

3,180,832
Patented Apr. 27, 1965

3,180,832
OIL COMPOSITIONS CONTAINING
ANTI-WEAR ADDITIVES

Michael J. Furey, Berkeley Heights, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

No Drawing. Filed Mar. 7, 1963, Ser. No. 263,425
7 Claims. (Cl. 252—56)

This invention relates to additives for hydrocarbon liquid compositions. Particularly, the invention relates to an additive mixture for hydrocarbon liquid compositions for reducing wear, wherein said additive mixture consists of an oil-soluble dimer acid with a diol or a polyol.

The present application is a continuation-in-part of Serial No. 816,704, filed May 29, 1959, entitled "Oil Compositions Containing Anti-Wear Additives," inventor: Michael J. Furey.

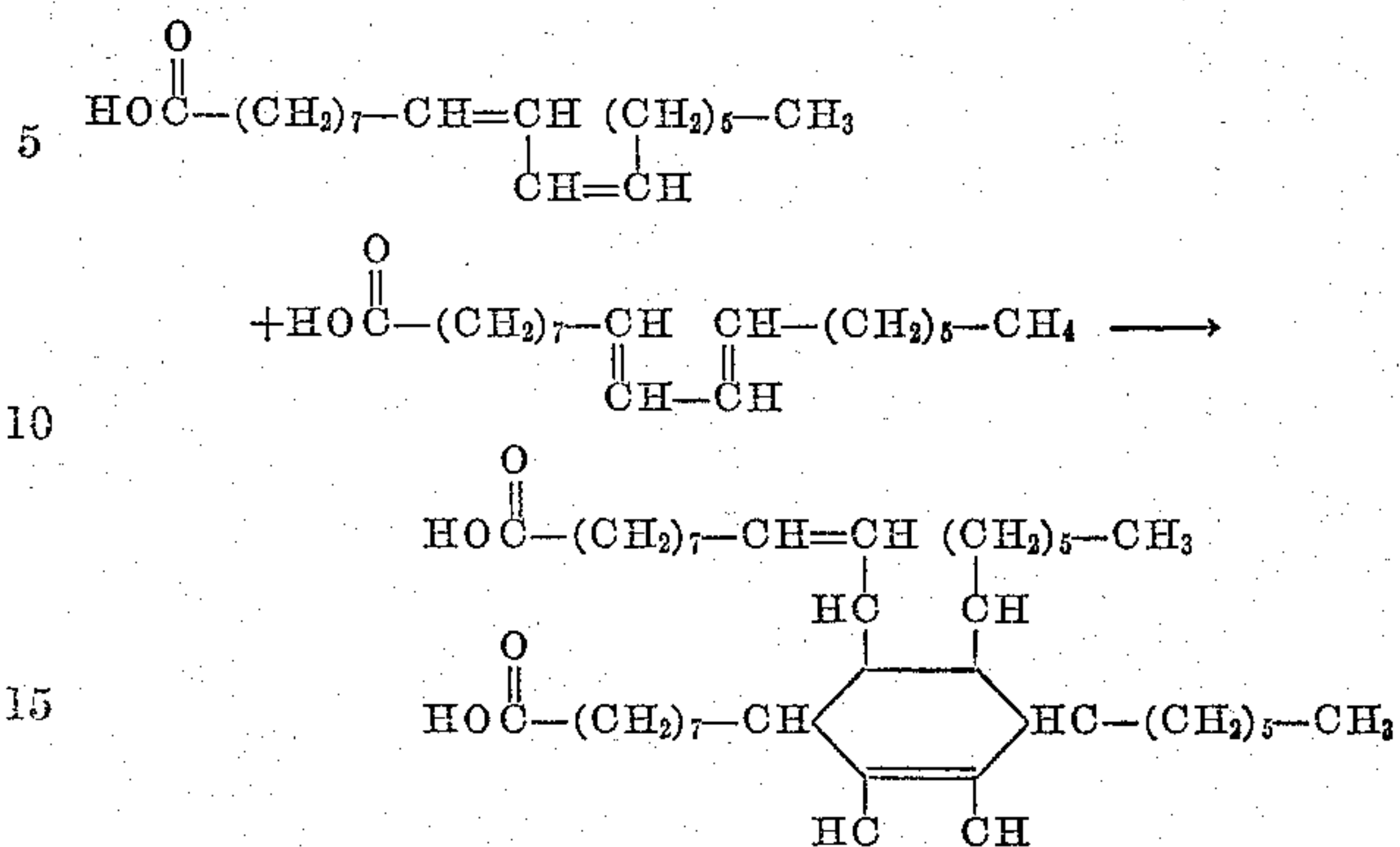
Many oil compositions are designed for lubricating under boundary conditions (e.g. crankcase oils, aviation oils and gear oils) where a serious problem is the prevention of wear of the metal surfaces that occurs under heavy loading. One common example of such heavy loading occurs in the operation of 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 the lubricant, a mixture of a dimer acid and a glycol, preferably in stoichiometric quantities.

