

UNITED STATES PATENT OFFICE

2,668,848

ESTER-TYPE SYNTHETIC LUBRICANTS

Martin B. Neuworth, Brentwood, Pa., assignor to
Socony-Vacuum Oil Company, Incorporated,
a corporation of New York

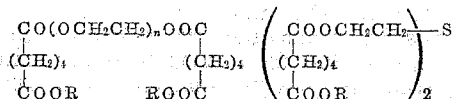
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This invention relates, broadly, to ester-type synthetic lubricants, and is more particularly concerned with the oily tetra-esters of adipic acid having high viscosity indices and low pour points.

Tetra-esters of adipic acid are the predominant constituents of the reaction products obtained from the esterification of a glycol or of thiodiglycol with an adipic acid monoester. These tetra-esters have the general structures:



wherein R is a branched-chain aliphatic group and n is an integer equal to one or more.

The tetra-esters of this invention are distinguishable from the polyester resins disclosed in U. S. Patent No. 2,035,528. In the patent, the resinous products are produced by reacting dicarboxylic acids with monohydric alcohols and with polyethyleneglycols in four different manners. A study of the working examples reveals that such reactions are carried out using a molar proportion of monoester to glycol of 1:1, respectively, or lower. In accordance with the present invention, however, it has been found that synthetic lubricants are produced only when a true, non-resinous ester is obtained. This necessitates a molar proportion of monoester to glycol of about 2:1, respectively.

As is well known to those familiar with the art, a large variety of esters have been proposed for use as synthetic lubricants. However, when these products have been utilized they have been found to be wanting in one or more characteristics. Thus, when these products have had high viscosity indices and low pour points, the viscosity has been poor. For example, it has been suggested to use the simple neutral esters of a number of dicarboxylic acids, including adipic acid. However, when the dicarboxylic acid has been esterified with a relatively high molecular weight branched-chain alcohol to obtain a high viscosity, the viscosity index has been relatively low while the pour point has been found to be too high for practical purposes. On the other hand, when normal alcohols of relatively high molecular weight have been used, although the viscosity indices of the products have been found to be desirable, the pour points have been found to increase tremendously. Accordingly, it will be appreciated that there has been a demand for ester-type synthetic lubricants having good viscosities, relatively high viscosity indices, and relatively low pour points.

In accordance with the present invention, it has now been discovered that it is possible to produce an ester-type synthetic lubricant pos-

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sessing all the desirable characteristics discussed hereinbefore. It has now been found that the reaction products obtained by the complete esterification of glycols or of thiodiglycol with adipic acid monoesters constitute excellent ester-type synthetic lubricants having high viscosities, high viscosity indices, and low pour points.

Accordingly, it is an object of the present invention to provide synthetic lubricants which are relatively inexpensive. A further object is to provide new ester-type synthetic lubricants. A more specific object is to afford ester-type lubricants having high viscosity indices and low pour points. Other objects will become apparent to those skilled in the art from the following detailed description.

Broadly stated, the present invention provides a new synthetic lubricant having a high viscosity index and a low pour point, which comprises the reaction product obtained by reacting an adipic acid monoester with an ethylene glycol or thiodiglycol in a molar proportion of about 2:1, respectively.

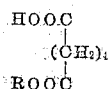
Any ethylene glycol can be utilized as the glycol reactant. Ethylene glycols are dihydric alcohols having the general formula



wherein n is an integer equal to one or more, and preferably, between one and six. Non-limiting examples of the ethylene glycols which can be used are ethylene glycol, diethylene glycol, triethylene glycol, tetraethylene glycol, and hexaethylene glycol. These glycols are readily available in commercial quantities and they are relatively inexpensive.

The thiodiglycol reactant utilizable herein has the structure, $\text{HOCH}_2\text{CH}_2-\text{S}-\text{CH}_2\text{CH}_2\text{OH}$. The manner of preparing this material is well known. The compound is also available in commercial quantities. Thiodiglycol is classified as a glycol reactant for the purposes of the present invention.

