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HYDROCARBON COMPOSITIONS CONTAINING ANTI-WEAR ADDITIVES

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The present invention is a continuation-in-part of Serial No. 263,425, filed March 7, 1963, now U.S. Patent No. 3,180,832, entitled "Oil Compositions Containing Anti-Wear Additives," inventor: Michael J. Furey.

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 fuels 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 a compound selected from the class consisting of polyamines and hydroxy amines and wherein the dicarboxylic acid is 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. It is preferred that the additives also have molecular weights below about 950, preferably below about 800 as determined by "Osmometer Method," Anal. Chem., vol. 33, No. 1, pp. 135–137, January 1961, Wilson.

The lubricity additives of the present invention preferably comprise reaction products of a polyamine or hydroxy amine and dicarboxylic acids that are obtained by the polymerization of dienoic or trienoic monocarboxylic acids. Thus, the invention is concerned with a novel class of lubricity additives which are specifically adapted for use in conjunction with oleophilic liquids such as hydrocarbon lubricants and jet fuels. In accordance with a specific adaptation of the present invention, middle distillate compositions such as jet fuels are improved with respect to their lubricity by incorporating therein an effective amount of a reaction product of a compound selected from the class consisting of polyamines and hydroxy amines and a dimer of linoleic acid. A very desirable compound is a reaction product of diethanol amine and a dimer of linoleic acid.

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 metal surfaces under heavy loading is a serious problem. 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 a compound selected from the class consisting of polyamines and hydroxy amines and wherein the dicarboxylic acid

is characterized by having at least 9 carbon atoms between the respective carboxylic groups.

Other additives, of course, may be added to the oil compositions of the present invention to form a finished oil. Such additives include 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 isononyl 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; etc.

As pointed out heretofore, the dicarboxylic acids utilized are those which contain at least 9 carbon atoms between the respective carboxylic groups. It is 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 dimer of linoleic acid, dodecanedioic acid, and 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 and must have at least two double bonds in its longest carbon chain, the bonds being separated by 3 carbon atoms, e.g., 9,12-octadecadienoic acid and 9,12,15-octa-decatrienoic acid.

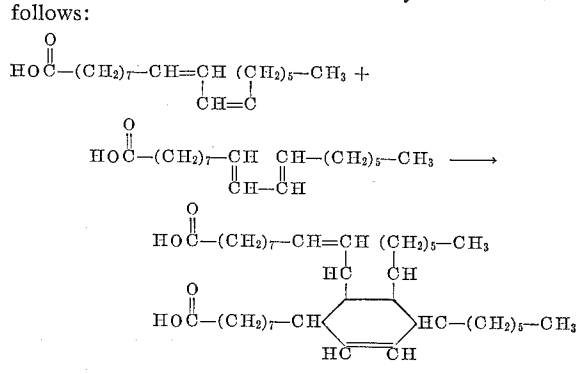
The mixture of high molecular weight unsaturated fatty acids comprises monomers, dimers, trimers and higher polymers in the ratio of from about 45% to about 55% of a monomers and dimers fraction having a molecular weight in the range of from about 300 to 600, and from about 45% to about 55% of a trimers and higher polymer fractions having a molecular weight in excess of 600. The fatty acid polymers result in part from a thermal polymerization of fatty acid type constituents of the castor oil, and in part from other reactions, such as the intermolecular esterification, of such acid to form high molecular weight products. The acid mixture, which is mainly a mixture of polymeric long chain polybasic carboxylic acids, is further characterized by the following specifications:

Acid No.	150–164
Saponification No.	175–186
Free fatty acids ——percent——	75–82
Iodine value	40 to 55
Non-saponifiables ——percent——	2.5 to 5

A fatty acid mixture such as above described is marketed by the W. C. Hardesty Company under the trade name "D–50 Acids," and as "VR–1 Acids" by Rohm and Haas Company.

Thus, as pointed out, a particularly desirable dicarboxylic acid to be used in forming the reaction product of the present invention is a dimer of linoleic acid.

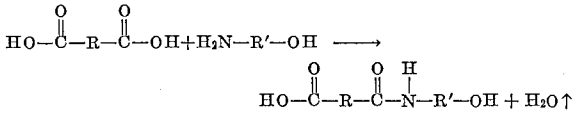
The formation of this dimer acid may be illustrated as follows:



In general, the dimer acid of linoleic acid with which 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 that the dimer acid is not necessarily 100% dimer acid.

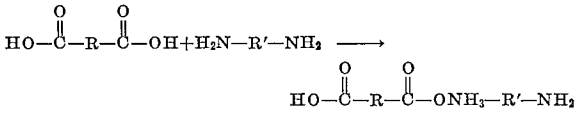
The amine compounds for use in conjunction with the diacids of the present invention are selected from the class consisting of polyamines and hydroxy amines such as amino alcohols, diamines, polyglycol amines, and dialkanol amines.

