

[54] LUBRICATING OIL ADDITIVE AND LUBRICATING OIL COMPOSITIONS CONTAINING SAME

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[58] Field of Search..... 252/51.5 A; 44/58

[57] ABSTRACT

An improved lubricating oil additive having, among other desirable properties, detergency and superior rust inhibitory characteristics and lubricating oil compositions containing said additive. The additive is a two component mixture comprising a high molecular weight amido-amine and a high molecular weight hydrocarbylamine. The preferred lubricating oil composition is a two-cycle engine oil composition comprising a major proportion of a hydrocarbon lubricating oil and a minor proportion of the two component additive of the invention.

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7 Claims, No Drawings

LUBRICATING OIL ADDITIVE AND LUBRICATING OIL COMPOSITIONS CONTAINING SAME

BACKGROUND OF THE INVENTION

Hydrocarbon lubricating oil compositions commonly have a number of desirable properties imparted thereto by the incorporation of additives. The principal properties imparted by the use of additives are improved detergency, anti-wear properties, and enhanced rust inhibiting characteristics. It is often required that separate detergency, anti-wear, and rust inhibiting additives be employed. Thus, in order to improve detergency, anti-wear, and rust inhibitory properties, the aggregate additive level often approaches a point where a number of undesirable results occur. For example, the detergency additive, the anti-wear additive and the rust inhibitor may be incompatible and interact to form a precipitate in the lubricating oil composition. The combined additives may also contribute to such deficiencies as storage instability where the additives flocculate when the lubricating oil composition is allowed to stand for a period of time, or poor water tolerance where in lubricating oil composition containing the additives forms emulsions or becomes turbid when contacted with water. Furthermore, in the special case of two-cycle engine oils which are mixed with the gasoline fuel, there is the added possibility that the two-cycle engine oil may not be readily miscible with gasoline.

SUMMARY OF THE INVENTION

It is therefore an object of this invention to provide an economical lubricating oil additive having detergency, anti-wear, and rust inhibiting properties.

It is another object of this invention to provide 3 oil compositions having enhanced detergency, anti-wear, and rust inhibiting properties.

It is yet another object of this invention to provide lubricating oil compositions having storage stability and good water tolerance.

It is a particular object of this invention to provide two-cycle engine oil compositions having detergency, anti-wear, and rust inhibiting properties as well as good storage stability, water tolerance, and ready miscibility with gasoline.

Yet other objects and advantages will be apparent to those skilled in the art from the following description.

The foregoing objects are achieved in accordance with the practice of this invention. Broadly, this invention consists of a lubricating oil additive comprising a mixture of a high molecular weight amido-amine and a hydrocarbylamine having a molecular weight in the range of about 425-10,000; and a hydrocarbon lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and a minor proportion of the foregoing additive mixture.

Thus, by the practice of this invention, there are provided a lubricating oil detergency, anti-wear, and anti-rust additive and hydrocarbon lubricating oil composition containing said additive which are characterized by excellent detergency, good wear characteristics, and rust inhibitory properties. In addition, the hydrocarbon lubricating oil compositions of this invention have such desirable properties as good storage stability, good water tolerance, and, in the case of two-cycle engine oil compositions, good gasoline miscibility.

DETAILED DESCRIPTION

High molecular weight amido-amines are known detergency additives for lubricating oil compositions and, in addition, often have good anti-wear properties. However, lubricating oil compositions containing such amido-amines do not have satisfactory anti-rust properties in the absence of a rust inhibitor. At times, even the addition of appreciable amounts of rust inhibitor do not impart sufficiently satisfactory anti-rust properties.

We have now discovered that an economical and superior lubricating oil detergency and anti-wear additive having unexpected rust inhibiting properties may be prepared by mixing a high molecular weight amido-amine and a hydrocarbylamine having a molecular weight in the range of about 425-10,000. The anti-rust characteristics of our additive mixture are surprising since neither the amido-amine alone nor the hydrocarbylamine alone has appreciable rust inhibiting properties. In fact, lubricating oil compositions containing our additive mixture and no other rust inhibitor often have anti-rust properties that are superior to those of lubricating oil compositions containing a high molecular weight amido-amine at the same concentration as our additive plus a rust inhibitor.

Broadly, the high molecular weight amido-amine component of our additive mixture is the condensation product of an alkylenepolyamine and less than the stoichiometric amount of a fatty monocarboxylic acid such that the resultant amido-amine has about 1-3 amino groups in addition to the amide groups. The fatty monocarboxylic acid moiety is aliphatic and contains about 12-30 carbons and preferably contains about 14-20 carbons. The fatty monocarboxylic acid may be either straight chain or branched chain, but mixtures of straight chain and branched chain acids are preferred. Examples of suitable fatty monocarboxylic acids are dodecanoic acid, eicosanoic acid, elaidic acid, triacontanoic acid, stearic acid, isosteric acid, ricinoleic acid, pentadecanoic acid, and alpha-ethyl dodecanoic acid. Preferred are mixtures of straight and branched chain fatty monocarboxylic acids containing about 14-20 carbons.