The adipic acid monoesters utilizable in accordance with the present invention have the structural formula:



wherein R is a branched-chain aliphatic group containing between about 6 and about 20 carbon atoms per radical, and, preferably, between about 8 and about 16 carbon atoms. Examples of adipic acid monoester reactants are 2-ethylbutyl hydrogen adipate, 2-ethylhexyl hydrogen adipate, 1-methyl-4-ethyloctyl hydrogen adipate, 2-methyl-octyl adipate, 2-methylheptyl adipate, and 1-(3-ethylamyl)-4-ethyloctyl hydrogen adipate. These monoesters can be pre-

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pared by any of several methods which have been proposed for the preparation of monoesters [see C. Contzen-Crovert, Bull. Sec. Chem. Belg., 35, 165-98 (1926) 1. Typically 2-ethylbutyl hydrogen adipate can be prepared as follows:

Example 1

The following reactants were placed in a 2-liter flask provided with a mechanical stirrer, a water trap, and a reflux condenser:

366 g. (2.5 mols) adipic acid
500 milliliters xylene

The mixture was heated to reflux and, after all of the adipic acid had dissolved, 129 g. (1.25 mols) of 2-ethylbutanol were added dropwise. Azeotropic distillation of water was continued for 20 hours, at which time the reaction was complete. The solution was allowed to cool and the unreacted adipic acid was filtered off. Then the xylene solution was washed with water to remove dissolved adipic acid, and it was dried. The xylene was stripped at a pot temperature of 135° C. under a pressure of 0.6 mm. The residual 2-ethylbutyl hydrogen adipate weighed 191 g. (83 per cent yield, based on the acid consumed).

In order to produce the non-resinous products of this invention, the adipic acid monoester reactant and the glycol reactant are reacted in a molar proportion about 2:1, respectively. Particularly when operating with thiodiglycol, a slight weight excess of glycol reactant can be used. Such a weight excess should not exceed 30 per cent. In all cases, however, the excess glycol reactant is removed by distillation, or other suitable means. To this extent, the molar proportion of reactants is critical.

The reaction products contemplated herein may be prepared by any of the conventional methods for effecting esterification. For example, the adipic acid monoester reactant can be mixed with glycol reactant, and the mixture heated in the presence of a dehydrating agent; or, vacuum can be employed to remove the water resulting from the esterification, thereby driving the reaction more nearly to completion. In the specific examples set forth hereinafter, the water of esterification was removed with a solvent with which the water formed an azeotropic mixture. Suitable solvents are the hydrocarbons of the benzene series boiling between 80° C. and 200° C., such as benzene, toluene, xylene, and cymene. Esterification catalysts can be employed in the reaction of the present invention. Preferred catalysts are the strong acids, such as sulfuric acid, hydrochloric acid, and aromatic sulfonic acids. These catalysts can be used in amounts varying from about 0.1 per cent to about 5 per cent by weight, based on the total weight of the reactants.

The time of reaction will depend on the reaction temperature and on the quantities of reactants involved. It is to be strictly understood that the method of esterification, and the time and temperature of the reaction are not critical factors in preparing the reaction products of the present invention.

The following specific examples are for the purpose of exemplifying the reaction products contemplated in the present invention. It is to be clearly understood that the invention is not to be considered as limited to the specific glycol reactants and adipic acid monoester reactants, or to the operations and manipulations described in the examples. As will be apparent to those

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skilled in the art, a wide variety of other reactants, as set forth hereinbefore, may be used to prepare a wide variety of products in accordance with this invention.

*Esters prepared from ethylene glycols**Example 2*

The following reactants were placed in a 1-liter reaction flask equipped with a mechanical stirrer, a thermometer, and a water trap provided with a water-cooled reflux condenser:

129 g. (0.5 mole) 2-ethylhexyl hydrogen adipate
42 g. (0.275 mole) triethylene glycol
1.3 g. p-toluene sulfonic acid monohydrate
200 milliliters xylene

Stirring was commenced and the reaction mixture was heated until the azeotropic water-xylene mixture evolved and the xylene was refluxing. The reaction was maintained under reflux at a temperature of 143° C. for 24 hours, at the end of which period, the evolution of water from the esterification ceased.

