United States Patent Office

3,287,273

Patented Nov. 22, 1966

1

3,287,273

LUBRICITY ADDITIVE-HYDROGENATED DICARBOXYLIC ACID AND A GLYCOL

Michael J. Furey, Berkeley Heights, and John K. Appeldoorn, Bernardsville, N.J., and Albin F. Turbak, Danville, Ill., assignors to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Sept. 9, 1965, Ser. No. 486,221
15 Claims. (Cl. 252—56)

This application is a continuation-in-part of application Serial Number 284,857, filed June 3, 1963 (now abandoned).

The present invention is broadly concerned with a novel class of lubricity additives, additive concentrates, and oleophilic liquid compositions containing the same. It is preferred that the oleophilic liquid compositions be substantially anhydrous. The invention is more specifically concerned with improving the lubricity of hydrocarbon liquids such as gasolines, aviation turbo fuel, kerosene, diesel fuel, lubricating oil and mineral lubricating oils. Other base fluids include liquid carbohydrates and esters such as dioctyl sebacate and didecyl adipate. The present invention also contemplates the use of the lubricity additives in solid products such as paraffin wax, lubricating grease and Carbowax. The invention in one specific aspect relates to improving the lubricity of middle distillates, particularly jet fuels.

The lubricity additives of the present invention comprise a reaction product between a dicarboxylic acid and an oil insoluble glycol, wherein the dicarboxylic acid is preferably characterized by having at least 9 carbon atoms between the respective carboxylic groups. It is preferred that the number of carbon atoms between the respective carboxylic groups of the dicarboxylic acid be in the range from about 12 to 42. The additives also have molecular weights below about 1700, preferably below about 1300 as determined by the "Osmometer Method," Anal. Chem., vol. 33, No. 1, pp. 135–137, January 1961, Wilson.

In one preferred embodiment of the present invention the lubricity additives preferably comprise predominantly partial esters of an oil insoluble glycol and dicarboxylic acids that are obtained by the polymerization of dienoic or trienoic monocarboxylic acids. In a second embodiment of the present invention, the lubricity additives preferably comprise diesters of an oil insoluble glycol and the dicarboxylic acids previously described. In still another embodiment of the present invention, the lubricity additives comprise esters of an oil insoluble glycol and hydrogenated dicarboxylic acids obtained as hereinbefore described.

In general, the compositions of the present invention improve the lubricity of distillate fuels boiling in the range from about 50° to 750° F. Such fuels include aviation turbo-jet fuels, rocket fuel (MIL–R–25576B), kerosenes, diesel fuels, and heating oils. Aviation turbo-jet fuels in which the dimer acid or hydrogenated dimer acid/glycol esters may be used normally boil between about 50° and about 550° F. and are used in both military and civilian aircraft. Such fuels are more fully defined by U.S. Military Specifications MIL–F–5624F, MIL–F–25656A, MIL–F–2554A, MIL–F–255558B, and amendments thereto, and in ASTM D–1655–62T. Kerosenes

2

and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D–396–48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the dimer acid or hydrogenated dimer acid/glycol esters may be employed are described in detail in ASTM Specification W–975–35T and later version of the same specification.

The additives of the present invention may be employed in conjunction with a variety of other additives commonly used in fuels such as those set forth above. Typical of such additives are oxidation inhibitors such as phenothiazine or phenyl-α-naphthylamine; rust inhibitors such as lecithin or petroleum sulfonates; sorbitan monooleate; detergents such as the barium salt of isonoyl phenol sulfide; pour point depressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; viscosity index improvers such as polymethacrylates; dispersants, dyes, dye stabilizers, haze inhibitors, antistatic agents, and the like.

