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LUBRICATING COMPOSITION

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11 Claims. (Cl. 252—56)

This invention relates to improved lubricating compositions. More particularly, it is concerned with gear lubricants which exhibit extreme pressure characteristics and which show substantially no adverse response to the presence of relatively small amounts of water.

The lubricants required for spur and hypoid gears must, in many cases, possess at least some extreme pressure characteristics. These lubricants may be formed by the incorporation into mineral oils or synthetic lubricants of one or more of a number of varying types of additives, such as the sulfides, which form an infinitesimal film on the metal surfaces; or by the use therein of phosphorus- or halogen-containing compounds which act in an analogous manner. Several types of agents (i. e., additives) known to possess extreme pressure characteristics have, however, the adverse property of low dispersibility in mineral oils or in synthetic lubricants miscible therewith such as the aliphatic diesters. These substances or additives are, moreover, readily soluble in water while the latter is ordinarily immiscible with most types of lubricating oils. Consequently, if mineral oil dispersions containing these classes of agents are contaminated with even small amounts of water, separation of the composition into two or more phases may result, the additive being dissolved in the contaminating water as one phase, while the lubricating oil settles out as the second phase. It is obvious that such a combination of conditions is highly undesirable for the effective and proper lubrication of gears, and the like.

These water-soluble extreme pressure agents have been employed under certain circumstances, such as in a relatively dry mix, which is applied to the gear teeth to form a film thereon, following which ordinary lubricating oils are then applied. Alternatively, the agents have been dispersed in mineral oils and like lubricants, by the use of certain dispersion agents, such as sulfonates, phosphatides, aliphatic carboxylic soaps, and the like. This, obviously, increases the cost of the final composition; also, these dispersing agents frequently modify the properties of the lubricating compositions adversely.

It is an object of the present invention to provide improved gear lubricants. It is another object of this invention to provide improved lubricating compositions exhibiting a minimum adverse response to the presence of water. It is a further object of this invention to prepare novel lubricating compositions containing certain classes of water-soluble extreme pressure agents which do not require the additional presence of dispersing agents. Other objects will become apparent during the following discussions.

Now, in accordance with the present invention, it has been found that the water-miscible polyoxyalkylene fluids are superior extreme pressure lubricants when modified by the solution therein of a minor, but effective amount to a water-soluble aliphatic hydroxy carboxylic acid.

The subject compositions referred to above have been

found to possess the unique property of complete miscibility even in the absence of dispersing agents when the composition is anhydrous or contains small amounts of water, e. g. less than about 5% by weight of the polyoxyalkylene fluid. However, it is preferred that the presence of water be held to a minimum, e. g. not exceeding 1% by weight, if possible, since the presence thereof largely decreases the extreme pressure effect of the subject classes of additives. By "water-soluble agents" is meant those agents of the recited classes having a solubility of at least 0.5% by weight in water at 20° C. Preferably the solubility is in the order of at least about 2.0%.

The water-miscible polyoxyalkylene fluids are distinguished from the corresponding classes of polyoxyalkylene fluids which are miscible in aliphatic hydrocarbons including mineral oils. Water miscibility is taken to mean the formation of clear uniphase mutual solutions when the fluid and water are mixed at room temperature (20° C.) in any proportions. The classes of materials with which this invention is concerned are those having an average molecular weight of at least about 250 and usually below about 1500. Polyoxyalkylene fluids of lower molecular weight, such as the diethylene glycol or tripropylene glycol monoethers, are suitable solvents for the subject classes of additives but do not exhibit proper lubricating characteristics or extreme pressure properties. For the most part, the polyoxyalkylene fluids which are miscible with water comprise mixtures of polymers of lower molecular weight epoxides and glycols. Polyethylene glycols having average molecular weights between about 250 and 750 are suitable. Monoesters of said glycols with fatty acids having less than about eight carbon atoms per molecule and monoethers of alcohol having less than about ten carbon atoms also may be utilized.

The preferred classes of water-miscible fluids for use in the present compositions comprise the copolymers of ethylene oxide and 1,2-propylene oxide, as well as the monoethers thereof, particularly when the oxide ratio is 75–25 to 10–90 ethylene oxide:1,3-propylene oxide. By the ratio from 75–25 to 10–90 is meant that, in the oxide mixture which may be used in forming the copolymers the amount of 1,2-propylene oxide in the mixture is from 1/3 to 9 times the amount of ethylene oxide present, by weight, the parts or proportion of the 1,2-propylene oxide being given last. These materials are described in two United States patents, namely, U. S. 2,425,755 to Roberts et al. and U. S. 2,425,845 to Toussaint et al. The materials preferred for use in the subject compositions are those having molecular weights of at least about 250 and preferably below about 1500. The unmodified diols falling within these limitations may be employed or the monoethers thereof may be used. In the preparation of the monoethers, alcohols having from 1 to about 10 carbon atoms are preferred, and still more preferably these are aliphatic monohydric alcohols having the above carbon chain limitations.

The subject polyoxyalkylene fluids may be prepared by polymerization of low molecular weight alkylene glycols to form a closely similar class of polymers. The epoxides and glycols are preferably those having from 1 to 4 carbon atoms each and it is further preferred that the epoxide linkage or the glycol radicals be attached to adjacent carbon atoms. Suitable glycols for use in the formation of water-miscible polymers include ethylene glycol, 1,2-propylene glycol, trimethylene glycol and butylene glycol.

