

UNITED STATES PATENT OFFICE

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SYNTHETIC LUBRICANTS

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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.

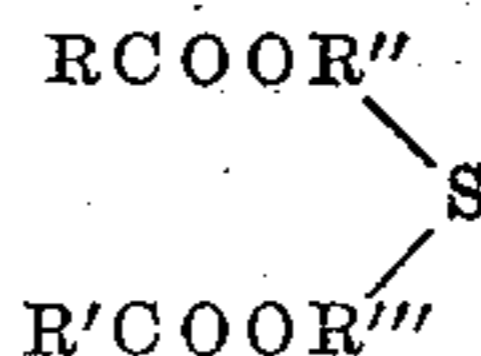
In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the 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 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

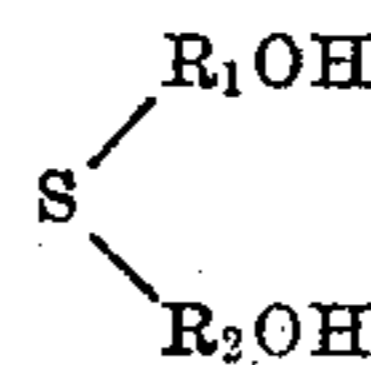
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which have been found to be useful as synthetic lubricating oils are esters of glycols containing a sulfur atom in a thioether linkage, such glycols being esterified by at least one branched chain saturated monocarboxylic acid. More exactly, the new esters may be defined by the formula:



where R and R' each represent an alkyl radical containing 8 to 20 carbon atoms, at least one of such radicals having a branched chain, and where R'' and R''' each represent an alkylene radical containing 2 to 5 carbon atoms or a series of alkylene radicals interconnected by oxygen atoms, the number of carbon atoms in each such alkylene radical being 2 to 4 and the number of interconnected oxygen atoms being not greater than 5.

Suitable glycols which contain no oxygen atoms in ether linkages are of the type—



These may be obtained by reacting two mols of a chlorinated alcohol with one mol of sodium sulfide under conditions which permit the separation of the by-product sodium chloride from the reaction product, or by reacting an olefin oxide with hydrogen sulfide. Glycols containing both sulfur and oxygen interlinked between carbon atoms may be formed by reacting thiodiglycol or similar compounds with alkylene oxides in various proportions. Typical examples of sulfur-containing glycols of the above types are as follows:

- 3-thia-2,4-dimethyl-1,5-pentanediol
- 3,9-di-oxa-6-thia-2,10-di-methyl-1,11-undecanediol
- 4-thia-1,7-heptanediol
- 5-thia-1,9-nonanediol
- 3,9-di-oxa-6-thia-1,11-undecandiol
- 3,6,12,15-tetra-oxa-9-thia-1,17-heptadecanediol

The acids which are used to esterify the above described glycols are saturated aliphatic monocarboxylic acids, at least one mol of such acid having a branched chain being used in the esteri-

fication: Typical examples of acids of this type which may be employed commercially are 2-ethylhexanoic acid, C₉ "Oxo" acid from diisobutylene, C₈ "Oxo" acid from C₇ propylene polymer, C₁₂ "Oxo" acid from C₁₁ propylene-butylene co-poly-

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

| Acid | Glycol | Flash Point, °F. | Kinematic Viscosity— | | ASTM Slope | Viscosity Index | ASTM Pour Point, °F. | Almen Machine Weights Carried (Gradual Loading) |
|--|----------------|------------------|----------------------|---------|------------|-----------------|----------------------|---|
| | | | 100° F. | 210° F. | | | | |
| 2-Ethylhexanoic..... | Thiodiglycol.. | 415 | 13.740 | 3.136 | 0.777 | 98 | <-75 | 7 |
| C ₉ "Oxo" acid..... | do..... | 425 | 17.400 | 3.866 | 0.725 | 134 | -65 | 5 |
| 2-Ethylhexanoic Caprylic acid..... | do..... | 420 | 10.503 | 2.784 | 0.751 | 122 | +25 | 8 |
| C ₉ "Oxo" acid Caprylic acid..... | do..... | 450 | 12.448 | 3.237 | 0.714 | 146 | -5 | 6 |
| Caprylic acid..... | do..... | 425 | 12.858 | 3.497 | 0.674 | 172 | +65 | 15 |

mer, and the like. When one of the acid radicals of the ester molecule is a saturated chain acid radical, typical acids which may be used include caprylic acid, capric acid, lauric acid, and the like. The "Oxo" acids are prepared by the oxidation of "Oxo" alcohols, which are formed by the reaction of carbon monoxide and hydrogen upon olefinic materials obtainable from petroleum products and hydrogenation of the resulting aldehydes. The C₉ "Oxo" acid is thus formed from a C₈ olefin, and the carbon atom of the carboxyl group is included in the number of carbon atoms indicated.

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

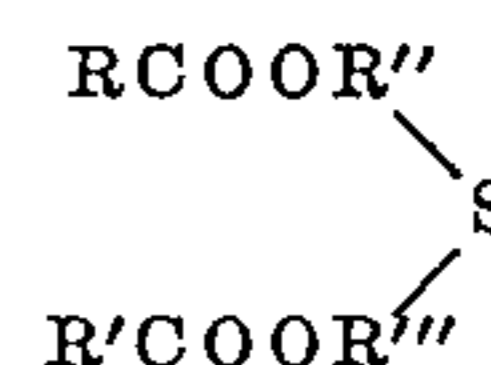
Data will be given below showing the properties of several examples of esters which illustrate the present invention, these esters having been prepared by esterifying thiodiglycol with 2-ethylhexanoic acid, C₉ "Oxo" acid, a mixture of equal molecular proportions of 2-ethylhexanoic acid and caprylic acid, and a mixture of equal molecular proportions of C₉ "Oxo" acid and caprylic acid, respectively. For comparison, the caprylic acid ester of thiodiglycol is included. In all cases the thiodiglycol was completely esterified. The following procedure was used in the esterification process in all cases:

Two mols of the acid or acid mixture and one mol of the glycol were mixed with ½% 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 off, after which it was washed with an aqueous 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. pressure to a bath temperature of 200-220° C.

The above data indicate that the esters of the present invention possess characteristics which render them suitable for general use as lubricating oils. The data show clearly that the presence of branched chain acid radicals has a pronounced effect in lowering the pour point of the esters. Extremely low pour points, of the order of -65° F. and below, were obtained when the ester contained two branched chain acid radicals. The esters may be blended with mineral lubricating oils, if desired, to give lubricants of improved viscosity index, pour point and load carrying capacity.

What is claimed is:

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



where R and R' are alkyl radicals containing 8 and 20 carbon atoms each, at least one of such radicals being a C₈ to C₁₁ "Oxo" radical, and where R'' and R''' are alkylene radicals containing 2 to 5 carbon atoms each.

2. A composition according to claim 1 in which both R and R' represent a C₈ "Oxo" radical.

3. A composition according to claim 1 in which R'' and R''' each represent—



4. As a new compound the di-C₉ "Oxo" acid ester of thiodiglycol.

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The following references are of record in the file of this patent:

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