Many oil compositions are designed for lubricating under boundary conditions (e.g., crankcase oils, aviation oils and gear oils) where the prevention of wear of the metal surfaces is a serious problem that occurs under heavy loading. One common example of such heavy loading occurs in the operation of the valve lifter mechanism of gasoline engines. Here, pressures of 50,000 to 100,000 p.s.i. can occur between the valve lifter and its actuating cam and metal wear is accordingly high. It has now been found that metal wear can be significantly reduced by adding to an oleophilic liquid such as a mineral oil lubricant, a reaction product between a dicarboxylic acid and an oil insoluble glycol wherein the dicarboxylic acid is preferably characterized by having at least 9 carbon atoms between the respective carboxylic groups. Preferred oil insoluble glycols include the alkane diols having relatively short carbon chains as, for example, from about 2 to 8, e.g., 2 to 5, carbon atoms. A very suitable glycol for the purposes of the present invention is ethylene glycol.

As pointed out heretofore, the preferred dicarboxylic acids utilized are those which contain at least 9 carbon atoms between the respective groups. It is greatly preferred that the number of carbon atoms between the carboxylic groups be in the range from about 12 to 42. Specific examples of these acids are the dimers of linoleic acid, oleic acid, the mixed dimer of linoleic and oleic acids and the dimer of dodecadienoic acid. It is also possible to employ the dimer of dicyclopentadiene dioic acid. While the foregoing acids are preferred, similar dicarboxylic acids such as "VR–1," described in U.S. 2,833,713, and "D–50," described in U.S. 2,470,849, may be used. The dienoic or trienoic monocarboxylic acid, that is polymerized to give the dicarboxylic polymer, can have from 12 to 30 carbon atoms. Extremely suitable dimer acids for use in the present invention are commercially available from Emery Industries Inc. under the trade name of Empol dimer acids. These dimer acids are available in various grades of dimer acid purity relative to trimer and monobasic acid content. For example, Empol 1014 dimer acid consists of 95% dimer acid, a trace of monobasic acids and the remainder essentially consists of trimer acid. Also available are Empol 1018 dimer acid (containing 17% trimer and a trace of monobasic acid),

Empol 1022 dimer acid (19 to 22% trimer and 2 to 5% monobasic acids) and Empol 1024 dimer acid (containing the same trimer acid content as Empol 1022 but containing only a trace amount of monobasic acid). The specifications and typical compositions of the Empol dimer acids discussed above are given in Table I:

TABLE I

	Empol 1014	Empol 1018	Empol 1022	Empol 1024
Neutralization Equivalent	288–294	287–299	289–301	289–301
Acid Value	191–195	188–196	186–194	186–194
Saponification Value	195–199	192–198	191–199	191–199
Color, Gardner 1953, Max	8	8	9	9
Monobasic Acids, Percent Max	1.5	1	2–5	1
Dimer Acid	95	83	77	79
Trimer Acid	4	17	20	21
Monobasic Acids	1	Trace	3	Trace
Dimer:Trimer Molar Ratio	36:1	7:1	6:1	6:1

The commercial dimer acids discussed above are generally produced by polymerization of unsaturated C_{18} fatty acids to form C_{36} dibasic dimer acids. Depending on the raw materials used in the commercial process, the C_{18} monomeric acid may be linoleic acid or oleic acid or mixtures thereof. The resulting dimer acids may therefore be the dimers of linoleic acid, oleic acid or a mixed dimer of linoleic and oleic acid. Representative formulas of the foregoing monomeric and dimer acids may be illustrated as follows. (It should be noted that the structure generally given for linoleic acid is that of 9,12-octadecadienoic acid but it is believed that prior to dimerization this acid isomerizes to the 9,11 structure, see in this regard the article "Dimer Acids," the Journal of the American Oil Chemists Society, vol. 39, December 1962, p. 535, J. C. Cowan.)