The subject classes of polyoxyalkylene fluids are improved by the solution therein of certain well-defined classes of water-soluble aliphatic hydroxy carboxylic acids. The preferred class of materials comprises the aliphatic hydroxy polycarboxylic acids. The following

acids are typical of the classes to be used in the subject compositions:

Hydroxy acids—
- Monohydroxy fatty acids:
  - Glycollic acid
  - Lactic acid
  - 1-ethylidene lactic acid
  - 2-ethylidene lactic acid
  - Ethylene lactic acid
  - Hydroxy caproic acid
  - α-Hydroxy butyric acid
  - Acetonic acid
  - Leucic acid
  - α-Hydroxy crotonic acid
  - α-Hydroxy valeric acid
- Polyhydric fatty acids:
  - Glyceric acid
  - Arabonic acid
  - Gluconic acid
  - Gulonic acid
  - Galactonic acid
  - Talonic acid
  - Mannonic acid
- Hydroxy polycarboxylic acids:
  - Citric acid
  - Tartaric acid
  - Trihydroxyglutaric acid
  - Saccharic acid
  - Tartronic acid
  - Malic acid

The corresponding sulfhydryl analogs of the above hydroxy acids may be used, such as thioglycollic acid and the like.

The proportion of the subject classes of additives to be utilized in these compositions will vary with the specific conditions to which the composition will be subjected, and the resulting demands thereon, as well as upon the maximum solubility of the additive at the minimum temperature to be encountered. Ordinarily, the proportion will be between about 0.1% and about 5% by weight of the additive based on the weight of the polyoxyalkylene fluid. However, smaller or larger amounts may also be used, and may, in some cases, be even preferred.

The following examples illustrate the advantages gained by the use of compositions of the present invention:

Example I

The extreme pressure characteristics of these compositions were tested in the 4-ball seizure load test at 1800 R. P. M. In this test the load is applied, after which the motor is turned on for a period of 10 seconds. In these tests, the lubricant employed was a copolymer of ethylene oxide and 1,2-propylene oxide having a viscosity of 260 at 100° F. and bearing the trademark "50–HB–260 UCON Fluid." This lubricant was modified by a solution therein of the substances listed in the table below. The table also indicates the maximum load leading to seizure which these compositions were capable of withstanding.

Composition	Four-Ball Seizure Load, kg.
Ucon fluid	59, 79
Ucon fluid+2% citric acid	126–141
Ucon fluid+2% tartaric acid	158–178
Ucon fluid+2% lactic acid	141–158

It will be seen that the presence of the hydroxy carboxylic acids more than doubled the extreme pressure maximum load of the Ucon fluid.

Example II

A second type of 4-ball wear test was utilized in an examination of the same compositions, the scar diameter of the balls being determined and averaged. The testing apparatus is described in "Engineering," vol. 136, July 13, 1933. The test conditions were 600 R. P. M., 7 kg. load for two hours at 80° C., using Atlas steel balls.

Fluid	Scar Diameter, mm.
50-HB-260 UCON Fluid	0.48
same+2% tartaric acid	0.21

Example III

An ethylene glycol polymer having an average molecular weight of about 600 bearing the trade name "Carbowax" can be modified with 1% by weight thioglycollic acid to give a lubricating composition having about double the load bearing capacity of the unmodified Carbowax.

Example IV

A polymer of 50% 1,2-butylene glycol and 50% ethylene glycol, having an average molecular weight of about 500 can be improved about 150% with respect to 4-ball load seizure by the presence of 0.5% glycollic acid.

Example V

A copolymer of ethylene oxide and propylene oxide containing about 60% oxyethylene radicals and 40% oxypropylene radicals, and having a viscosity of about 660 SSU at 100° F. is improved about 180% in the spur gear loading test by dissolving 0.25% α-hydroxy valeric acid therein. The spur gear assembly is run at 3000 R. P. M., ambient temperature.

This case is a division of our copending application, Serial No. 354,622, filed May 12, 1953, now U. S. Patent 2,744,871 which is a continuation-in-part of copending application Serial No. 299,742, filed July 18, 1952, now abandoned.

We claim as our invention:

1. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of citric acid.

2. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of mono-hydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of tartaric acid.

3. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average

molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of lactic acid.

4. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic hydroxy carboxylic acid.

5. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic monohydroxy carboxylic acid.

6. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic polyhydroxy carboxylic acid.

7. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic hydroxy polycarboxylic acid.

8. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible

mixture of heteric oxyethylene oxy-1,2-propylene diols in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said diols containing in a single molecule both oxyethylene and oxy-1,2-propylene groups and said mixture having an average molecular weight of at least 300 attributable to said groups, and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic hydroxy carboxylic acid.

9. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible polyoxyalkylene fluid having an average molecular weight between about 250 and about 1500 and a minor amount, sufficient to improve the extreme pressure properties thereof, of a water-soluble aliphatic hydroxy carboxylic acid.

10. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy oxyethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio from about 1 part to about 9 parts by weight of 1,2-propylene oxide for each part by weight of ethylene oxide, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and between about 0.1% and about 5% by weight of a water-soluble aliphatic hydroxy carboxylic acid.

11. A lubricating composition adapted for extreme pressure use comprising a major amount of a water-miscible mixture of monohydroxy ethylene oxy-1,2-propylene aliphatic monoethers in which the ethylene oxide and 1,2-propylene oxide are combined therein as oxyethylene and oxy-1,2-propylene groups in a ratio which is at least one-third part of 1,2-propylene oxide for each part of ethylene oxide by weight, said mixture having an average molecular weight of at least 300 attributable to said groups, the aliphatic monoether group containing from 1 to 10 carbon atoms, the aliphatic monoethers of said mixture containing in a single molecule both the oxyethylene and oxy-1,2-propylene groups, and between about 0.1% and about 5% by weight of a water-soluble aliphatic hydroxy carboxylic acid.

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