The reaction mixture was cooled and washed free of acid with a dilute aqueous solution of sodium carbonate, and then with water. The xylene solution was dried with anhydrous sodium sulfate, following which, the xylene was removed by distillation at a pot temperature of 200° C. under a pressure of one millimeter. The 130 grams of esterification reaction product (80.3 per cent yield, based on the adipic acid monoester reactant) had the following properties:

Flash point	-----°F--	435
Saponification number	-----	357
Saponification number (theory)	-----	352
Density 4 ²⁰	-----	1.0103
Neutralization number	-----	0.5

Example 3

Using the same apparatus as in Example 2, the following reactants were charged:

129 g. (0.5 mole) 2-ethylhexyl hydrogen adipate
75 g. (0.25 mole) hexaethylene glycol
200 milliliters xylene

The mixture was heated to reflux and the azeotropic removal of water was continued until its evolution ceased. Then, 1.3 g. p-toluene sulfonic acid monohydrate was added and the reaction was continued under reflux for three hours. The product, treated and isolated as described in Example 2, weighed 164 grams (83.5 per cent yield, based on the adipic acid monoester reactant). This reaction product had the following properties:

Flash point	-----°F--	460
Saponification number	-----	291
Saponification number (theory)	-----	285
Density 4 ²⁰	-----	1.0298
Neutralization number	-----	1.0

Example 4

The following reactants were placed in a 1-liter flask provided with a mechanical stirrer, a water trap and a reflux condenser:

150 g. (0.652 mole) 2-ethylbutyl hydrogen adipate
25 g. (0.391 mole) ethylene glycol
1.5 g. p-toluene sulfonic acid monohydrate
150 milliliters xylene

The reaction mixture was heated for 20 hours under reflux conditions, at which time the azeotropic distillation of water ceased. The xylene

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solution was cooled, and washed free of acid with dilute sodium carbonate aqueous solution and, finally, with water. After being dried over anhydrous sodium sulfate, the solution was stripped of xylene at a pot temperature of 200° C., under a pressure of 0.6 mm. The reaction product, which weighed 132 g. (87 per cent yield) had the following properties:

Flash point -----°F--	385
Saponification number -----	445
Saponification number (theory) -----	462
Density ⁴⁰ -----	1.0216
Neutralization number -----	0.1

Examples 5, 6, 7 and 8

The following reaction products were prepared in a manner similar to that of the previous examples:

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The utility of these products as synthetic lubricants is demonstrated by the results obtained in the Lauson Engine Test. In accordance with this test, a single-cylinder Lauson liquid-cooled engine, with splash lubrication, is operated at a speed of about 1825 R. P. M. The oil is maintained at about 270° F. The engine is inspected at 20-hour intervals and makeup oil is added at these times. After 100-hour operation of the engine, the oil is tested for acidity and viscosity, and the piston cleanliness and the detergency of the engine are evaluated on the basis of 100. Also, the copper-lead bearings of the engine are weighed before and after the test, and the loss in weight in grams is reported. The product of Example 2, containing 0.75 per cent by weight of an oxidation inhibitor described in U. S. Patent No. 2,381,377, and a Pennsylvania SAE #20 motor

TABLE I

	5	6	7	8
Adipic Acid Monoester.....	2-ethyl-hexyl	2-ethylbutyl	1-methyl-4-ethyloctyl	1-(3-ethylamyl)-4-ethyloctyl
Glycol.....	Diethylene	Triethylene	Triethylene	Diethylene
Flash Point.....	495° F.	420° F.	415° F.	465° F.
Saponification Number.....	374	366	298	236
Saponification Number (Theory).....	382	392	325	268
Density ⁴⁰	0.9963	1.0428	0.9885	0.9569

It will be seen from the data presented in the foregoing examples, that the ethylene glycol reaction products of the present invention are prac-

oil, similarly inhibited (for purposes of comparison), were subjected to the Lauson Engine Test. The results obtained are tabulated in Table III.

TABLE III

	Hours	N. N.	Kinematic Viscosity at 210° F., cs.	Cleanliness		Bearing Loss, grams	
				Piston	Detergency	Top	Bottom
2.....	0	2.5	6.42				
	100	10.8	9.26	92	88	0.035	0.033
SAE #20.....	0	0	8.5				
	100	3.5	10.21	78	65	0.064	0.036

tically neutral materials having a specific gravity of about one, or slightly greater. In all cases, the saponification number agrees closely with the theoretical value for a product which is completely esterified. Further, these products have flash points that fall within a range which renders them comparable to light lubricating oils.

