Patented Nov. 13, 1951

2,575,196

UNITED STATES PATENT OFFICE

2,575,196

MIXED ESTERS OF POLYHYDRIC ALCOHOLS AND DIBASIC ACIDS

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No Drawing. Application October 1, 1948, Serial No. 52,430

7 Claims. (Cl. 260—485)

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This invention relates to a new class of compounds which have been 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, from 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 interests 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, and high viscosity indices. 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 nonvolatile 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

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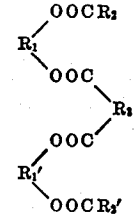
which have been found to be particularly suitable for use as lubricating oils are complex esters prepared by reacting one molecular proportion of a monobasic aliphatic acid with one molecular proportion of a glycol, thereby forming a half ester of the glycol, after which two molecular proportions of such half ester are reacted with one molecular proportion of a dibasic aliphatic acid. The esters are formed by simple reaction of the component parts, without heating or otherwise treating the product to form a polymerized or resinous material. It is usually desirable to employ an esterification catalyst such as p-toluenesulfonic acid. The reactions are conducted by the usual esterification methods, removing water as formed, as by means of a water trap attached to a refluxing condenser. A reaction medium or water-entraining medium, such as naphtha, benzene, toluene, or the like, is usually employed.

The new class of compounds may be broadly defined by the following general formula:



where R_1 and R_1' are glycol radicals which may consist of saturated aliphatic hydrocarbon groups, straight chain or branched, containing 2 to 20 carbon atoms each, or they may each represent a series of saturated aliphatic hydrocarbon radicals interlinked by one or more oxygen or sulfur atoms, or 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 pair of oxygen and/or sulfur atoms in the chain, and provided further that the total number of carbon, oxygen and sulfur atoms in each radical is from 5 to 80 and the number of sulfur atoms in each radical is not greater than two. R_2 and R_2' of the formula each represent

an aliphatic hydrocarbon radical, straight chain or branched, saturated or unsaturated, containing 1 to 22 carbon atoms, or they may represent organic radicals consisting of groups of short aliphatic hydrocarbon radicals interlinked by oxygen atoms, provided that the number of oxygen atoms in each radical is not greater than 5 and provided that there is at least one carbon atom between the carboxyl group and the first oxygen atom and at least two carbon atoms between each pair of oxygen atoms, the total number of carbon and oxygen atoms in the radical being from 3 to 22, or the radicals R_2 and R_2' may represent organic radicals each consisting of an aliphatic hydrocarbon chain containing a single interlinking sulfur atom, such sulfur atom being separated from the carboxyl group by at least one carbon atom, the total number of carbon and sulfur atoms in the radical being from 3 to 22, R_3 of the formula is an aliphatic hydrocarbon radical, straight chain or branched, saturated or unsaturated, containing 0 to 30 carbon atoms, or it may be an organic radical consisting of a series of saturated aliphatic hydrocarbon radicals interlinked by one or more atoms of oxygen or sulfur, or both oxygen and sulfur, provided there are at least two carbon atoms between each pair of oxygen or sulfur atoms, provided there are not more than two sulfur atoms in each chain, provided there is at least one carbon atom between the carboxyl group and the first oxygen or sulfur atom, and provided that the total number of carbon, oxygen, and sulfur atoms in the entire radical R_3 is from 3 to 80. The molecular weight of the entire ester should be at least 300 and the viscosity at 210° F. should not be greater than 150 seconds (Saybolt) to provide a product having lubricating properties.

Among the various components of the complex esters of the present invention, certain preferences may be pointed out as giving the optimum of desired properties from the standpoint of service as a lubricant. The preferred glycols are the polyethylene glycols of the formula

$$HO(CH_2CH_2O)_nCH_2CH_2OH$$

where n is 1 to 26. The preferred monobasic acids are the fatty acids containing 2 to 10 carbon atoms per molecule. The preferred dibasic acids are the straight chain dibasic acids of the paraffinic group having from 6 to 10 carbon atoms per molecule.

Among the monobasic acids which may be employed in the preparation of the esters of the present invention the following may be listed as illustrative:

Acetic acid
Propionic acid
Butyric acid
Valeric acid
Caproic acid
Caprylic acid
Lauric acid
Palmitic acid
Stearic acid
Oleic acid
β-Methoxypropionic acid
β-Ethoxypropionic acid
β-tert.-Octoxypropionic acid
β-Ethylmercaptopropionic acid
β-tert.-Octylmercaptopropionic acid
β-tert.-Dodecylmercaptopropionic acid

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 20 carbon atoms. These may include, for example, ethylene glycol, propylene glycol, butylene glycols, pinacone, trimethylene glycol, tetramethylene glycol, pentamethylene glycol, and the like. Since the glycols may also contain oxygen or sulfur atoms, compounds such as diethylene glycol, triethylene glycol, the polyethylene glycols of the formula

$$HO(CH_2CH_2O)_nCH_2CH_2OH$$

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

$$HO(\underset{\displaystyle R_1}{\underset{|}{CH}}-\underset{\displaystyle R_2}{\underset{|}{CH}}O)_nCH-\underset{\displaystyle R_2}{\underset{|}{CH}}OH$$

where R_1 or R_2 is a methyl group and the other is hydrogen, and where n is 1 to 20, may likewise be employed. 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 also may be used glycols containing both oxygen and sulfur in similar linkages; such a compound is bis-[2-(2-hydroxyethoxy)ethyl]sulfide.