The dicarboxylic acid amino alcohol reaction product may be prepared by reacting one mole of dimer acid with one mole of an amino alcohol as follows:



The prefered amino alcohols are those alcohols having from about 2 to 20 carbon atoms and R′ may be derived from an aliphatic, alicyclic or aromatic hydrocarbons. Specific amino alcohols which are desirable are monoethanolamine; N-aminoethyl ethanolamine; p-amino phenol; 4-amino-1-butanol; 5-amino-1-pentanol; 10-amino-1-decanol; and amino isopropanol.

The diacid diamine reaction products in accordance with the present invention may be made by reacting one mole of a dicarboxylic acid with one mole of a diamine as follows:

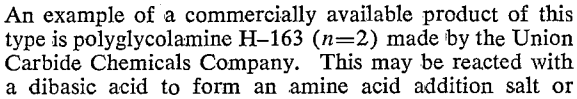


R may be a bivalent aliphatic, alicyclic or aromatic hydrocarbon radical containing from 9 to 42 carbon atoms. R′ may be a bivalent aliphatic, alicyclic or aromatic hydrocarbon radical containing from 2 to 50 carbon atoms. Examples of suitable diamines are thylene diamine; propylene diamine; 1,4 butane diamine and 1,6 hexane diamine. In general, the preferred structure for both the diacids and diamines is α–ω.

The polyglycolamines for use in conjunction with the present invention have the following general structure:

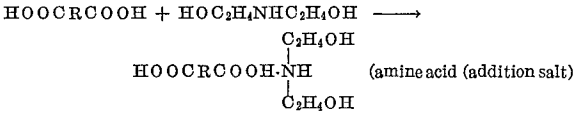
$$HO—[C_2H_4O]_nC_3H_6NH_2$$

An example of a commercially available product of this type is polyglycolamine H–163 (n=2) made by the Union Carbide Chemicals Company. This may be reacted with a dibasic acid to form an amine acid addition salt or possibly even a partial ester.



It is preferred that the number of carbon atoms in the amine be in the range from 2 to 20 and that the amine be either a primary or secondary amine.

The dicarboxylic acid dialkanol amine reaction product for use in conjunction with the present invention has the following general formula:



Here again the number of carbon atoms in the dialkanol amine may vary in the range from about 2 to 20.

It is well-known in the art to improve the quality of jet fuels by various refining techniques in order to remove from these fuels undesirable constituents such as polar compounds, sulfur compounds, and nitrogen compounds. These compounds are removed in order to improve engine performance and lengthen the hours the engine can be operated without major overhauling, but it has been found that when the voscosity of these fuels is relatively low and wherein certain impurities are removed to below a maximum, the finished pure fuel lacks lubricity, which is essential in order to keep the engine parts from excessive wear and a relatively short life. These engine parts among others comprise the fuel pumps, the gears, the bearings and any other parts wherein scuffing and wear is a problem.

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 dicarboxylic acid/polyamine or dicarboxylic acid/hydroxy amine reaction products 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–25554A, MIL–F–2558B, and amendments thereto, and in ASTM D–1655–62T. Kerosenes and heating oils will normally have boiling ranges between about 300° and about 750° F. and are more fully described in ASTM Specification D–936–48T and supplements thereto, where they are referred to as No. 1 and No. 2 fuel oils. Diesel fuels in which the dicarboxylic acid/polyamine or dicarboxylic acid/hydroxy amine reaction products may be employed are described in detail in ASTM Specification D–975–35T and later versions of the same specification.

Particularly desirable base fuels wherein the present additives 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.

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 these additives are rust inhibitors, anti-emulsifying agents, corrosion inhibitors, anti-oxidants, dispersants, dyes, dye stabilizers, haze inhibitors, antistatic agents and the like. It will frequently be found convenient to prepare additive concentrates for use in the various types of fuels and thus add all of the additives simultaneously.

The additives of the present invention, as pointed out heretofore, are also very effective in increasing the load carrying capacity of other fuels and fuels such as xylene, kerosene, and synthetic oils as well as mineral lubricating oils. The synthetic oils will include diester oils such as di(2-ethylhexyl) sebacate; complex ester oils and either monobasic acids or monohydric alcohols; silicone oils; sulfide esters; organic carbonates; and other synthetic oils known to the art. Warming the oil and additive materials may be necessary in order to obtain solution.

The present invention may be more fully understood by the following examples further illustrating the same.

Example 1

0.1 mole C_{36} dimer acid (56.5 g.) and 0.1 mole diethanolamine (10.5 g.) were mixed in 200 ml. benzene and refluxed at 82° C. for 4 hours. Only 0.1 ml. H_2O was collected, indicating that esterification of the alcohol did not occur. The benzene was stripped under vacuum at 34–38° C. to leave a yellow clear viscous liquid as the product. A 0.1% solution of this product dissolved in a straight mineral oil was prepared. This oil was a solvent-extracted distillate having a viscosity of 34.9 cps. at 77° F. and a viscosity index of 110.