In a different environment, it is well-known in the art to improve the quality of jet fuels by removing from these fuels undesirable constituents such as polar compounds, sulfur compounds, and nitrogen compounds; but it has been found that, the viscosity of these fuels being relatively low, when these impurities are removed, the finished pure fuel lacks lubricity, which is essential in order to keep certain engine parts from excessive wear. These engine parts among others comprise the fuel pumps wherein scuffing and wear is a problem.

Therefore, another objective of the present invention is to 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/glycol mixtures 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-25558B, 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-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/glycol mixtures may be employed are described in detail in ASTM Specification D-975-35T and later versions of the same specification.

The additives of the present invention may also 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 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 dimer acids for use in conjunction with the present

invention are dimers of linoleic acid. The formation of this dimer acid may be illustrated as follows:

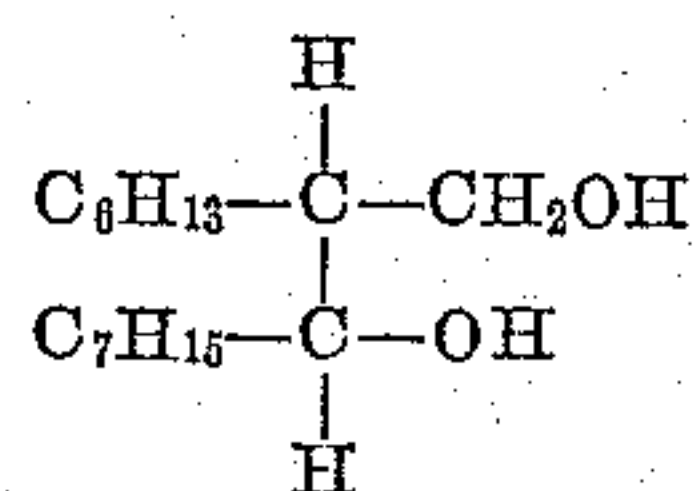


While the invention is described using an admixture of a dimer acid and a glycol, it is to be understood that the dimer acid is not necessarily 100% dimer acid, for example, the following compositions of acid are commercially available:

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

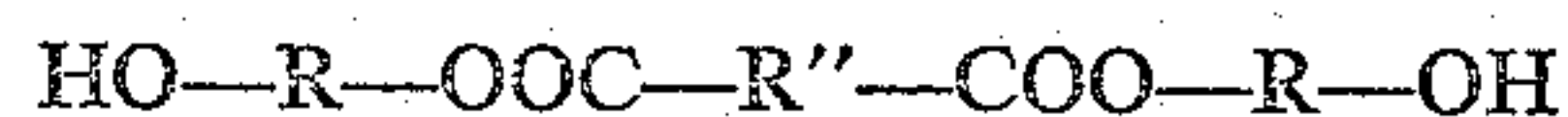
It is preferred for the purpose of the present invention that the amount of dimer acid present in the acid composition be at least 50% and more preferably about 75% by weight.

