1 in which R and R' are β -tertiary-octylmercaptoethyl groups and R'' is a polyethylene glycol radical.

4. As a new composition of matter the hexamethylene glycol ester of β -tert.-octylmercapto-propionic acid.

5. As a new composition of matter the triethylene glycol ester of β -tert.-octylmercapto-propionic acid.

6. As a new composition of matter the tetraethylene glycol ester of β -tert.-octylmercapto-propionic acid.

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