As shown by the data in the following table, the dimer acid/diethanolamine salt is quite effective in reducing metallic contact and friction. These tests were run on the ball-on-cylinder machine at 240 r.p.m. with steel-on-steel

for 32 minutes. The device is described fully in the paper "Metallic Contact and Friction Between Sliding Surfaces" by M. J. Furey and published in A.S.L.E. Transactions, vol. 4, No. 1, pp. 1–11 (1961).[1]

TABLE I.—EFFECT OF DIMER ACID/DIETHANOLAMINE SALT ON METALLIC CONTACT AND FRICTION

Load (g.m.s.)	Mean Hertz Pressure (p.s.i.)	Percent Metallic Contact		Friction (g.m.s.)	
		Base Oil	Base Oil+ +0.1% Additive	Base Oil	Base Oil +0.1% Additive
240	54,400	92	13	27	12
1,000	88,000	98	38	105	68
4,000	141,000	98	98	354	293

From the above, it is apparent that the additives of the present invention are effective in reducing both metallic contact and friction.

If the additives of the present invention 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 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 from about 0.001 to 0.2% by weight, preferably in the range 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 in the range preferably from about 0.1 to 2.0% by weight.

[1] The system—consisting basically of a fixed metal ball loaded against a rotating cylinder—is one of pure sliding. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between the two surfaces. In general, the electrical resistance fluctuates very rapidly from a very high value to a very low value, suggesting that metallic contact is discontinuous. The average recorded resistance, therefore, is a time average and is consequently related to the percent of the *time* that metallic contact occurs—referred to as "percent metallic contact." It has been found that there is an excellent correlation between "percent metallic contact" and wear in this system. The friction between the ball and cylinder is measured by means of a small differential transformer and is recorded continuously. With this apparatus, the entire region from hydrodynamic (no metallic contact) to pure "boundary" lubrication (continuous metallic contact) can be readily investigated. In these tests, metallic contact and friction at a given load and speed are recorded with time. The test specimens—½ inch balls and 1¼ inch diameter cylinders—were made of AISI 52100 steel. All the tests were run at the same temperature—77° F.—and at one speed—240 r.p.m. (56 cm. per sec. sliding velocity). The loads were varied from 240 to 4000 grams, corresponding to mean Hertz pressures of 54,700 to 141,000 p.s.i.

Example 2

Additional reaction products were prepared by the technique described in Example 1. The results of these preparations are tabulated in the following table.

TABLE II.—REACTION PRODUCTS OF C_{36} DIMER ACID AND POLYAMINES OR HYDROXY AMINES

Amine Compound	Solvent	Reaction Temp., ° C.	Reaction Time (hrs.)	[1] H_2O Evolved (ml.)	Nature of Product
1,6 Hexane Diamine	None	[2] 78	0.5	[3]	Viscous amber fluid.
Do	Benzene	82	4	0.2	Amber gel.
Do	Toluene	111	5	1.5	Somewhat darker amber gel.
Do	Xylene	138	1	2.4	Dark amber gel.
Ethylene Diamine	Benzene	82	5	1.4	Viscous, lt. amber fluid.
Do	Toluene	111	1.5	2.9	Viscous amber fluid.
Ethanolamine	Benzene	82	4	[3]	Amber fluid.
Diethanolamine	do	82	4	0.1	Lt. amber or yellow fluid.
Triethanolamine	do	82	5	1.8	Amber fluid.

[1] Since all reactions involved 0.1 gm. mole, theoretical H_2O evolution for losing 1 mole of H_2O is 1.8 ml.
[2] Acid heated to 66° C. and diamine then added with stirring. Temp. climbed to 78° C. max.
[3] Not known.

None of the above products was soluble to the extent of 1% in the mineral oil used. At 0.1% however the diethanolamine derivative was satisfactory and the best of the lot. Blends were also made at 0.2% in xylene. It was found that the diethanolamine derivative was best, being almost completely soluble. The other two alkanolamine derivatives (ethanolamine and triethanolamine products) were fairly soluble though not as good.

Thus, in base fuels requiring low solubility or in base fuels wherein the solubility is greater, these compounds will function to improve the lubricity characteristics of the base fuel.

What is claimed is:

1. An oleophilic liquid composition of improved lubricity comprising a major amount of an oleophilic liquid selected from the group consisting of lubricating oil and normally liquid hydrocarbon fuel, and dissolved therein about 0.001 to 4.9% by weight of a lubricity additive which reduces friction and has a molecular weight of less than 950, which is a reaction product of equi-molar amounts of an unsaturated hydrocarbon dicarboxylic acid containing 9 to 42 carbon atoms between the carboxylic acid groups, and an amine selected from the group consisting of lower alkylene diamines and hydroxy hydrocarbon amines containing 2 to 20 carbon atoms.

2. A composition according to claim **1**, wherein said acid is a C_{36} dimer acid and said amine is a dialkanol amine.

3. A composition according to claim **1**, wherein said liquid is a fuel, said acid is the dimer of linoleic acid, and said amine is diethanolamine.

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