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PHENYLENEDIACETATE ESTER

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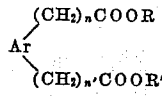
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This invention relates to a new class of compounds which have been found to be particularly suitable for use as synthetic lubricants because of their high viscosity indices and high load carrying capacity.

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 point 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 high load carrying capacity. 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 point 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.

The new compounds of the present invention which have been found to be particularly suitable for use as lubricating oils are aralkyl esters of the formula



where Ar is an aromatic nucleus which may be a benzene or diphenyl nucleus, which may or may not be partially or fully hydrogenated and may or may not contain one or more alkyl side chains,

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the total number of carbon atoms in all of the side chains, however, being not greater than 16; where n and n' are integers from 1 to 9; and where R and R' are aliphatic hydrocarbon radicals, saturated or unsaturated, straight chain or branched, or radicals consisting of a series of saturated aliphatic hydrocarbon radicals linked through 1 to 5 atoms of oxygen and/or sulfur in each group, the number of sulfur atoms in each group being not greater than 2, and each pair of oxygen and/or sulfur atoms being separated by a chain of at least two carbon atoms with at least two carbon atoms between the carboxyl group and the first oxygen or sulfur atom in the ester group, the total number of carbon, oxygen and sulfur atoms in the two ester groups being from 8 to 40. The two carboxyalkyl groups may be joined to the aromatic nucleus in any relative positions, and mixtures of esters may be employed in which the carboxyalkyl groups are joined in various positions, as in the case of derivatives of mixtures of two or more of the isomeric xylenes. Esters in which the R and R' groups are of branched chain structure are especially desirable, since branching in these groups tends to give a compound of low pour point.

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. The dibasic acids from which esters of the present invention are derived may be prepared by chlorinating an alkylaromatic hydrocarbon or by chloralkylating an aromatic hydrocarbon to introduce two chloralkyl groups, then converting the chlorinated compound into a nitrile, and hydrolyzing the latter. Thus, a xylene may be converted into a phenylenediacetic acid by chlorination, followed by the steps outlined above; or a di(chloromethyl)benzene may be formed by two successive treatments of benzene with formaldehyde and hydrogen chloride; or a di(chloromethyl)benzene may be formed by first chlorinating toluene to give benzyl chloride and following this by a single chlormethylation step. Dibasic acids of this type may also be prepared by condensing 2 mols of a dibasic acid anhydride or 2 mols of a dibasic acid monoacyl chloride with the aromatic compound in the presence of a Friedel-Crafts catalyst, followed by reduction of the carbonyl groups to methylene groups.

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

m-Phenylenediacetic acid
p-Phenylenediacetic acid

m-Phenylenedipropionic acid
1-ethyl-2,4-phenylene-β-dipropionic acid
1-methyl-2,4-phenylene-β-diacetic acid
1-tert.-octyl-2,4-phenylenediacetic acid
1,2,3,4-tetrahydro-1,4-phenylenediacetic acid
Hexahydro-1,3-phenylenediacetic acid
1-tert.-butyl-2,4-hexahydrophenylenediacetic acid
4,4'-diphenylenediacetic acid
4,4'-dodecahydrodiphenylenediacetic acid

The monohydric alcohols which may be employed in esterifying any of the dibasic acids falling within the scope of the above formula and illustrative examples are typified by 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 especially 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.

For the production of esters having low pour points it is advantageous to employ branched chain alcohols, such as those derived by the Oxo process described above.

In the table below will be shown data obtained in tests of the properties of two typical esters illustrating the present invention. The di-n-decyl m-phenylene diacetate was prepared as follows:

A mixture was prepared consisting of 34.3 grams (0.7 mol) of sodium cyanide and 400 ml. of 75% aqueous ethanol, and to this mixture while being agitated at refluxing temperature was added gradually 80 grams (0.303 mol) of m-xylylene dibromide. The hot solution was filtered and added to 900 ml. of water and the whole was extracted with ether, after which the ether was evaporated yielding 42.7 grams (90.5%) of product, which was m-xylylene dinitrile. This was hydrolized to the dibasic acid by refluxing with a mixture of 280 ml. of concentrated sulfuric acid and 400 ml. water per mol of dinitrile. The solid acid precipitated from the aqueous solution upon the addition of 750 ml. of ice water.

The acid prepared above was esterified by the following method: In a 1-liter round bottomed reaction flask, fitted with a reflux condenser and a water trap, was placed a charge consisting of one mol of a dibasic acid, two mols of n-decanol, 4.5 grams of p-toluene sulfonic acid monohydrate, and 100 ml. of toluene. The mixture was refluxed until no more water collected in the trap. The resulting solution was washed with three 100 ml. portions of saturated aqueous sodium carbonate solution and one 100 ml. portion of water. After drying over "Drierite" (anhydrous calcium sulfate) the material was filtered and stripped to a bath temperature of 200–225° C. at a pressure of about 5 mm.

The di-n-decyl p-phenylene diacetate was prepared as follows: To a mixture of 253 grams (2 mols) benzyl chloride and 70 grams (2.3 mols) paraformaldehyde was added 70 grams of pulverized zinc chloride and hydrogen chloride was bubbled in for a period of four hours while the temperature was kept below 60° C. The product was decanted, and benzene was added to the reaction flask to wash out the remaining traces of the product; the total product including the benzene washings was washed with water and filtered to remove solid material. The product was further washed with dilute sodium carbonate solution and water. The product, consisting of p-xylylene dichloride dissolved in benzene, was treated with sodium cyanide as in the case of m-xylylene dibromide and then hydrolyzed to form the corresponding dibasic acid. This acid was esterified with n-decanol by the method described above.

Ester	Flash Point, (°F.)	Pour Point (°F.)	Kinematic, 100° F.	Viscosity, 210° F.	Viscosity Index	Almen Machine Weights Carried (Gradual Loading)
Di-n-decyl, m-diphenylenediacetate	415	30	25.510	5.025	136	12
Di-n-decyl, p-phenylenediacetate		35	27.700	5.782	153	15

The above data indicate that the esters constituting the subject matter of the present invention possess characteristics, particularly with regard to viscosity index and load carrying capacity, 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 load carrying capacity.

What is claimed is:

1. As a new composition of matter di-n-decyl phenylenediacetate.

2. As a new composition of matter di-n-decyl m-phenylenediacetate.

3. As a new composition of matter di-n-decyl p-phenylenediacetate.

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