The alkylenepolyamine moiety of the amido-amine broadly contains about 2-8 amino groups and preferably about 3-6 amino groups. The alkylenepolyamine may broadly contain about 2-16, and preferably about 4-12, carbons. Examples of suitable alkylenepolyamines are ethylenediamine, propylenediamine, diethylenetriamine, hexamethylenediamine, triethylenetetramine, tetraethylenepentamine, and pentaethylenhexamine. The preferred alkylenepolyamine is tetraethylenepentamine.

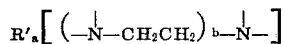
As set forth above, the amido-amine component of our additive mixture is prepared by condensing the alkylenepolyamine with less than the stoichiometric amount of the fatty monocarboxylic acid so that the resultant amido-amine contains about 1-3 amino groups in addition to the amide groups. It is therefore apparent that, from a consideration of the number of amino groups in the alkylenepolyamine, one skilled in the art could readily determine the mole ratio of polyamine to be condensed with fatty monocarboxylic acid to obtain the desired amido-amine. Broadly, however, the mole ratio of alkylenepolyamine to monocarboxylic acid is from about 1:1 to about 1:7 and preferably from about 1:1 to about 1:5. The most preferred amido-amine is

the condensation product of one mole of tetraethylenepentamine and about three moles of a mixture of branched and straight chained fatty monocarboxylic acids containing about 14-20 carbons. Such an amido-amine is manufactured by the Oronite Additives Division of the Chevron Chemical Company and marketed under the designation Oronite 340-D.

The hydrocarbylamine component of our additive mixture is broadly a high molecular weight branched chain aliphatic hydrocarbon monoamine or an alkylenepolyamine having a molecular weight in the range of about 425-10,000 and preferably in the range of about 450-5,000, as well as mixtures of said monoamine and said alkylenepolyamine. Preferred, however, are high molecular weight alkylenepolyamines. The alkylenepolyamines contain about 2-8, and preferably about 2-6 amino nitrogens.

The high molecular weight branched chain aliphatic hydrocarbon monoamine has the empirical formula R-NHA wherein A is either hydrogen or lower alkyl, preferably of from 1 to about 3 carbons, and R is a branched chain aliphatic hydrocarbon substantially free of olefinic unsaturation and of from about 420-1500 average molecular weight. Examples of suitable branched chain aliphatic hydrocarbon monoamines are polypropenylamine, polyisobutenylamine, N-polyisobutenyl dimethylamine, N-polyisobutenyl methylethylamine, N-polypropenyl diethylamine, N-polyisobutenyl N-methylaniline, N-polyisobutenyl morpholine, N-polyisobutenyl piperidine, and N-poly(1-butene) propylamine.

The preferred hydrocarbylamines, as stated above, are high molecular weight alkylenepolyamines. Most preferred are alkylenepolyamines having the empirical formula



wherein b is an integer of from 1 to about 5; a is an integer of from 1 to about 3 and preferably from 1 to about 2; and R' is a branched chain aliphatic hydrocarbon of about 420-1500 average molecular weight and is preferably polypropylene or polyisobutylene. Examples of suitable alkylenepolyamines are N,N'-di(polypropenyl) diethylenetriamine; N,N'-di(polyisobutenyl) diethylenetriamine; N,N'-di(polyisobutenyl) triethylenetetramine; N,N'-di(polypropenyl) tetraethylenepentamine; N,N'-di(polyisobutenyl) tetraethylenepentamine, N,N',N''-tri(polyisobutenyl)tetraethylenepentamine; N,N'-di(poly-1-butenyl) triethylenetetramine; and N,N'-di(polyisobutenyl) di(trimethylene) triamine. A particularly suitable alkylenepolyamine meeting the above requirements is Oronite OGA-472 manufactured by the Oronite Additives Division of Chevron Chemical Company. Oronite OGA-472 is an approximately 70 volume percent solution of the alkylenepolyamine in a mixed aromatic hydrocarbon/aliphatic alcohol solvent.

The lubricating oil additives of this invention comprise a mixture of the foregoing amido-amine and hydrocarbylamine wherein the volume ratio of said amido-amine to said hydrocarbylamine is from about 1:10 to about 10:1 and preferably from about 1:3 to about 3:1. The most preferred lubricating oil additive has an approximately 1:0.7 volume ratio of amido-amine to hydrocarbylamine.

