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LUBRICATING OIL AND ADDITIVE COMPOSITION

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8 Claims. (Cl. 252—31)

This invention relates to lubricating oils and, more particularly, to lubricating oils containing elemental sulfur. Still more particularly, it relates to a combination of a phosphatide and an acylated amine, which act together to stabilize the suspension of elemental sulfur in a lubricating oil.

The prior art has shown that elemental surfur may be suspended in lubricating oils at ambient temperatures for a reasonable period of time and that the incorporation of sulfur in oils imparts a slippery characteristic, effects a polished surface in pronounced wear areas and imparts a high oiliness characteristic to the lubricating oils. At lower temperatures, however, and especially around 0° F., the sulfur tends to fall out of solution. This problem has been circumvented by incorporating the sulfur into an active sulfur compound and then adding this compound as a sulfur producing additive to the lubricating oils. These active sulfur compounds, however, have certain distinct disadvantages, the most pronounced of which is the difficulty encountered in preparing them and the substantial increase in cost to produce an equivalent amount of active sulfur compound with respect to the required amount of elemental sulfur. Also, the active sulfur compounds usually impart an undesirable dark color to the lubricant and give an objectionable odor to the finished lubricant. Another objectionable feature is that these compounds frequently have an irritating effect on the skin and this makes them obviously less desirable to handle.

The advantages of having a lubricating oil with available elemental sulfur are many. One of the most important advantages is the fact that free, elemental sulfur reacts with the metal to form a metallic salt which, in turn, imparts a slippery characteristic to the wear peaks. These wear peaks are characteristic of various areas where two metal parts are rubbing against each other in an environment of insufficient lubrication. Thus, the metal sulfide is very beneficial in these pronounced wearing areas and tends to retard the wearing action by effecting a smooth rubbing surface. This phenomenon can also be explained by the fact that the free sulfur reacts with the metal to form a corrosive salt which in turn corrodes away the wear peaks, thus giving a polished appearance.

Also, elemental sulfur is beneficial in cutting oils in that it tends to impart a high degree of oiliness characteristic to the lubricant. Such oils with a high oiliness characteristic tend to impart a smoother finish to the metal work pieces and also add to the life of work tools, such as dies, taps, reamers, and broaches. This function can best be explained by the fact that sulfur tends to modify the surface tension of the oil in such a manner that the oil adheres more satisfactorily to the cutting edge of the tool and produces a more efficient lubricated work area.

Another important advantage in the effective use of elemental sulfur as a lubricating additive is the relatively lower cost of sulfur as compared to an active sulfur compound. Usually the active sulfur compounds are rather stable and require a relatively high temperature to make the sulfur available for efficient use. Therefore, the effective use of a lubricant is dependent on the instability of the active sulfur compound. As a result, a larger equivalent amount of the active sulfur compound is usually required in ordinary operating conditions to give comparative results as compared to an effective, elemental sulfur containing lubricant.

Also, the composition of this invention has utility in other fields where the suspension of insoluble materials is desirable. One of such fields is the ink industry; where, for example, the invention can be useful to suspend pigments, act as a surface-active agent, etc.

It is therefore an object of this invention to provide an improved additive for lubricating oils.

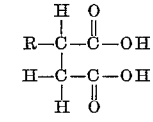
Another object of this invention is to provide a more efficient suspension agent.

Another object of this invention is to provide a more efficient and better lubricating oil.

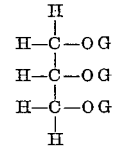
Still another object of this invention is to provide a lubricating oil with elemental sulfur.

More particularly, it is the object of this invention to provide an additive which facilitates the stable suspension of elemental sulfur in lubricating oils.

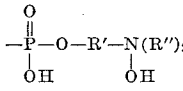
These and other objects of this invention are accomplished by an additive combination comprising (A) from about 5 percent by weight to about 90 percent by weight of an oil-soluble acylated amine prepared by the process which comprises mixing one equivalent of a substituted succinic compound selected from the class consisting of substituted succinic acids having the structural formula



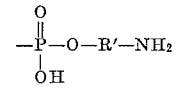
and the substituted succinic anhydride thereof, in which R is a hydrocarbon radical having at least 50 aliphatic carbon atoms, with at least about one-half an equivalent of an alkylene polyamine and heating the resulting mixture at a temperature above about 80° C. to effect acylation; and (B) from about 90 percent by weight to about 5 percent by weight of a phosphatide having the general structural formula



where G is selected from the class consisting of fatty acyl radicals, phosphorus containing radicals having the structural grouping



and phosphorus containing radicals having the structural grouping



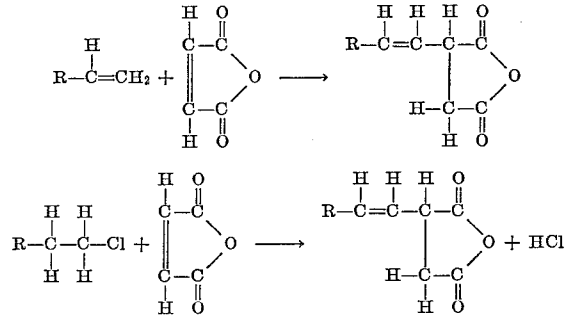
in which R′ is a lower alkylene radical having from 1 to about 10 carbon atoms and R″ is a lower alkenyl radical having from 1 to about 4 carbon atoms, and at least one of the G radicals is a said phosphorus containing radical; and (C) from about 0.01 percent by weight to about 48 percent by weight of a mineral oil. The combination of the acylated amine and the phosphatide is notably effective to permit the suspension of sulfur in oil.

