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DIALKYLALKENYLSUCCINATES

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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 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 alkenyl dibasic and tribasic carboxylic acids in which the alkenyl group contains 3 to 24 carbon atoms and in which the total number of carbon atoms in the molecule, exclusive of the alkenyl group, is

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from 4 to 7. To form the esters of the present invention these acids may be esterified with primary monohydric alcohols containing 1 to 18 atoms or with monohydric alcohols containing oxygen or sulfur in ether or thioether linkages. In the latter case the oxygen or sulfur atoms are separated by a chain of at least two carbon atoms, and there is always a chain of at least two carbon atoms between the hydroxyl group and the first atom of oxygen or sulfur. It is not desirable to employ an alcohol containing more than two sulfur atoms, but there is no limit to the number of oxygen atoms which may be present. However, it is desirable, when employing alcohols containing oxygen or sulfur atoms, to employ alcohols in which the total number of carbon, oxygen and sulfur atoms, exclusive of the hydroxyl group, is from 4 to 20. The esterifying groups in a given ester may be alike or different, but the acid and esterifying alcohols should be so chosen that the resulting ester has a molecular weight of at least 300.

The alkenyl dicarboxylic and tricarboxylic acids employed in preparing the esters of the present invention may be conveniently prepared by condensing monoolefins with suitable acids or acid anhydrides, employing an elevated temperature, for example, 160° C. or higher, the acids or anhydrides having a double bond between two carbon atoms conjugated with one or more carboxyl groups. The condensation process results in the formation of an alkenyl substituted saturated polycarboxylic acid or acid anhydride. For example, when an olefin is condensed with maleic anhydride there is formed an alkenylsuccinic acid anhydride. Examples of acids or acid anhydrides which may be reacted with olefins in this manner are the following: maleic, citraconic, ethylmaleic, glutaconic, itaconic, methylitaconic, dimethylitaconic, hydromuconic, aconitic and methylaconitic.

For introducing the alkenyl groups desired in accordance with the present invention any monoolefin having from 3 to 24 carbon atoms may be employed. Such olefins include normal and branched chain olefins and polymers of the same, as well as mixtures of olefins occurring in technical products. Examples of suitable olefins include propylene, n-butylene, isobutylene, 2-ethyl-1-butene, diamylene, 1-decene, 1-tetradecene, 1-octadecene, C_{16}–C_{18} olefins from the Fischer synthesis, C_{17}–C_{18} polypropylene, C_{24} polypropylene, C_{24} dechlorinated wax, cracked gasoline, and similar products.

All of the alkenyl substituted dicarboxylic or tricarboxylic acids or anhydrides of the type described above may be esterified by reaction with an alcohol, employing the usual esterification methods, preferably with the aid of an esterification catalyst such as p-toluene sulfonic acid, and

a water entraining agent. Typical examples of suitable alcohols which may be employed are the following:

Methyl alcohol
Ethyl alcohol
n-Propyl alcohol
n-Butyl alcohol
Isobutyl alcohol
n-Amyl alcohol
Isoamyl alcohol
n-Octyl alcohol
2-ethylhexyl alcohol
Cetyl alcohol
Oleyl alcohol
Ethylene glycol mono-n-butyl ether
Ethylene glycol mono-2-ethylbutyl ether
Ethylene glycol mono-2-ethylhexyl ether
Ethylene glycol monoisooctyl ether
β-n-Butylmercaptoethanol
β-Tert.-octylmercaptoethanol
β-n-Dodecylmercaptoethanol
Diethylene glycol mono-n-butyl ether
Diethylene glycol mono-2-ethylbutyl ether
Diethylene glycol mono-2-ethylhexyl ether
Propylene glycol mono-butyl thioether
Propylene glycol mono-tert.-octyl thioether
Propylene glycol mono-n-dodecyl thioether
n-Butylmercaptoethoxyethanol
Tert.-octylmercaptoethoxyethanol
n-Dodecylmercaptoethoxyethanol
n-Butylmercaptopropoxypropanol
Tert.-octylmercaptopropoxypropanol
n-Dodecylmercaptopropoxypropanol
Propylene glycol mono-n-butyl ether
Dipropylene glycol monomethyl ether
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 "Cellosolves."

