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SYNTHETIC LUBRICANT

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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 and high viscosity indices.

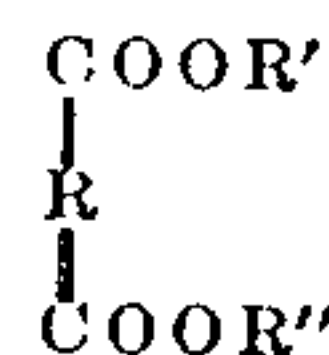
In the lubricant art, considerable progress has been realized in recent years in the production of lubricants characterized by one or more specific properties and adapted for particular uses. In the main, this progress can be attributed to two developments: the first, new refining procedures, and the 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, lower pour points, and higher flash points than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit high viscosity indices and in many cases very low pour points. Those esters which do not exhibit a pour point which is sufficiently low for use without additive may be made useful by simply adding a pour depressant, as in the case of mineral oils. The esters possessing both high viscosity indices and low pour points 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

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which accumulates and interferes 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 particularly suitable for use as lubricating oils are esters of dicarboxylic acids which contain one or more atoms of oxygen and/or sulfur in ether or thioether linkages, and in which the alcohol residue is a long chain aliphatic hydrocarbon radical or a hydrocarbon radical containing oxygen and/or sulfur in ether or thioether linkages. More precisely, the new class of compounds may be defined by the general formula



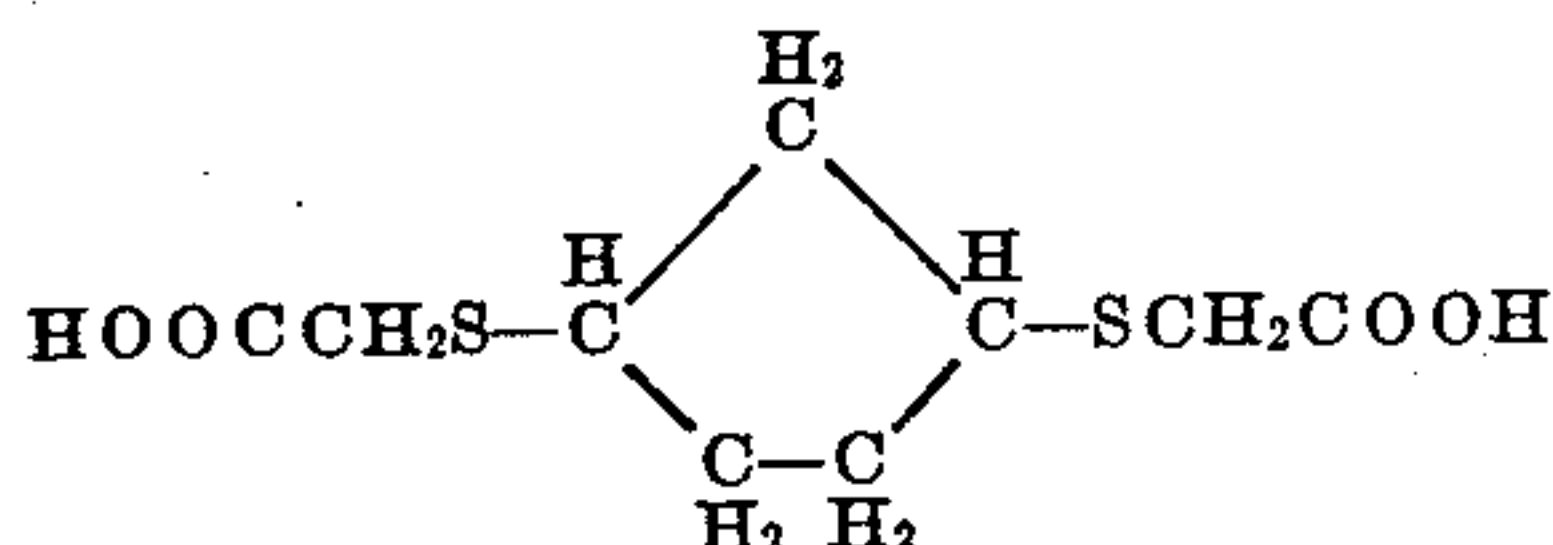
where R is an organic group which consists of hydrocarbon radicals interlinked by at least one atom of oxygen and/or sulfur, the total number of carbon and oxygen or sulfur atoms in the group being from 3 to 85 and the number of sulfur atoms being not greater than 2. In this group there is at least one carbon atom between each carboxyl group and the nearest oxygen or sulfur atom and at least two carbon atoms between any two oxygen and/or sulfur atoms. The hydrocarbon radicals in group R may be of any hydrocarbon type, whether aliphatic, cycloaliphatic, aromatic, or aliphatic-aromatic, whether straight or branched, and whether saturated or unsaturated, although compounds in which such hydrocarbon radicals are saturated aliphatic radicals are generally preferred. R' and R'' of the formula are organic groups, alike or unlike, and may consist of aliphatic hydrocarbon radicals containing a total in the two groups of 16 to 40 carbon atoms, or they may be groups each consisting of a series of saturated aliphatic hydrocarbon radicals interlinked by 1 to 5 oxygen