These products have high viscosity indices and very low pour points. Their excellence as synthetic lubricants is illustrated by the following data:

TABLE II

Example	Kinematic Viscosity, cs.		Viscosity Index	Pour Point, ° F.
	at 100° F.	at 210° F.		
2.....	30.39	6.02	148	-65
3.....	48.71	9.21	149	-60
4.....	20.64	4.54	154	-65
5.....	24.11	5.11	152	-65
6.....	32.48	6.56	153	-65
7.....	46.42	7.71	133	-65
8.....	83.34	10.77	119	-55

It is apparent that the synthetic lubricant is appreciably superior to the mineral lubricating oil in regard to cleanliness of the engine, minimum bearing corrosion, and low viscosity increase at the end of the test period.

Esters prepared from thiodiglycol

Example 9

The following reactants were placed in the reaction vessel described in Example 2:

208 g. (0.8 mole) 2-ethylhexyl hydrogen adipate
61 g. (0.4 mole+25% excess) thiodiglycol
2 g. p-toluene sulfonic acid monohydrate
2000 milliliters xylene

The reaction mixture was heated to reflux temperature to remove the water of esterification. The reaction was continued for 7 hours at 143-155° C., at the end of which time the evolution of water of esterification had ceased.

The reaction mixture was cooled and washed free of acid with a dilute aqueous solution of sodium carbonate and then with water. The

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xylene solution was dried with anhydrous sodium sulfate. Xylene was removed by distillation under atmospheric pressure. Finally, the residue was subjected to distillation at 200° C. pot temperature, under 0.4 millimeter pressure, to remove the excess thiodiglycol. The 169 grams of product (69% yield based on the adipic acid monoester reactant) had the following properties:

Sulfur, percent	5.7
Sulfur, percent (theory)	5.3
Density ⁴²⁰	1.0095
Saponification number	321
Saponification number (theory)	372

Example 10

A large prepilot plant of the product of Example 9 was made in the the manner described therein. The 20 gallons of finished product obtained had the following properties:

Sulfur, per cent	5.27
Sulfur, per cent (theory)	5.31
Density ⁴²⁰	1.0036
Saponification number	336
Saponification number (theory)	372

This material was soluble in mineral lubricating oils. It had a very good inhibitor response. For example, the product responded to viscosity index improvement when a commercial acrylic acid ester resin, known as Acryloid 710, was blended therewith. This reaction product was unusually stable toward hydrolysis and showed excellent dielectric properties.

Example 11

The following reactants were reacted at 158-160° C. for 6 hours, as described in Example 9:

244 g. (0.8 mole) 1-methyl-4-octylethyl hydrogen adipate
61 g. (0.4 mole+25% excess) thiodiglycol
2 g. p-toluene sulfonic acid monohydrate
200 milliliters xylene

After washing the product, removing the solvent, and removing excess thiodiglycol at 200° C. pot temperature under 0.6 millimeter, the product obtained weighed 239 grams, 87.5 per cent yield based on the adipic acid monoester reactant. It had the following properties:

Sulfur, per cent	4.87
Sulfur, per cent (theory)	4.66
Density ⁴²⁰	0.9851
Saponification number	253
Saponification number (theory)	366

Example 12

The following reactants were reacted at 149-155° C. for 3½ hours, in the manner described in Example 9:

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385 g. (1.0 mole) 1-(3-ethylamyl)-4-ethyloctyl hydrogen adipate
73 g. (0.5 mole+20% excess) thiodiglycol
3.8 g. p-toluene sulfonic acid monohydrate
300 milliliters xylene

After washing, drying, and removing the solvent, the reaction product was subjected to distillation at 200° C. pot temperature, under 0.7 millimeter pressure, to remove excess thiodiglycol. Then, the product was stirred, at room temperature (about 25° C.), with 10 grams of ignited aluminum oxide powder. Subsequently, an additional 10-gram portion of aluminum oxide powder was added, and stirring was continued for another hour. This treatment was used to remove any residual acidity of the product. The material was filtered with suction through filtering clay. The 369 grams of product (86 per cent yield, based on the adipic acid monoester reactant) had the following properties:

Sulfur, per cent	3.92
Sulfur, per cent (theory)	3.75
Density ⁴²⁰	0.9597
Saponification number	230
Saponification number (theory)	262