The polyols of the present invention are those which may contain from *a* up to about 50 carbon atoms. A satisfactory glycol has 16 carbon atoms and the general formula:



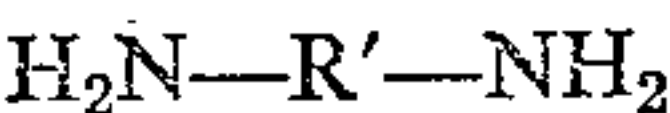
wherein the C₆ and C₇ alkyl groups are branched. This material was prepared by aldolization of iso-octyl aldehyde, followed by hydrogenation. The iso-octyl aldehyde that was used, was an isomeric mixture of branched chain aldehydes (predominantly methyl branched) prepared in the first stage of the well-known Oxo process. Here a C₇ monoolefin (prepared from butylene and propylene feed, is reacted with hydrogen and carbon monoxide under pressures of 1,000 to 3,000 p.s.i. and temperatures of about 300° to 400° F. in the presence of a cobalt carbonyl catalyst to form iso-octyl aldehyde.

Other diols are useful for the present invention. For instance, a dihydroxy compound can be prepared by esterifying one mole of dimer acid with two moles of a glycol, thus:



wherein R is the radical of a glycol and R' is the hydrocarbon part of the dimer acid. The diol represented by the above formula is suitable to be used with dimer acid according to the present invention. Other suitable diols are oxa alkane diols obtained for example by hydrolysis of ethylene oxide, propylene oxide or other epoxy compounds. These diols may have molecular weights between 200 and 2000. An example is 3,6,9-trioxa-1,4,7,10-tetramethyl undecane-1,11-diol.

In place of the polyols, oil-soluble diamines may be used such as those having the general formula



wherein R' is an alkyl radical of 10 to 40 carbon atoms, e.g. 1,12-dodecyl diamine and 1,9-heptadecyl diamine.

The preferred glycols which give excellent results are those containing from about 2 to 5 carbon atoms, for example, ethylene glycol and 1,4-butane diol.

The oil compositions of the invention will comprise a major proportion of oil and about 0.01 to 2.0%, preferably 0.1 to 1.0 wt. percent of the additive mixture of the invention. As discussed above, this additive mixture generally will have substantially equimolar proportions of dimer acid and glycol although it is to be understood that compositions encompassed within the invention can have a slight excess of either material. Thus, broadly speaking there may be present about 0.8 to 1.2 molar proportions of the glycol per molar proportion of dimer acid. Also additive concentrate compositions containing up to 30 wt. percent of the additive mixture may be prepared as solutions or dispersions, depending of course upon the maximum oil-solubility of the additive mixtures.

Among the liquid hydrocarbons which may be used as base fuels are mineral lubricating oils or synthetic lubricating oils. The synthetic oils will include diester oils such as di(2-ethylhexyl) sebacate; complex ester oils such as those formed from dicarboxylic acids, glycols 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 if the additives are solid at normal temperature.

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 dipressants such as copolymers of vinyl acetate with fumaric acid esters of coconut oil alcohols; viscosity index improvers such as polymethacrylates; etc.

The invention will be further understood by reference to the following examples which illustrate a preferred form of the invention.

EXAMPLE 1

A crankcase lubricating oil composition was prepared by simple mixing into oil, equimolar proportions, 0.258 wt. percent of the C₁₆ alkane diol previously described and 0.568 wt. percent of the dimer of linoleic acid (also previously described). The oil itself was a mineral lubricating oil of 100 SUS at 100° F., having a viscosity index of about 95, and prepared by solvent extraction of a Mid-Continent crude.