and/or sulfur atoms (not more than 2 sulfur atoms), the total number of carbon, oxygen, and sulfur atoms in the two groups being from 8 to 40. When the groups contain oxygen or sulfur atoms, there should be at least two carbon atoms between any two such non-carbon atoms and between the carboxyl group and the nearest atom of oxygen or sulfur. The hydrocarbon group at the end of a chain may contain one or more carbon atoms. To produce a composition which will have a sufficiently high viscosity to be useful as a lubricant the components of the composition should be chosen so that the molecular weight thereof is at least 300. It is also preferable to prepare compounds having a viscosity not greater than 150 seconds (Saybolt) at 210° F.

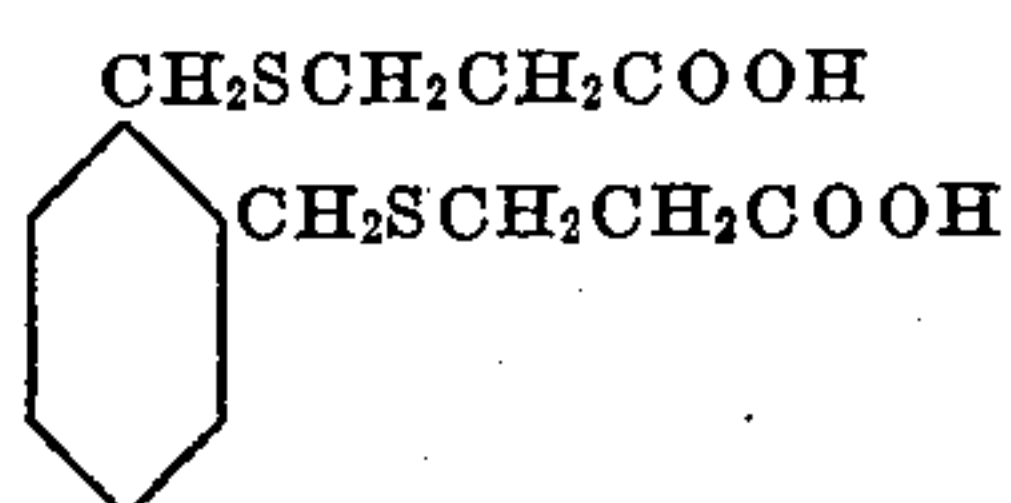
The esterification process can be carried out by the usual methods, preferably employing an esterification catalyst, such as p-toluene sulfonic acid, and a water-entraining agent.

Illustrative examples of the dibasic acids which may be employed in the synthesis of the esters of the present invention are the following: diglycolic acid, thiodiglycolic acid, ethylene-bis-glycolic acid, β -oxydipropionic acid, o-di(2-thia-4-carboxybutyl) benzene, 4,7-di-oxa--1,10-decanedioic acid, 4,7,10,13-tetra-oxa-1,16-hexadecanedioic acid, 4,10-di-oxa-7-thia-1,13-tridecanedioic acid, 4,7,10,13,16-penta-oxa-1,19-nonadecanedioic acid, and 4,7-di-thia-1,10-decanedioic acid.

In addition to the above, it has been found advantageous to prepare esters from dibasic acids which are addition products of unsaturated dibasic acids and alcohols or mercaptans or of monobasic hydroxy and/or mercapto aliphatic acids and diolefins. For example, two mols of thioglycolic acid and one mol of cyclopentadiene may be reacted together to form a product probably having a composition of the type



and such an acid may be reacted with alcohols to form esters suitable for use in accordance with the present invention. Similarly, thioglycolic acid may be reacted with vinyl cyclohexene or other diolefins. In a similar manner, addition products may be formed between unsaturated acids, e. g., maleic acid, and alcohols or mercaptans. The addition product of a maleic acid ester and dodecyl mercaptan is an example of such a product. Such addition products may be conveniently formed by bubbling air through a mixture of the mercapto-acid and olefin or refluxing the unsaturated ester with the mercaptan in the presence of an acid catalyst such as SnCl_4 . Also, carboxylic acid derivatives of substituted benzenes may be employed. An example of this type of product is the compound



The monohydric alcohols employed in esterifying the dibasic acids described above are typified by the following:

Methyl alcohol
Ethyl alcohol

- n-Propyl alcohol
- n-Butyl alcohol
- Isobutyl alcohol
- n-Amyl alcohol
- 5 Isoamyl alcohol
- n-Octyl alcohol
- 2-ethylhexyl alcohol
- Cetyl alcohol
- 10 Oleyl alcohol
- Ethylene glycol mono-n-butyl ether
- Ethylene glycol mono-2-ethylbutyl ether
- Ethylene glycol mono-2-ethylhexyl ether
- Ethylene glycol monoisooctyl ether
- 15 β -n-Butylmercaptoethanol
- β -Tert.-octylmercaptoethanol
- β -n-Dodecylmercaptoethanol
- Diethylene glycol mono-n-butyl ether
- 20 Diethylene glycol mono-2-ethylbutyl ether
- Diethylene glycol mono-2-ethylhexyl ether
- Propylene glycol mono-butyl thioether
- Propylene glycol mono-tert.-octyl thioether
- 25 Propylene glycol mono-n-dodecyl thioether
- n-Butylmercaptoethoxyethanol
- Tert.-octylmercaptoethoxyethanol
- n-Dodecylmercaptoethoxyethanol
- n-Butylmercaptopropoxypropanol
- 30 Tert.-octylmercaptopropoxypropanol
- n-Dodecylmercaptopropoxypropanol
- Propylene glycol mono-n-butyl ether
- Dipropylene glycol monomethyl ether
- 35 Dipropylene glycol monoethyl ether
- Dipropylene glycol mono-n-butyl ether
- Tripropylene glycol monomethyl ether
- Tripropylene glycol monoethyl ether
- Tripropylene glycol mono-n-butyl ether
- Propylene glycol monoisopropyl ether
- Dipropylene glycol monoisopropyl ether
- Tripropylene glycol monoisopropyl ether

Many of the above listed ether alcohols, formed by the reaction of ethylene oxide or propylene oxide with aliphatic alcohols, are known in the industry as "Dowanols," "Carbitols," or "Cello-solves."

A group of alcohols especially adapted for use in connection with the present invention are the so-called "Oxo" alcohols, prepared by the reaction of carbon monoxide and hydrogen upon the olefins obtainable from petroleum products and hydrogenation of the resulting aldehydes. Materials such as diisobutylene and C_7 olefins are suitable for this purpose; also higher molecular weight olefinic materials are sometimes employed. The alcohols obtained in this manner are primary alcohols and normally have a branched chain structure.

In the table below will be shown data obtained in tests of the properties of several typical esters illustrating the present invention. The esterification process was carried out in each case by the following procedure: A mixture of one mol of dibasic acid, 2.2 mols of alcohol, 0.5 weight percent of p-toluene-sulfonic acid monohydrate, and 100 to 200 mls. of a water-entraining agent such as naphtha, benzene, toluene or the like, is refluxed until no more water is collected in an esterification water trap. The product is washed until neutral with saturated aqueous Na_2CO_3 solution and then with water. After drying over a desiccant, such as anhydrous CaSO_4 , the material is stripped at a pressure of 5 mm. to a bath temperature of 200-225° C.

The data obtained in the tests of properties of the esters obtained as described are shown in the following table:

two carbon atoms between each pair of said oxygen atoms and at least one carbon atom between the carboxyl group and the nearest of said oxygen