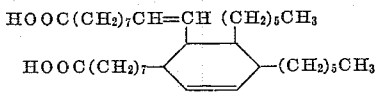
(a)

$$CH_3(CH_2)_4CH{=}CHCH_2CH{=}CH(CH_2)_7COOH \xrightarrow[300^\circ\ C.]{\Delta}$$

9,12 linoleic acid

$$CH_3(CH_2)_5CH{=}CHCH{=}CH(CH_2)_7COOH \xrightarrow[\text{Diels-Alder}]{\text{2 molecules 9,11 acid}}$$

9,11 linoleic acid

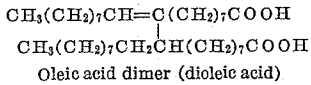


Linoleic acid dimer (dilinoleic acid)

(b)

$$CH_3(CH_2)_7CH{=}CH(CH_2)_7COOH \xrightarrow[\text{Diels-Alder}]{\text{2 molecules oleic acid}}$$

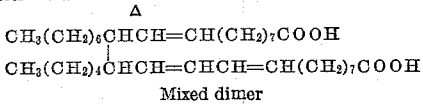
Oleic acid



Oleic acid dimer (dioleic acid)

(c)

9,11 linoleic acid + oleic acid $\xrightarrow[\text{Diels-Alder}]{\Delta}$



Mixed dimer

It should be noted that the above structural formulae only indicate one of the several possible structural isomers. It is believed that the commercial dimer acids would contain mixtures of such structural isomers.

The dimer acid of linoleic acid with which one embodiment of the present invention is concerned is a C_{36} dimer acid and is described in U.S. Patent 2,424,588, issued July

29, 1947, and entitled "Lubricant Composition"; inventors: W. J. Sparks et al. It is to be understood as indicated in the specifications for the commercial dimer acid that the dimer acid utilized in the practice of the present invention is not necessarily 100% dimer acid.

For example, the following compositions of acid were reacted with ethylene glycol wherein Compositions A, B and C produced a satisfactory product and Composition D produced a reaction product which was not soluble. Composition A exhibited the highest solubility in hydrocarbons. The content of each of the foregoing compositions is shown in Table II.

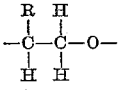
TABLE II

	Composition Wt. Percent			
	A	B	C	D
Dimer Acid	95	75	76	21
Trimer Acid	4	22	23	79
Monomer Acid	1	3	1	0

Thus, it is essential that the amount of dimer acid present in the acid composition be at least 50% and preferably above 75%, such as 95% by weight. It is to be understood that, under certain circumstances, these dicarboxylic acids can be substituted acids such as with bromine, fluorine or a hydroxy group.

The lubricity additives of the present invention comprising a reaction product between a dimerized dicarboxylic acid and an oil insoluble glycol may be produced by various techniques. The oil insoluble glycol reacted with the dicarboxylic acid may be an alkane diol or an oxa-alkane diol, straight chain or branched. The alkane diol has from about 2 to 8 carbon atoms, preferably 2 to 5 carbon atoms in the molecule.

The oxa-alkane diol can have 4 to 100 carbon atoms with periodically repeating groups of



wherein R is H or CH_3.

The preferred alkane diol is ethylene glycol and the preferred oxa-alkane diol is 4-oxa-heptane diol-2,6. As pointed out, the preferred dimeric dicarboxylic acids are the dimers of linoleic acid, oleic acid or the mixed dimer of linoleic and oleic acids, which may also contain some monomer as well as trimer. Other specific satisfactory glycols are, for example, propylene glycol, polypropylene glycol, polyethylene glycol and the like.

The molar quantities of the dicarboxylic acid and glycol reactants may be adjusted so as to secure either a complete diester or a partial ester.

Turning now to the embodiment wherein a diester of a dimeric dicarboxylic acid is used, as previously indicated, the molar quantities of reactants are adjusted in this embodiment so as to secure a complete diester. For example, one process is to reflux an excess of the diol with the selected dioic acid at 80° C. in the presence of benzene as diluent and toluene sulfonic acid as catalyst until the theoretical amount of water has been produced in a water-trap in the reflux condenser. The diluent is then stripped off under vacuum at 40° C. The general reaction equation is as follows:

$$HOOC{-}R{-}COOH + XHO{-}R'{-}OH \rightarrow HO{-}R'OOC{-}R{-}COOR'{-}OH + XH_2O$$

wherein R is the hydrocarbon skeleton of the dicarboxylic acid having more than 9 carbon atoms between the acid groups. R′ is either the hydrocarbon skeleton of a C_2 to C_8 glycol or the oxa-alkane diol and X is 2 or greater.