The base oil without additive and the above composition containing the additives of the invention were each tested according to the procedure described in an article, by M. J. Furey and J. F. Kunc, entitled "A Radiotracer Approach to the Study of Engine Valve Train Lubrication." This article was published in the July 1958 issue of Lubrication Engineering Journal of the American Society of Lubrication Engineers, pages 302 to 309. Briefly described, this test was carried out as follows: A laboratory V-8 gasoline engine was equipped with radioactive steel valve lifters. The engine was run using the oil composition for a period of 3 hours at 1000 r.p.m. with no load and with the valve lifters under normal spring tension, while the jacket outlet temperature of the circulating water was controlled at 180° F., and the oil temperature was between 180-190° F. After 3 hours' operation, the amount of wear occurring on the radioactive steel valve lifters was determined by first measuring the total amount

of radioactive wear debris contained in the used oil by means of a scintillation detector connected to a scaler. A standard solution containing a known weight of a radioactive valve lifter was also counted. From this, the concentration of lifter wear debris in the oil sample is calculated.

The above test procedure was repeated on the base oil per se (i.e. without any additive) as a reference, followed by another test using the base oil containing 0.826 wt. percent of the previously described dimer of linoleic acid. Then the base oil was once more run in the test, followed by still another test wherein the base oil contained 0.826 wt. percent of the previously described C₁₆ alkane diol. By thus running the base oil without addition before each of the additive-containing oils were run, any carry-over effect from previous additives is eliminated. The result of the test of each additive-containing oil was calculated as percent wear relative to the wear encountered by the preceding reference test. The compositions tested and the results obtained are summarized in the following table:

Table I
INFLUENCE OF GLYCOLS AND DIMER ACIDS ON VALVE LIFTER WEAR

Additive in Mineral Lubricating Oil, Wt. Percent	Relative Valve Lifter Wear, Percent
None (Each reference oil tested equals 100% wear).....	100
0.258% C ₁₆ Glycol + 0.568% Linoleic dimer acid.....	13
0.826% Linoleic dimer acid.....	40
0.826% C ₁₆ Glycol.....	25

The above data show that the mixture of the C₁₆ glycol and the C₃₆ dimer acid in a 1:1 molar ratio greatly reduced the valve train wear when used at a total concentration of 0.826 wt. percent. At the same total concentration, both the dimer acid and glycol showed a much lesser effect, when used alone. This shows that neither the glycol or the dimer acid alone was nearly as effective as the combination of these two materials. The above described radioactive valve train test has been found to correlate well with actual valve train wear that occurs during normal driving. Furthermore, remarkably, when the reference oil was run after the test oil that contained the additive mixture of the present invention, the rate of wear of the valve lifters remained at about 13% of reference for 3 hours, before returning to 100%; but when the reference oil was run after the other test oils containing only one of the additive ingredients, the rate of wear rose immediately to 100% of reference, i.e. there was no carry-over of beneficial effect, except with the oil containing the additive mixture of the present invention.

EXAMPLE 2

Another test was carried out to measure the metallic contact and friction between sliding, lubricated surfaces. The apparatus used is described in the Journal, entitled "ASLE Transactions," vol. 4, pages 1-11 in 1961. "ASLE" is American Society of Lubrication Engineers. In essence, the system consists basically of a fixed metal ball loaded against a rotating cylinder. The extent of metallic contact is determined by measuring both the instantaneous and average electrical resistance between two surfaces.

In a severe test at 480 r.p.m. and with a Hertz load of 141,000 lbs./sq. in., the following results were obtained.

No.		Percent Metal Contact	Percent Decrease in Friction
1.....	Lube oil with viscosity of 100 S.U.S. at 100° F.....	100	0
2.....	Same oil as No. 1, with 1% equimolar mixture of dimer acid and 1,12-octadecane diol.....	85	13

From the above it is apparent that the additive appreciably reduced the friction and metallic contact.