The lubricating oil compositions of this invention broadly comprise a major proportion of a hydrocarbon lubricating oil and a minor proportion of the inventive additive mixture. In practice, lubricating oil compositions comprising a major proportion of a hydrocarbon lubricating oil and about 1-30 volume percent, and preferably about 2-20 volume percent, of the additive find particular utility. Most preferred are lubricating oil compositions comprising a major proportion of a hydrocarbon lubricating oil and about 4-12 volume percent of the additive mixture. The lubricating oil compositions of this invention may also contain minor amounts of conventional materials such as dyes, alcohols, viscosity index improvers, antioxidants, and light petroleum hydrocarbon fractions. The lubricating oil compositions of this invention have general utility as such, but their use as two-cycle engine oils is particularly advantageous.

The efficacy of the additive mixture of this invention and of lubricating oil compositions containing said additive mixture regarding detergency and rust inhibitory properties was determined by means of engine tests and the Boating Industry Association (BIA) rust test. In the BIA rust test, selected steel panels which have been matched with regard to surface and edge finish are thoroughly cleaned with cold naphtha and then by dipping in boiling naphtha followed by dipping in boiling anhydrous methanol. The panel, at 70°F, is dipped in the lubricating oil composition to be tested, which is at 70°F, for 10 minutes and is then drained vertically in 70°F still air for 10 minutes. The panel is immersed vertically into a 70°±10°F salt water solution having a composition of one-half pound of chemically pure sodium chloride in 1 gallon of distilled water. To pass the test, the panel should show no visible rust after the test period except for the area within one-eighth inch of the panel edges or within one-eighth inch of any holes.

The following specific examples will serve to further illustrate the instant invention.

EXAMPLE I

A lubricating oil additive is prepared from equal volumes of the amido-amine designated Oronite 340-D and the 70 volume percent alkylenepolyamine solution designated Oronite OGA-472. A hydrocarbon lubricating oil composition is prepared comprising a major proportion of a hydrocarbon lubricating oil and 8.4 volume percent of the foregoing additive mixture. A gasoline composition is prepared having a 50:1 fuel:oil ratio wherein the gasoline contains 0.5 ml. of tetraethyl lead per gallon and wherein the oil is the lubricating oil composition containing 8.4 volume percent of the instant additive mixture. An air cooled two-cycle engine is operated on the gasoline composition for a 100-hour period after which time the engine is dismantled and rated for cleanliness and wear. The piston cleanliness is rated 8 on a scale of 1-10 wherein a 10 rating is perfect. Crankcase cleanliness is rated as "clean." Engine wear is negligible. It is apparent from the foregoing that the lubricating oil additive of the instant invention is an effective detergency and anti-wear additive.

EXAMPLE II

A number of two-cycle engine oil compositions are prepared containing the two component additive mixture of this invention. The amido-amine component of the additive is Oronite 340-D and the hydrocarbyla-

mine component is an alkylenepolyamine solution, namely, Oronite OGA-472. For comparison, a similar two-cycle engine oil composition is prepared containing only the amido-amine component Oronite 340-D. The lubricating oil compositions contain minor amounts of conventional materials such as long chain fatty alcohol; Stoddard Solvent, a well known light petroleum fraction; and, in all but one composition, a separate anti-rust additive. The two-cycle engine oil compositions are then subjected to the BIA rust test for various periods of time and thereafter evaluated as "pass" or "fail." The makeups of the two-cycle engine oil compositions and the results of the BIA rust tests are shown in Table I.

TABLE I

	1	2	3	4
Hydrocarbon Oil, vol. %	71.32	71.32	71.41	71.50
Oronite 340-D, vol. %	8.40	4.20	4.20	4.20
Oronite OGA-472, ^a vol. %	—	4.20	4.20	4.20
Long Chain Fatty Alcohol, vol. %	0.10	0.10	0.10	0.10
Stoddard Solvent, vol. %	20.00	20.00	20.00	20.00
Anti-Rust Additive, vol. %	0.18	0.18	0.09	—
BIA Rust Test:				
8 Hours	Pass	Pass	Pass	Pass
24 Hours	Fail	—	—	Pass
71 Hours	—	Pass	Pass	—

^a70 volume percent solution of alkylenepolyamine.

The data in Table I show that prior art two-cycle engine oil composition 1 containing only the amido-amine detergency additive plus a separate rust inhibitor fails the rust test after 24 hours. In contrast, two-cycle engine oil compositions 2, 3, and 4 containing the two component additive mixture of the instant invention pass the rust test after 71 hours if a separate anti-rust additive is present and pass the rust test after 24 hours if no separate anti-rust additive is present. It is therefore apparent that the instant two component lubricating oil additive has unexpectedly superior rust inhibiting properties than does the amido-amine component alone plus a separate rust inhibitor.