Particularly desirable base fuels wherein the additives of the present embodiment are most effective are those base fuels wherein the viscosity is below about 3 centistokes and which fuels are substantially free of polar compounds, sulfur compounds, and nitrogen compounds. In essence, the concentration of these compounds is less than about 0.01% by weight, which is secured when the jet fuel is highly refined, such as by hydrofining.

If the diester additives of the present embodiment are used as an additive concentrate, the concentrate may consist essentially of from about 25 to 75% of the additives, the remainder being a satisfactory solvent such as kerosene, a Varsol, a naphtha and the like. The preferred concentrate contains about 50 to 60% of the additive in the solvent.

When the diester additive is used in conjunction with oleophilic liquid, the concentration may vary appreciably. For example, when the additive is used in a fuel, the concentration is in the range of from about 0.001 to 0.4% by weight, preferably in the range of from about 0.01 to 0.09% by weight. On the other hand, if the additive is used with a hydrocarbon lubricating oil, the concentration may vary in the range from about 0.001 to 4.9% by weight, preferably in the range from about 0.1 to 2.0% by weight.

The embodiment relating to the glycol diesters of dimer acids may be more easily understood by reference to the following examples.

EXAMPLE 1

In order to further illustrate the invention, a number of tests were carried out using the additives of the present invention in base jet fuels and the load carrying capacity of the fuels determined.

One mole of C_{36} dimer acid (Empol 1014—previously identified) was reacted with 2 moles each of either of two glycols (ethylene and neopentyl) by refluxing in benzene in the presence of p-toluene sulfonic acid monohydrate as a catalyst. The water evolved was measured and the benzene solutions were water washed. On evaporation of the benzene under vacuum at 35° to 40° C., the resultant products were found to be dark amber, clear, viscous fluids quite soluble in hydrocarbons.

Effect on scuffing

As shown by the data below, the addition of 0.1% of the C_{36} dimer acid/ethylene glycol diester to a jet fuel greatly increased the load-carrying capcaity as measured by the Ryder gear test. The dimer acid alone has little effect.

Fluid:	Ryder rating (#/in.)
Base jet fuel [1]	400
Base+0.1% diester of C_{36} dimer acid and ethylene glycol	[2] 1,100
Base+0.1% C_{36} dimer acid	480

[1] Highly isoparaffinic fuel of 375° to 500° F. boiling range, high thermal stability, low freezing point and low sulfur content.

[2] Run under more severe condition of 5# load steps rather than 2#. Under this condition (5# step), the base fails on the first step.

As shown by the above data, the addition of 0.1% of the diester increases the antiscuffing properties of jet fuel as measured by the Ryder gear test (E. A. Ryder, ASTM Bulletin 184, 41 (1952). The ratings represent the load in pounds/inch of tooth width to produce a given amount (22½%) of gear scuffing. It can also be seen that the C_{36} dimer acid itself has substantially no effect.

EXAMPLE 2

Another test was carried out with the following results:

	Additive wt. percent	Ryder Scuff Test #/in.
Neutral Mineral Oil, Viscosity 43 SUS at 210° F.	0	1,170
Mineral Oil with Diester of Ethylene Glycol and Dimer of Linoleic Acid	0.5	3,200

Thus, it is apparent that the diester is very effective.

EXAMPLE 3

The preparation and tests of Example 1 are repeated except that the C_{36} dimer acid is obtained from oleic acid. The ethylene glycol diester of the dioleic acid is observed to have the effect of improving the antiscuffing properties of jet fuel as measured by the Ryder gear test.