Components of Ester		Flash Point, °F.	Kinematic Viscosity		ASTM Slope	Viscosity Index	ASTM Pour Point, °F.
Acid	Alcohol		100° F.	210° F.			
Diglycolic	n-Decyl	410	16.360	3.696	0.731	130	80
Do	C ₁₁ "Oxo"	390	21.840	4.083	0.773	91	<-35
β-Oxydipropionic	n-Decyl		25.540	5.298	0.673	150	<-35
Do	C ₁₃ "Oxo"	415	226.900	25.160	0.565	126	-20
Ethylene-bis-glycolic	C ₁₀ "Oxo"	445	19.230	3.990	0.743	120	<-35
Do	Butyl Carbitol	440	23.950	4.590	0.732	121	<-35
4,7-Di-oxa-1,10-decane-dioic	C ₁₂ -C ₁₃ "Oxo"	410	22.97	4.97	0.672	155	0
Do	Butyl Carbitol		16.600	3.962	0.694	158	<-35
4,7,10,13-Tetra-oxa-1,16-hexadecanedioic	C ₈ "Oxo"	355	13.700	3.487	0.702	154	<-35
4,7,10,13,16-Pentaoxa-1,19-nonadecanedioic	do	425	32.610	6.578	0.634	152	<-35
Thiodipropionic	2-Ethylhexyl	410	11.596	2.911	0.760	113	<-35
Do	C ₈ "Oxo"	395	13.890	3.480	0.710	148	<-35
Do	C ₉ "Oxo"		18.410	4.133	0.705	148	<-35
Do	C ₁₀ "Oxo"		19.880	4.385	0.695	152	<-35
Do	Butyl Carbitol		17.180	4.007	0.698	155	<-35
4,7-Di-thia-1,10-decane-dioic	β-(tert.-Octyl-mercapto)-ethanol		74.062	9.892	0.670	119	<-35
4,10-Di-oxa-7-thia-1,13-tridecanedioic	Butyl Carbitol	485	26.580	5.449	0.670	149	<-35
Adduct:	C ₈ "Oxo"	415	22.840	4.782	0.692	146	<-35
2 mols Thioglycolic	n-Decyl		32.210	5.973	0.681	138	<-35
1 mol Isoprene							
Adduct:	do		19.660	4.306	0.703	148	<-35
2 mols Thioglycolic							
1 mol Cyclopentadiene	do		21.410	4.680	0.683	154	<-35
Adduct:							
2 mols Thioglycolic	Isoamyl	415	13.990	3.642	0.683	167	-10
1 mol Vinylcyclohexene							
Adduct:	Butyl Carbitol		20.660	4.722	0.666	164	<-35
1 mol Thioglycolic							
1 mol Undecylenic	Butyl Cellosolve		16.55	4.061	0.677	169	5
Adduct:							
1 mol Thioglycolic	C ₈ "Oxo"	455	30.610	5.993	0.664	146	-15
1 mol Oleic							
Adduct:	n-Decanol	475	24.760	5.156	0.676	150	30
1 mol Maleic							
1 mol n-Dodecylmercaptan	C ₈ "Oxo"	460	23.970	4.742	0.714	133	25
Adduct:							
1 mol Maleic	Tripropylene glycol monoisopropyl ether.	355	57.91	8.31	0.683	120	5
1 mol n-Dodecylmercaptan							
Adduct:	C ₈ "Oxo"	440	32.910	5.882	0.697	131	10
1 mol Itaconic							
1 mol n-Dodecylmercaptan	Butyl Carbitol	415	55.950	9.822	0.599	144	50
Adduct:							
1 mol Itaconic	C ₁₁ -C ₁₂ "Oxo"	395	50.84	7.63	0.689	120	<-35
1 mol tert.-Dodecyl mercaptan							
Adduct:	Tripropylene glycol monoisopropyl ether.	360	134.9	11.315	0.754	71	-5
1 mol Itaconic							
1 mol tert.-Dodecyl mercaptan	Butyl Carbitol	460	31.780	6.477	0.634	153	-10
Adduct:							
1 mol Oleic	C ₁₁ -C ₁₂ "Oxo"		27.660	5.197	0.709	131	-40
1 mol Thioglycolic							
o-Di(2-thia-4-carboxy-butyl) benzene							

The above data indicate that the esters constituting the subject matter of the present invention possess characteristics, particularly with regard to viscosity index and pour point, which indicate their suitability 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 and pour point.

What is claimed is:

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



where R is an organic group consisting of saturated aliphatic hydrocarbon radicals inter-linked by at least two oxygen atoms, the total number of carbon and said oxygen atoms in the group R being from 3 to 85, the number of oxygen atoms being at least 2, in which there are at least

atoms; where R' and R'' are organic groups selected from the class consisting of (1) saturated branched chain aliphatic hydrocarbon radicals containing a total in the two groups of 16 to 40 carbon atoms and (2) radicals consisting of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 non-carbon atoms in each group of the class of elements consisting of oxygen and sulfur, the number of sulfur atoms being not greater than 2, and the total number of carbon and said non-carbon atoms in the two groups R' and R'' being from 8 to 40, there being at least 2 carbon atoms between each pair of said non-carbon atoms and between the carboxyl group and the nearest such non-carbon atom; the components of the composition being so chosen that the molecular weight thereof is at least 300.

2. A composition according to claim 1 in which the groups R' and R'' are each saturated branched chain aliphatic hydrocarbon radicals and contain a total in the two groups of 16 to 40 carbon atoms.

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3. A composition according to claim 1 in which each of the groups R' and R'' consists of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 non-carbon atoms of the class of elements consisting of oxygen and sulfur.

4. As a new composition of matter the ester formed by reacting one molecular proportion 4,7-di-oxa-1,10-decanedioic acid and two molecular proportions of butyl carbitol.

5. As a new composition of matter the ester formed by reacting one molecular proportion of 4,7,10,13 - tetra-oxa - 1,16 - hexadecanedioic acid with two molecular proportions of C₈ "Oxo" alcohol.

6. As a new composition of matter the ester formed by reacting one molecular proportion of 4,7,10,13,16-penta-oxa-1,19-nonadecanedioic acid with two molecular proportions of C₈ "Oxo" alcohol.

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