EXAMPLE III

A two-cycle engine oil composition is prepared containing the same two component additive mixture of the instant invention as is described in Example I. For comparison, similar oil compositions containing essentially the same level of the individual components are also prepared. None of the compositions contains a separate anti-rust additive. The two-cycle engine oil compositions are subjected to the BIA rust test. The makeups of the oil compositions and the results of the rust tests are shown in Table II.

TABLE II

	5	6	7
Hydrocarbon Oil, vol. %	71.5	71.5	71.5
Oronite 340-D, vol. %	8.4	—	4.2
Oronite OGA-472, ^a vol. %	—	8.4	4.2
Long Chain Fatty Alcohol, vol. %	0.1	0.1	0.1
Stoddard Solvent, vol. %	17.5	17.5	17.5
Isopropyl Alcohol, vol. %	2.5	2.5	2.5

TABLE II-Continued

	5	6	7
BIA Rust Test:			
8 Hours	Fail	Fail	Pass
24 Hours	Fail	Fail	Pass

^a70 volume percent solution of alkylenepolyamine.

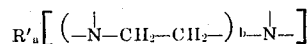
From Table II it is seen that two-cycle engine oil compositions 5 and 6 containing the individual components of the instant additive fail the BIA rust test after 8 and 24 hours. Engine oil composition 7, containing an essentially equivalent amount of the two component additive of our invention, passes the BIA rust test after 8 hours and 24 hours. The data therefore illustrate the unexpected rust inhibiting properties, absent from the individual amido-amine and alkylenepolyamine components, that are present when the two components are combined.

In addition to excellent detergency and anti-wear properties and the unexpected rust inhibiting characteristics of lubricating oil compositions of this invention, said lubricating oil composition have good storage stability and water tolerance. In addition, two-cycle engine oil compositions containing the additive mixture of this invention exhibit ready solubility in gasoline. This invention therefore provides a lubricating oil additive mixture that imparts to hydrocarbon lubricating oil compositions, and particularly to two-cycle engine oil compositions, a number of desirable properties. Lubricating oil compositions containing the two component additive of this invention thus have good detergency and anti-wear characteristics and, unexpectedly, excellent rust inhibitory properties. The lubricating oil compositions also exhibit good storage stability and water tolerance characteristics.

While this invention has been illustrated by the presentation of specific examples, it will be understood that the scope of the invention is limited only by the appended claims.

We claim:

1. A lubricating oil additive comprising a mixture of an amido-amine and a hydrocarbylamine, in which
 - a. the amido-amine/hydrocarbylamine volume ratio varies from about 1/10 to about 10/1,
 - b. the amido-amine is the condensation product of an alkylenepolyamine containing about 2-6 amino nitrogens and 2-16 carbon atoms and less than the stoichiometric amount of a fatty monocarboxylic acid containing about 14-20 carbon atoms, the mole ratio of said alkylenepolyamine to said fatty monocarboxylic acid being from about 1:1 to about 1:5, and
 - c. the hydrocarbylamine has a molecular weight from about 450 to about 5000 and is selected from the group consisting of branched chain aliphatic hydrocarbon monoamines and alkylenepolyamines, and wherein the alkylenepolyamine has the empirical formula



wherein R' = a branched chain aliphatic hydrocarbon selected from the group consisting of polypropylene and polyisobutylene and having an average molecular weight ranging from about 450 to about 1500,

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a = an integer having the value of 1 or 2,
b = an integer having the value of from 1 to about 5.

2. The lubricating oil additive of claim 1 wherein the amido-amine is the condensation product of 1 mole of tetraethylenepentamine and about 3 moles of a mixture of branched and straight chain fatty monocarboxylic acids containing about 14-20 carbons.

3. The lubricating oil additive of claim 1 wherein the volume ratio of said amido-amine to said alkylenepolyamine is from about 1:3 to about 3:1.

4. The lubricating oil additive of claim 2 wherein the volume ratio of said amido-amine to said al-

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kylenepolyamine is about 1:0.7.

5. A hydrocarbon lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and about 1-30 volume percent of the additive of claim 1.

6. A hydrocarbon lubricating oil composition comprising a major proportion of a hydrocarbon lubricating oil and about 2-20 volume percent of the additive of claim 3.

7. A two-cycle engine oil composition comprising a major proportion of a hydrocarbon lubricating oil and about 4-12 volume percent of the additive of claim 4.

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