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ESTERS OF TRIMETHYLADIPIC ACID

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7 Claims. (Cl. 260—485)

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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.

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.

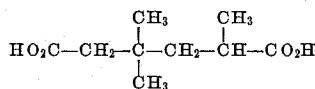
Recently, in an effort to obtain superior lubricants endowed with specific and superior characteristics, a new field has been explored, namely, the synthesis of lubricants from various materials. Esters represent one class of materials which have attracted unusual interest as synthetic lubricants. In general, they are characterized by higher viscosity indices and lower pour point than mineral oils of corresponding viscosity. The esters described in the present specification have been found to exhibit these desirable 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 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 constitute a class of esters which have been found to possess properties indicating their usefulness as synthetic lubricating oils are fully esterified trimethyladipic acids, the acids having been esterified by monohydric alcohols which contain oxygen or sulfur atoms in ether or thioether linkages. The ester groups which replace the hydrogen atoms of the two carboxyl groups of the acid contain straight chain or branched chain

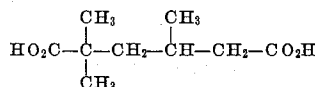
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hydrocarbon groups and may be alike or unlike in chain length or other characteristics.

Trimethyladipic acid, which undoubtedly consists of a mixture of two isomeric forms having the structures



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may be readily prepared by oxidizing dihydroisophorone with nitric acid, a detailed method for carrying out the preparation being described hereinafter. The trimethyladipic acid may be readily esterified by refluxing with a suitable alcohol or mixture of alcohols in the presence of a catalyst such as p-toluenesulfonic acid monohydrate and a suitable medium for entraining water during the reaction.

The monohydric alcohols which may be employed in preparing the trimethyladipic acid esters of the present invention are aliphatic alcohols of the general formula



where R is (1) an alkyl group of 1 to 18 carbon atoms, or (2) an organic group consisting of a series of saturated aliphatic hydrocarbon radicals interlinked by oxygen or sulfur atoms or both, the number of oxygen and sulfur atoms not exceeding 5, and the total number of carbon, oxygen and/or sulfur atoms being from 4 to 18, with the provision that there are at least two carbon atoms between each pair of oxygen or sulfur atoms and between the atom X and the first oxygen or sulfur atom; X is oxygen or sulfur; and R' is a saturated aliphatic hydrocarbon group of 2 to 3 carbon atoms, alcohols in which R' represents the group $-\text{CH}_2\text{CH}_2-$ being generally preferred. The total number of carbon, oxygen and/or sulfur atoms in the two alcohol residues attached to the acid radical should be at least 12.

Among the ether-alcohols and thioether-alcohols which have been found to be particularly suitable for use as esterifying alcohols in the preparation of the compounds of the present invention may be mentioned the following, it being understood that these are illustrative only

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and that the invention is not to be considered as limited to the use of such compounds:

Ethylene glycol mono-n-butyl ether
 Ethylene glycol mono-2-ethylbutyl ether
 Ethylene glycol mono-2-ethylhexyl ether
 Ethylene glycol mono-tert.-octyl 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

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prepared by esterifying the trimethyladipic acid obtained in the above described process in accordance with the following procedure: A mixture containing 1 mol of trimethyladipic acid, 5 2.2 mols of alcohol, 0.7% by weight of p-toluenesulfonic acid monohydrate, and a water entraining material such as benzene, toluene, naphtha or the like was refluxed until no more water collected in the water trap connected to the refluxing condenser. Then the mixture was washed 10 three times with a saturated solution of sodium carbonate and once with water. After drying over a desiccant such as Drierite (anhydrous calcium sulfate) the product was stripped at 15 210–225° under 5 mm. pressure.

The esters obtained by the above typical reaction method were found to have the properties set forth in the table.

Table

Alcohols Used in Esterification	Kinematic Viscosity		ASTM Slope	Viscosity Index	ASTM Pour Point
	100° F.	210° F.			
Butyl carbitol.....	16.050	3.701	0.724	136	°F. $\begin{matrix} < -35 \\ < -35 \\ -20 \\ 0 \end{matrix}$
2-Ethylhexyl carbitol.....	17.640	3.987	0.711	145	
Tripropylene glycol monoisopropyl ether.....	170.000	18.130	0.618	118	
β -tert.-Octylmercaptoethanol.....	616.900	41.940	0.593	111	

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," "Cellosolves," or "Carbitols."

Data will be given below showing properties of four examples of esters of trimethyladipic acid which illustrate the present invention. All of these esters are prepared by esterifying trimethyladipic acid, the latter being prepared by the following method: In an all glass apparatus consisting of a 3-liter flask fitted with a stirrer, condenser and dropping funnel was placed 1.5 liters (16 mols) of 50% aqueous nitric acid solution. This material was heated to boiling and 350 g. (2.5 mols) of dihydroisophorone was added dropwise at such a rate that refluxing continued rapidly. The refluxing was continued for several hours after the addition of the dihydroisophorone was complete, after which the resulting solution was nearly neutralized with sodium hydroxide and the top layer resulting from this procedure separated. After washing this product three or four times with a saturated sodium chloride solution, about 100–200 cc. benzene was added and the water removed by azeotropic distillation. The solvent was then removed by vacuum stripping to give 307 g. of product. (The crude acid may be used as such or the material may be distilled.)

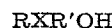
The esters described in the table below were

The above data indicate that the esters of trimethyladipic acid prepared from alcohols containing ether or thioether linkages contain characteristics with regard to viscosity index and pour point which indicate their suitability for general use as a lubricating oil, and particularly under conditions where the use of non-volatile additives is not desirable.

The esters of the present invention not only possess good lubricating qualities in themselves, but they 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 fully esterified trimethyladipic acid, formed by esterifying trimethyladipic acid with at least one monohydric aliphatic alcohol of the general formula



where R is a member of the class consisting of (1) alkyl groups containing 1 to 18 carbon atoms each, and (2) organic groups each consisting of a series of aliphatic hydrocarbon radicals interlinked by non-carbon atoms selected from the group consisting of oxygen and sulfur, the number of said non-carbon atoms not exceeding 5 and the total number of carbon atoms and said non-carbon atoms in radical R being from 4 to 18, wherein there are at least two carbon atoms between each pair of said non-carbon atoms and between the atom X and the first such non-carbon atom; X is an element of the group consisting of oxygen and sulfur; and R' is a saturated aliphatic hydrocarbon group of 2 to 3 carbon atoms; the total number of carbon and said non-carbon atoms in the two R(XR')_n groups attached to the acid radical being at least 12.

2. A composition according to claim 1 in which X of the formula is oxygen.

3. A composition according to claim 1 in which X of the formula is oxygen and in which all of the interlinking non-carbon atoms in radical R are oxygen atoms.

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4. A composition according to claim 3 in which the radical R' is the group $-\text{CH}_2\text{CH}_2-$.

5. A composition according to claim 1 in which the esterifying alcohol is butyl carbitol.

6. A composition according to claim 1 in which the esterifying alcohol is 2-ethylhexyl carbitol.

7. A composition according to claim 1 in which the esterifying alcohol is tripropylene glycol monoisopropyl ether.

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REFERENCES CITED

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2,448,259	Finch	Aug. 31, 1948

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