EXAMPLE 4

The preparations and tests of Example 1 are repeated except that the C_{36} dimer acid is obtained from the mixed dimer of oleic and linoleic acids. The ethylene glycol diester of the dioleic acid is observed to have the effect of improving the antiscuffing properties of jet fuel as measured by the Ryder Gear Test.

Turning now to the embodiment of the present invention relating to the use of partial esters of dicarboxylic acids having at least 9 carbon atoms between the carboxylic acid groups in the molecule, the partial esters of the aforementioned acids generally consist of a mixture containing a major portion of the monoester with minor proportions of the diester and unreacted acid. The preparation of these partial esters can best be illustrated by reference to the following equation:

$$\text{HOOC—R—COOH} + \text{YHO—R'—OH} \rightarrow \text{HO—R'OOC—R—COOH} + H_2O$$

wherein R is the hydrocarbon skelton of the dicarboxylic acid having more than 9 carbon atoms between the acid groups, R′ is either the hydrocarbon skeleton of a C_2 to C_8 glycol or the oxa-alkyl skeleton of an oxa-alkane diol and Y is less than 2.

The procedure used in preparing the partial ester consisted of weighing out the dimer acid and glycol in equimolar quantities and carrying out the esterification in benzene under reflux conditions (80° C.) with a small amount of paratoluene sulfonic acid as a catalyst. A condenser and trap were used—the refluxing being stopped when the theoretical amount of water was collected. (The water azeotropes off with the benzene.) Then the benzene solution was cooled and water washed to remove the catalyst. The benzene was then stripped off under vacuum at 35° to 40° C., leaving the product usually a clear, dark amber viscous fluid.

EXAMPLE 5

The procedure outlined immediately above was used to make 6 different monoesters. In each case, 0.1 mole of C_{36} dimer acid (Empol 1014—essentially linoleic dimer acid), 0.1 mole of glycol and 1.5 grams paratoluene sulfonic acid were mixed with 1 pint of benzene and then the reaction was carried out. Monomeric esters of the following glycols were made:

Glycol

Ethylene
Triethylene
Neopentyl (2,2-dimethyl,1,3 propane diol)
1,4 butane diol
1,6 hexane diol
1,12 dihydroxy octadecane

Each of the above monoesters was quite soluble in hydrocarbons.

Effect of monomeric esters on load-carrying capacity of jet fuels

As shown by the data below, the addition of 0.1% of several of the monoesters increases the antiscuffing properties of jet fuel as measured by the Ryder Gear Test (E. A. Ryder, ASTM Bulletin 184, 41 (1952)). The ratings represent the load in pounds/inch of tooth width to produce a given amount (22½%) of gear scuffing. It can be seen that the ethylene glycol derivative is by far the most effective, while the neopentyl compound is the least effective. It can also be seen that the C_{36} dimer acid itself has substantially no effect.

Effect of monomeric esters of C_{36} dimer acid and glycols on load-carrying capacity of jet fuels

Run	Additive in Base Jet Fuel [1]	Ryder Rating (#/in.)
A	None	400
B	0.1% C_{36}/Ethylene Glycol Monoester	1,530
C	0.1% C_{36}/Triethylene Glycol Monoester	1,100
D	0.1% C_{36}/Neopentyl Glycol Monoester	770
E	0.1% C_{36}/1,6 Hexane-Diol Monoester	1,800
F	0.1% C_{36} Dimer Acid	480
G	Run B except Dimer Acid Hydrogenated	2,290

[1] Highly isoparaffinic fuel of 375° to 500° F. boiling range, high thermal stability, low freezing point and low sulfur content.

Furthermore, it has also been found that the ethylene glycol monoester blend (at 0.1% concentration) passes a critical thermal stability test for jet fuels. This is a 5 hour test in which the fuel, held at 300° F. in bulk, is pumped through a heat exchanger to reach 500° F. and then through a filter. The requirements are that no deposits should form on the metal heat exchanger tube and that there should be no (or little) pressure drop across the filter. Many conventional load-carrying additives fail to test.