Illustrative examples of the dibasic acids which may be employed in the synthesis of the complex esters of the present invention are the following:

Oxalic acid
Malonic acid
Succinic acid
Glutaric acid
Adipic acid
Pimelic acid
Suberic acid
Azelaic acid
Sebacic acid
Brassylic acid
Pentadecanedicarboxylic acid
Tetracosanedicarboxylic acid
C_4—C_{24} Alkenylsuccinic acids
Diglycolic acid
Thiodiglycolic acid

The C_4—C_{24} alkenyl succinic acids listed above are prepared by condensing olefins or mixtures of olefins with maleic anhydride.

If desired, various addition agents may be incorporated in the esters of the present invention for the purpose of improving their properties with respect to their usefulness as lubricants. For example, antioxidants, viscosity index improvers, thickeners, dyes, etc., may be added.

Data will be given below showing the preparation of several examples of complex esters within the scope of the present invention, indicating the adaptability of these esters to lubricating service. All of these esters were prepared by a general esterification method which may be described in detail as follows: In a 1-liter round bottom reaction flask, fitted with a reflux condenser and water trap, were placed one mol of monobasic acid, one mol of glycol, 2.5 grams of p-toluenesulfonic acid monohydrate (catalyst), and 100 ml. toluene. The mixture was refluxed until no more water collected in the water trap. After cooling, 0.5 mol of dibasic acid was added and the refluxing process resumed until again no more water collected in the trap. The mixture was washed with three 100 ml. portions of saturated aqueous sodium carbonate solution and one 100 ml. portion of water. After drying with "Drierite" (anhydrous calcium sulfate) the material was filtered and stripped at a pressure of about 5 mm. to a bath temperature of about 225° C.

The results of tests of various properties of

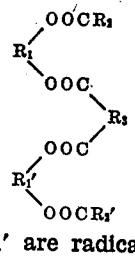
esters prepared by the above general method are shown in the table of data as follows:

Component of Ester	Flash Point (° F.)	Kinematic Viscosity		ASTM Slope	Viscosity Index	ASTM Pour Point (° F.)
		100° F.	210° F.			
Valeric acid Adipic acid Tetraethylene glycol	435	42.480	8.487	0.588	153	<−35
Valeric acid Adipic acid Triethylene glycol	395	30.030	6.346	0.628	157	<−35
Caproic acid Adipic acid Tetraethylene glycol	460	44.538	8.848	0.582	153	<−35
Caprylic acid Adipic acid Tetraethylene glycol	475	43.335	8.678	0.583	153	<−35
Caprylic acid Adipic acid Triethylene glycol	470	37.240	7.493	0.610	152	<−35
Acetic acid Sebacic acid Tetraethylene glycol	440	82.200	13.409	0.567	141	<−35
Propionic acid Sebacic acid Tetraethylene glycol	415	51.846	9.922	0.573	150	<−35
Butyric acid Sebacic acid Tetraethylene glycol	435	54.56	10.60	0.559	152	<−35
Valeric acid Sebacic acid Tetraethylene glycol	445	58.852	11.576	0.542	152	<−35
Caproic acid Sebacic acid Tetraethylene glycol	465	56.150	10.995	0.551	152	<−35
Butyric acid Thiodipropionic acid Thiodiglycol	375	37.330	7.111	0.636	150	<−35
Butyric acid Thiodipropionic acid Tetraethylene glycol	390	42.470	7.734	0.633	144	−40
Butyric acid Adipic acid (0.25 mol) Sebacic acid (0.25 mol) Tetraethylene glycol	375	37.840	7.493	0.614	151	−45
Acetic acid Adipic acid Ethylene glycol	395	116.3	14.030	0.631	121	−15
Butyric acid Adipic acid Polyethylene glycol (300 mol wt.)	435	62.155	11.476	0.560	148	−35

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 and particularly for use where the presence of additives is not desirable. The esters of the present invention may 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_1 and R_1' are radicals of the formula $-(CH_2CH_2X)_nCH_2CH_2-$ in which X is a member of the group consisting of oxygen and sulfur and n is an integer from 1 to 7; where R_2 and R_2' are alkyl groups containing 1 to 7 carbon atoms each; and where R_3 is a radical selected from a group consisting of (1) radicals of the formula $-(CH_2)_m-$ where m is an integer from 4 to 8, (2) radicals of the formula $-(CH_2)_nO(CH_2)_n-$ where n is an integer from 2 to 4, and (3) radicals of the formula $-(CH_2)_pS(CH_2)_p-$ where p is an integer from 2 to 4.

2. A composition according to claim 1 in which R_1 and R_1' represent radicals of the formula $-(CH_2CH_2O)_nCH_2CH_2-$ where n is an integer from 2 to 3.

3. A composition according to claim 1 in which R_3 is a radical of the formula $-(CH_2)_m-$ where m is an integer from 4 to 8.

4. A composition according to claim 3 in which m is 4.

5. As a new composition of matter a compound according to claim 1 in which R_1 and R_1' of the formula each represent the radical

$$-(CH_2CH_2O)_3CH_2CH_2-$$

R_2 and R_2' of the formula each represent the radical

$$-(CH_2)_2CH_3$$

and R_3 of the formula represents

$$-CH_2CH_2-S-CH_2CH_2-$$

6. A composition according to claim 1 in which R_1 and R_1' of the formula represent radicals of the formula

$$-(CH_2CH_2O)_3CH_2CH_2-$$

in which R_2 and R_2' of the formula represent methyl radicals, and in which R_3 of the formula represents the radical

$$-(CH_2)_8-$$

7. A composition according to claim 1 in which R_1 and R_1' of the formula represent the radical

$$-(CH_2CH_2O)_3CH_2CH_2-$$

in which R_2 and R_2' of the formula represent

$$-(CH_2)_2CH_3$$

and in which R_3 of the formula represents the radical

$$-(CH_2)_8-$$

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