The thiodiglycol ester reaction products of the present invention have high viscosity indices and low pour points. Their excellence as synthetic lubricants is illustrated by the following data:

TABLE IV

Example	Kinematic Viscosity, cs.		Viscosity Index	Pour Point, ° F.
	at 100° F.	at 210° F.		
9	31.88	6.34	150	<-65
10	31.95	6.24	147	<-65
11	53.62	8.46	131	<-65
12	91.21	11.32	117	-55

A great advantage of the thiodiglycol reaction products of this invention is that they have good inherent anti-oxidation properties. In other words, they function satisfactorily as lubricants without the necessity of blending antioxidants therewith. This quality is demonstrated by the results of the Lauson Engine Test, wherein the product of Example 10 containing no oxidation inhibitors was tested and compared with uninhibited Pennsylvania SAE #20 motor oil. The results obtained for each run are set forth in Table V.

TABLE V

	Hours	N. N.	Kinematic Viscosity at 210° F., cs.	Cleanliness		Bearing Loss, grams	
				Piston	Detergency	Top	Bottom
10	0	nil	6.24				
	100	1.2	6.39	76	68	0.004	0.000
SAE #20	0	0.1	8.51				
	100	4.8	11.10	85	78	0.646	0.557

The products of the present invention are useful also as plasticizers and as intermediates in organic synthesis. The oil-solubility of the thiodiglycol reaction products suggests their use as

extenders for lubricating oils and as additives to impart valuable properties thereto.

Although the present invention has been described with preferred embodiments, it is to be understood that modifications and variations may be resorted to, without departing from the spirit and scope of this invention, as those skilled in the art will readily understand. Such variations and modifications are considered to be within the purview and scope of the appended claims.

This application is a continuation-in-part of co-pending application Serial No. 6,019, filed February 3, 1948, now abandoned, by the same inventor.

What is claimed is:

1. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 6 and about 20 carbon atoms, with a glycol reactant selected from the group consisting of an ethylene glycol having the formula, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, wherein n is an integer varying between one and six, and thiodiglycol, in a molar proportion of about 2:1, respectively.

2. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 8 and about 16 carbon atoms, with a glycol reactant selected from the group consisting of an ethylene glycol having the formula, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, wherein n is an integer varying between one and six, and thiodiglycol, in a molar proportion of about 2:1, respectively.

3. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing about 8 and about 16 carbon atoms, with an ethylene glycol having the formula



wherein n is an integer varying between one and six, in a molar proportion of about 2:1, respectively.

4. The non-resinous reaction product obtained by reacting 2-ethylhexyl hydrogen adipate with an ethylene glycol having the formula



wherein n is an integer varying between one and six, in a molar proportion of about 2:1, respectively.

5. The non-resinous reaction product obtained by reacting 1-methyl-4-ethyloctyl hydrogen adi-

pate with an ethylene glycol having the formula, $\text{H}(\text{OCH}_2\text{CH}_2)_n\text{OH}$, wherein n is an integer varying between one and six, in a molar proportion of about 2:1, respectively.

6. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 8 and about 16 carbon atoms, with thiodiglycol, in a molar proportion of about 2:1, respectively.

7. The non-resinous reaction product obtained by reacting 2-ethylhexyl hydrogen adipate with thiodiglycol, in a molar proportion of about 2:1, respectively.

8. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 8 and about 16 carbon atoms, with triethylene glycol, in a molar proportion of about 2:1, respectively.

9. The non-resinous reaction product obtained by reacting 2-ethylhexyl hydrogen adipate with triethylene glycol, in a molar proportion of about 2:1, respectively.

10. The non-resinous reaction product obtained by reacting 1-methyl-4-ethyloctyl hydrogen adipate with triethylene glycol, in a molar proportion of about 2:1, respectively.

11. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 6 and about 20 carbon atoms, with an ethylene glycol having the formula



wherein n is an integer varying between 3 and 6, in a molar proportion of about 2:1, respectively.

12. The non-resinous reaction product obtained by reacting an adipic acid monoester having the formula, $\text{ROOC}(\text{CH}_2)_4\text{COOH}$, wherein R is a branched-chain aliphatic radical containing between about 6 and 20 carbon atoms, with thiodiglycol, in a molar proportion of about 2:1, respectively.

MARTIN B. NEUWORTH.

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