EXAMPLE 6

The procedures and tests of Example 5 are repeated with the exception that the dimer of oleic acid is utilized as the dicarboxylic acid. The addition of 0.1% of the resulting monoesters is found to increase the antiscuffing properties of jet fuel.

EXAMPLE 7

The procedures and tests of Example 5 are repeated with the exception that the mixed dimer of linoleic and oleic acids is utilized as the dicarboxylic acid. The addition of 0.1% of the resulting monoesters is found to increase the antiscuffing properties of jet fuel.

Another method for the preparation of desired monoester products involves heating a stirred mixture of equimolar proportions of diol and dioic acid for 4 hours at 100° C. and then to add 1.5 molar proportion of dioic acid with further stirring and heating at 80° C. as above.

Another technique is to heat one molar proportion of the dioic acid at 50° to 100° C. and to introduce, portionwise beneath the surface of the acid, 0.01 to 0.75 molar proportion, preferably 0.2 to 0.5 molar proportion, of ethylene oxide or propylene oxide.

A further technique is to heat together one molar proportion of diol and two molar proportions of dioic acid at 95° to 125° C. in the presence of kerosene as diluent for 4 to 28 hours.

The preferred technique is to reflux the mixture as utilized in Examples 5 through 7.

EXAMPLE 8

A number of compositions were prepared using various percentages of the lubricity additives of the present invention and were tested by means of the "Ryder Scuff Test." The particular lubricity agent used was an ester

of a linoleic dimer reacted with ethylene glycol under refluxing conditions as described hereinbefore. The results of these tests are illustrated in the following table:

Run	Oil	Additive, Wt. Percent	Ryder Scuff Test Lbs. per Inch
A	Di(2-ethylhexyl) sebacate	0	1,900
		0.5	3,080
B	C_{8-10} Oxo adipate	0	1,700
		0.1	2,000
C	Blend of 69% No. A with 17.3% C_8 azelate and 13.7% C_{10} adipate.	0	1,700
		0.2	2,470
D	Blend of 55% trimethylolpropane triester of pelargonic acid and 45% complex ester of neopentyl glycol, trimethyl pentanol and sebacic acid.	0	2,500
		0.5	2,960
E	Aviation grade mineral oil, viscosity 100 SUS at 210° F.	0	2,700
		0.5	3,610
F	Neutral mineral oil, viscosity 43 SUS at 210° F.	0	1,170
		0.1	2,530
G	No. F with additive made using 2 moles of diol for 1 mole of dioic acid.	0	1,170
		0.5	3,200

From the above, it is readily apparent that the additive of the present invention materially reduced scuffing in every case.

It has now further been found that especially effective lubricity additives can be prepared from the reaction product of an oil insoluble glycol and a hydrogenated dicarboxylic acid having at least 9 carbon atoms between the carboxylic acid groups. While either the dicarboxylic acid or the ester product may be hydrogenated, it is preferred that the dicarboxylic acid be hydrogenated prior to esterification. This hydrogenation may be accomplished by any suitable process known to the art. For example, the acid may be reduced with hydrogen gas over platinum catalyst at a temperature in the range from 20° to 100° C. in a steel bomb. The hydrogen pressure in the system may range from about 10 to 300 pounds. Another method by which hydrogenation may be accomplished is by the use of lithium hydride using conventional techniques at ambient temperatures. As before, the preferred dicarboxylic acids for use in this embodiment consist of the dimer of linoleic acid, the dimer of oleic acid and the mixed dimer of linoleic and oleic acids. Additionally, the preferred oil insoluble glycols include alkane diols or oxa-alkane diols having straight or branched chains. The alkane diol may have from about 2 to 8 carbon atoms, preferably 2 to 5 carbon atoms in the molecule. A preferred alkane diol is ethylene glycol and a preferred oxa-alkane diol is 4-oxa-heptane diol-2,6. Other specific satisfactory glycols are, for example, propylene glycol, polypropylene glycol, polyethylene glycol and the like. Diesters and partial esters of the hydrogenated dicarboxylic acids may be prepared by any of the methods previously disclosed in previous embodiments of the present invention.