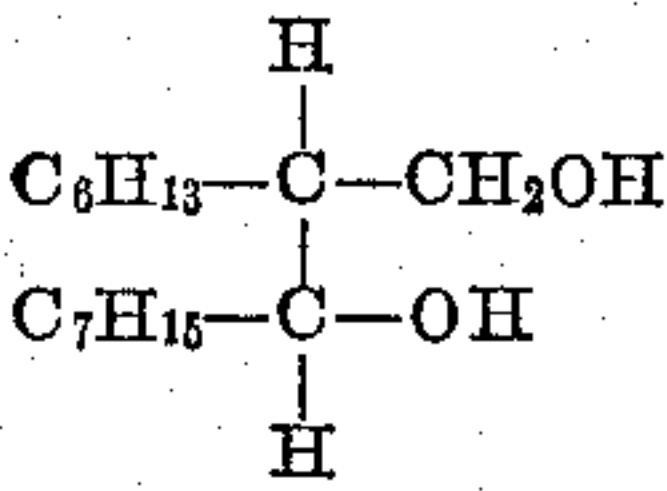
EXAMPLE 3

Additional tests were carried out using the additive of the present invention in a jet fuel (U.S. Military Specification MIL-F-5624F) with the following results:

Additive in Jet Fuel	Ryder Scuff Rating (#/in.)
None	400.
0.1% C ₁₆ glycol+C ₃₆ dimer acid	1,433.
0.1% C ₃₆ dimer acid	480 (No sig. effect).
0.1% hexylene glycol+C ₃₆ dimer acid	776 (Sig. but not large).

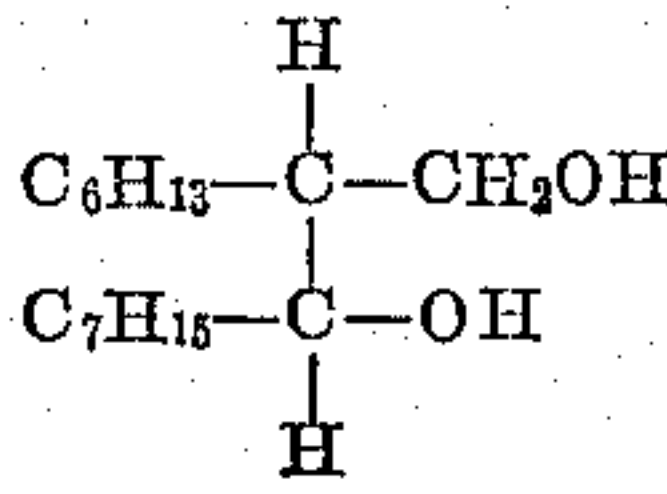
What is claimed is:

1. A water-free lubricating oil composition comprising a major amount of mineral lubricating oil containing as the sole anti-wear agents 0.1 to 5.0 wt. percent of an additive mixture consisting of linoleic dimer acid and an alkane glycol of the general formula:



in substantially equimolar proportions.

2. A water-free lubricating oil composition comprising a major amount of lubricating oil and about 0.1 to 30 wt. percent of an additive mixture of a linoleic dimer acid and a polyol having the general formula:



and wherein there is about 0.8 to 1.2 molar proportions of said polyol per molar proportion of said linoleic dimer acid.

3. A liquid hydrocarbon oil composition comprising a major amount of a liquid hydrocarbon oil and about 0.01 to 2 wt. percent of an additive mixture of a linoleic dimer acid and a diol wherein said diol has from 2 to 50 carbon atoms in the molecule and wherein there is about 0.8 to 1.2 molar proportions of said diol per molar proportion of said linoleic dimer acid.

4. Composition as defined by claim 3 wherein said diol is ethylene glycol.

5. Composition as defined by claim 4 wherein said dimer acid has constituents of at least 50% pure dimer acid.

6. Composition as defined by claim 3 wherein said diol has from about 2 to 5 carbon atoms in the molecule.

7. Composition as defined by claim 6 wherein about 0.01 to 1.0 weight percent of said additive mixture is used.

References Cited by the Examiner

UNITED STATES PATENTS

2,334,158	11/43	Von Fuchs et al.	252—56
2,424,588	7/47	Sparks et al.	252—56
2,497,968	2/50	Young et al.	252—56 X

DANIEL E. WYMAN, *Primary Examiner*.

JOSEPH R. LIBERMAN, *Examiner*.