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 the tests of various properties of a number of esters illustrating the present invention which indicate the usefulness of these esters as synthetic lubricating oils. All of these esters were derived from alkenylsuccinic acids having alkenyl groups of varying length. In some cases the two esterifying groups are of quite different chain length. Where two alcohols are shown, one mol of each alcohol was reacted with one mol of the acid. The general method employed in preparing anhydrides of the alkenylsuccinic acids consisted in heating maleic anhydride in the presence of an olefin in a bomb overnight at a temperature of 220° C., after which the product was heated in a vacuum to strip off the excessive olefin and any unreacted maleic anhydride. The esterification was carried out by refluxing a mixture consisting of 1 gram mol of the alkenylsuccinic acid, 2.2 gram mols of alcohol (or 1.1 gram mols each of two different alcohols), 2.5 grams of p-toluene sulfonic acid monohydrate (catalyst) and 100 ml. toluene or similar hydrocarbon medium in an apparatus fitted with a reflux condenser and water trap until no more water collected in the trap, after which the resulting mixture was washed with a sodium carbonate solution and water, dried by means of a desiccant, and stripped of solvent by heating under vacuum.

The results of tests of the properties of various esters are shown in the following table:

Esters of alkenyl succinic acids

Olefins Employed in Alkylation	Alcohol	Flash Point (°F.)	ASTM Pour Point (°F.)	Kinematic Viscosity		ASTM Slope	Viscosity Index
				100° F.	210° F.		
Isobutylene	n-Decyl	390	<−35	15.572	3.490	0.752	115
2-Ethyl-1-butene	do	380	<−35	33.980	5.671	0.727	117
Do	Butyl carbitol		<−35	34.720	5.570	0.742	108
Diamylene	n-Decyl	450	−20	180.500	16.820	0.659	106
1-Decene	Ethyl		<−35	6.990	2.188	0.751	131
C_{10}–C_{12} olefin	n-Amyl	390	<−35	26.91	4.111	0.838	19
Do	C_8 Oxo	395	−20	53.948	6.165	0.813	51
Do	Butyl carbitol	410	<−35	38.660	5.631	0.769	89
Do	Butyl cellosolve	395	<−35	31.35	4.697	0.805	57
Do	n-Decyl	425	<−35	37.800	5.752	0.750	99
Do	Methyl+n-decyl	365	<−35	35.420	5.146	0.791	73
Do	Methyl+C_{11}–C_{13} Oxo	435	(?)+30	59.753	6.799	0.791	65
Do	n-Amyl	370	<−35	29.11	4.496	0.809	53
C_{12}–C_{14} olefin	2-Ethylhexyl	435	−45	42.72	5.65	0.803	69
Do	n-Decyl	400	<−35	40.73	6.238	0.728	110
Do	Butyl cellosolve	410	<−35	33.56	5.000	0.791	72
Do	Butyl carbitol	430	<−35	35.540	5.681	0.739	109
Do	Ethyl		−25	13.720	3.175	0.767	106
1-Tetradecene	n-Amyl	460	<−35	28.970	5.257	0.718	126
C_{14}–C_{18} olefin	n-Decyl	490	−10	35.530	6.246	0.687	132
Do	Methyl+n-decyl	395	−25	33.620	5.702	0.720	120
Do	Ethyl+n-decyl	435	−25	28.260	5.127	0.723	123
Do	Isobutyl+n-Tetradecyl	460	+35	38.770	6.467	0.695	126
Do	n-Decyl	415	−15	235.7	21.61	0.625	112
C_{16}–C_{18} Fischer olefins	do	420	−20	152.10	14.010	0.692	96
C_{17}–C_{18} Polypropylene	do	460	+25	37.270	6.562	0.676	134
1-Octadecene	do	480	+65	76.363	11.085	0.628	130
C_{24} Dechlorinated wax	Methyl+n-decyl	435	+65	84.400	11.245	0.645	123
Do	C_8 Oxo	435	+65	75.963	10.283	0.660	122
Do	n-Decyl	395	−10	271.100	19.960	0.680	93
C_{24} Polypropylene	Methyl+n-decyl	455	−5	230.500	15.442	0.741	65
Do							

The above data indicate that the esters constituting the subject matter of the present invention possess characteristics, particularly with regard to the pour point, viscosity-temperature characteristics, viscosity index, and slope on the ASTM chart D341–32T, which indicate clearly 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 characteristics.

What is claimed is:

1. As a new composition of matter an aliphatic alcohol diester of an alkenylsuccinic acid containing a single alkenyl group of 4 to 24 carbon atoms, in which the alcohol radicals are selected from the group consisting of (1) alkyl groups of 2 to 14 carbon atoms and (2) alkoxy radicals of the type

$$C_4H_9(OCH_2CH_2)_nOH$$

where n is an integer from 1 to 2.

2. Di-n-decyl isobutenylsuccinate.
3. Di-n-decyl ethylbutenylsuccinate.
4. Diethyl decenylsuccinate.

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