In order to further illustrate the advantages obtained by utilizing a hydrogenated dicarboxylic acid to form an ester product for use as a lubricity additive, a number of tests were carried out on several additives including a monoester prepared from a hydrogenated C_{36} dimer acid (Empol 1014).

EXAMPLE 9

A number of additives were added to base jet fuels and the load carrying capacity of the fuels determined. As shown by the data below, the addition of 0.1% of each of the monoesters of C_{36} dimer acid increases the antiscuffing properties of jet fuel as measured by the Ryder Gear Test. The ratings represent the load in pounds/inch of tooth width to produce a given amount (22½%) of gear scuffing. It can be seen that the hydrogenated dimer acid derivative shows greatly superior results.

Effect of monomeric esters of C_{36} dimer acid and glycols on load-carrying capacity of jet fuels

Run	Additive in Base Jet Fuel [1]	Ryder Rating (#/in.)
A	None	400
B	0.1% C_{36} Dimer Acid/Ethylene Glycol Monoester	1530
C	0.1% C_{36} Dimer Acid	480
D	Run B except Dimer Acid Hydrogenated	2290

[1] Highly isoparaffinic fuel of 375° to 500° F. boiling range, high thermal stability, low freezing point and low sulfur content.

The importance of maintaining control over the molecular weight of the reaction products of the present invention was investigated. I should be noted that the diesters and partial esters heretobefore described have terminal hydroxy groups arising either from the carboxylic acid groups that have not been esterified or from the unreacted portion of the glycol. It is possible that under the conditions of esterification that these groups react further causing condensation of 2 or more ester molecules forming condensation polymers of relatively high molecular weight. Such polymers are described in U.S. Patent 2,424,588, previously cited. In this patent, the condensation reaction between molecules is allowed to proceed until polymers having molecular weight as high as 20,000–25,000 are obtained. It is possible to control the amount of condensation by following the amount of water produced in the reaction mixture and stopping the reaction when the theoretical amount of water for the desired polymer state has been obtained. The effect of increasing the polymeric state of the reaction product between a C_{36} dimer acid (Empol 1014—dilinoleic acid) was determined as per the following Example 10.

EXAMPLE 10

The comparative lubricity of additive compositions containing various degrees of polymerization between the ethylene glycol ester of a C_{36} dimer acid was determined. Reaction products of varying degrees of polymerization were obtained by stopping the esterification reaction at various points based on the amount of water collected. Compounds having essentially one ester molecule, 2 ester molecules and 4 ester molecules were prepared. The respective physical characteristics of these compounds are given in the following table:

Reaction product of ethylene glycol and C_{36} dimer acid

	Number Molecules Ester Condensed [1]	Acid Number (Theoretical)	Molecular Weight (Theoretical)
Product A	1	94(100)	716(609)
Product B	2	39(50)	1,264(1,200)
Product C	4	21(25)	1,975(2,364)

[1] Based on water removed from the reaction mixture.

It is seen from the above table that Product A consisted essentially of a monomeric monoester of ethylene glycol and the C_{36} dimer acid. Product B, on the other hand, consisted of a dimer of the monoester wherein 2 molecules of the monoester have condensed. The slightly lower acid number than theoretical and the slightly higher molecular weight than theoretical can be attributed to small amounts of higher polymer condensation products. Similarly, Product C is seen to be a tetramer of the monoester and also is observed to contain small amounts of more highly condensed mateiral.

The above materials were tested in order to determine the effect on the lubricity properties of a fluid to which they have been added. The test results are given below:

Additive in solvent 100 neutral:	Relative Valve Lifter Wear [1]
None	100
1% of Product A	8
1% of Product B	12
1% of Product C	85

[1] In a 28 hour test using a 1962 V–8 Olds engine equipped with 16 radioactive valve lifters. Test conditions:
(a) Speed—1500 r.p.m.
(b) Jacket outlet temperature—180° F.
(c) No load.

Examination of the above data clearly indicates that both the monomeric and dimeric ester reaction products (Products A and B, respectively) show a substantial reduction in the valve lifter wear. The tetramer condensation product, however, shows a far lesser effect on reduction of valve lifter wear in this test. Thus, in order to achieve best results in improving lubricity, it is necessary that the dicarboxylic acid-glycol ester be formed in such a manner so that no more than about 3 molecules of the ester condense. For purposes of clarity, the following equation is believed to represent the method of formation of the above polyesters:

$$n\text{HOOC—R—COOH} + n\text{HO—R'—OH} \rightarrow \text{HO}\left[\text{OC—R—COO—R'—O}\right]_n\text{H} + n\text{H}_2\text{O}$$

As indicated, for the purposes of the present invention, it is necessary that n have a value no greater than about 2 in order to prepare operative esters for use as lubricity additives.

It is similarly possible to form polyesters of the diesters of the dicarboxylic acids of the present invention.

What is claimed is:

1. A new composition of matter, suitable for addition to a composition selected from the group consisting of hydrocarbon liquids and synthetic ester lubricants, which comprises an ester, formed by reacting an oil-insoluble glycol having between about 2 and about 8 carbon atoms per molecule with a hydrogenated dimer of a C_{12} to C_{18} unsaturated monocarboxylic acid, said ester being selected from the group consisting of monomeric esters having the formulae:

HOOC—R—COOR'—OH

HO—R'—OOC—R—COO—R'—OH

and esters formed by reacting a hydrogenated dimer of said carboxylic acid with said glycol in the mole ratio of 2 to 1 respectively, wherein R is the hydrocarbon radical of the said dimer acid and R' is the hydrocarbon radical of said glycol.

2. A composition of matter as in claim **1** wherein the acid is the hydrogenated mixed dimer of linoleic and oleic acids.

3. A composition of matter as in claim **1** wherein the acid is the hydrogenated dimer of linoleic acid.

4. A composition of matter as in claim **1** wherein the acid is the hydrogenated dimer of oleic acid.

5. A composition of matter as in claim **1** wherein the glycol is ethylene glycol.

6. A composition of matter as in claim **1** wherein the glycol is ethylene glycol and the acid is the hydrogenated mixed dimer of linoleic and oleic acids.

7. A composition of matter comprising a major amount of a liquid selected from the group consisting of hydrocarbon liquids and synthetic ester lubricants, and a minor amount of the composition of claim **1**.

8. A composition of matter as in claim **7** wherein the liquid is a jet fuel and the ester is present in an amount ranging between about 0.001 and about 0.4 wt. percent.

9. A composition of matter as in claim **7** wherein the liquid is a mineral lubricating oil and the ester is present

in an amount ranging between about 0.001 and about 4.9 wt. percent.

10. A composition of matter as in claim **8** wherein the ester is a partial ester.

11. A composition of matter as in claim **9** wherein the ester is a partial ester.

12. A composition of matter as in claim **8** wherein the acid is the hydrogenated dimer of linoleic acid.

13. A composition of matter as in claim **8** wherein the acid is a hydrogenated dimer of oleic acid.

14. A composition of matter as in claim **8** wherein the acid is a hydrogenated mixed dimer of linoleic and oleic acids.

15. A composition of matter as in claim **8** wherein the glycol is ethylene glycol.

References Cited by the Examiner

UNITED STATES PATENTS

2,424,588	7/1947	Sparks et al.	252—56
2,562,878	8/1951	Blair	260—485
2,870,112	1/1959	Mertzweiller	260—468
2,976,245	3/1961	Copes	252—56
3,029,204	4/1962	Matuszak et al.	252—56
3,036,099	5/1962	Barrett et al.	260—407 X

FOREIGN PATENTS

847,399	7/1960	Great Britain.

DANIEL E. WYMAN, *Primary Examiner.*

W. H. CANNON, *Assistant Examiner.*