A particular example of the additive composition of this invention is one consisting essentially of from about 35 to about 45% by weight of component (A), from about 8 to about 18% by weight of component

(B) and from about 38 to about 48% by weight of component (C).

The reaction by which component (A) is prepared involves an amidation of a dicarboxylic acid (or anhydride thereof) with a polyamine, and can result in a simple acyclic diamide, a cyclic diamide, a polymeric amide or a combination of any of these types of products. It will be noted also that the amide groups may react further to form imide groups and it is believed that a substantial amount of imide formation takes place in the process. Furthermore, there is reason to believe that in certain instances an appreciable proportion of amine carboxylic salt is present in the product.

The substituted succinic acids and anhydrides which are contemplated as a reactant in the process are readily available from the reaction of maleic anhydride with a high molecular weight olefin or a chlorinated high molecular weight olefin. The product from such a reaction is the corresponding alkenyl succinic anhydride. The reaction involves merely heating the two reactants at a temperature of about 150–200° C. The reactions in each case are illustrated by the following equations:



It is recognized that the reactions may not go precisely as indicated in the above equations, especially with respect to the particular carbon atom of the olefin chloride reactant which ultimately becomes attached to the maleic acid or anhydride reactant; but, other than this, the equations are believed to be illustrative. For the purposes of this invention, this substituent should, however, be a substantially aliphatic group and in most cases of course it will be an alkenyl or allkyl group. In some cases, however, it may well be desirable to employ a substituted succinic anhydride in which the substituent is derived, for example, from a copolymer of styrene and isobutylene, or of a substituted styrene and some lower aliphatic olefin. In these latter cases the copolymer will be substantially aliphatic, that is, the composition of a copolymer will be predominantly aliphatic, i.e., more than about 80 percent of the monomeric units will be those of the aliphatic monomer.

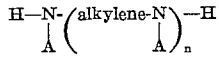
The size of the copolymer group appears to determine the effectiveness of the additive of this invention as a dispersant in lubricating oils. It is critically important that this substituent be large, that is, that it have at least about 50 carbon atoms in its structure; it may range in size up to one having a molecular weight of 100,000 or even higher. As stated before, these substituent groups are substantially aliphatic hydrocarbon radicals, including both alkyl and alkenyl radicals.

The most common sources of these substantially aliphatic hydrocarbon substituents are the polyolefins such as polyethylene, polypropylene, polyisobutylene, etc. A particularly preferred polyolefin is polyisobutylene. Thus, the condensation of a polyisobutylene having a molecular weight of 750 with maleic anhydride yields an alkenyl succinic anhydride which upon further reaction with an ethylene amine produces an especially effective lubricating oil dispersant. Polyisobutylenes of this particular molecular weight are quite economically available and the effectiveness of products prepared from this material makes them desirable for use in the process of this invention.

Other sources of such hydrocarbon substituents are the polymers of higher 1-mono-olefins such as, 1-hexene, 1-octene, 1-dodecene, 1-octadecene, and others which may contain as many as 30 carbon atoms. Interpolymers of the 1-mono-olefins may also be used provided they are substantially aliphatic. Such interpolymers contemplated are those of 1-mono-olefins with isoprene, butadiene, piperylene, vinyl cyclohexene, chloroprene, vinyl chloride, styrene, vinyl acetate, chlorostyrene, and vinyl alkyl ethers. Interpolymers are preferred in which the composition thereof comprises at least 80 percent, on a molar basis, of 1-mono-olefin units.

Ordinarily, the substituted succinic anhydride is reacted directly with the alkylene polyamine; although, in some circumstances, it may be desirable first to convert the anhydride to the acid before reaction with the amine. In other cases, it may be desirable to prepare the substituted succinic acid by some other means and to use an acid prepared by such other means. In any event, either the acid or the anhydride may be used in a process of this invention.

The term "alkylene polyamine" is used in a generic sense to denote a class of polyamines conforming to the following structure:



in which n is an integer preferably less than about 10, A is a hydrocarbon radical or hydrogen radical or an amino hydrocarbon radical, and the alkylene radical is preferably a lower alkylene radical having less than 8 carbon atoms. Specific amines which are contemplated are exemplified by: ethylene diamine, triethylene tetramine, propylene diamine, decamethylene diamine, octamethylene diamine, di(hepta-methylene) triamine, tripropylene tetramine, tetraethylene pentamine, trimethylene diamine, tetraethylene hexamine, di(trimethylene) triamine, 2-heptyl-3-(2-aminopropyl) imidazoline, 1,3-bis(2-aminoethyl) imidazoline, pyrimidine, 1-(2-aminopropyl) piperazine, 1,4-bis(2-aminoethyl) piperazine, and 2-methyl-1-(2-aminobutyl) piperazine. Higher homologues such as are obtained by condensing two or more of the above illustrated alkylene amines are likewise useful.

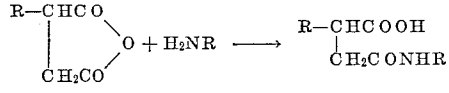
The ethylene polyamines are especially useful in this invention. They are described in detail under the heading "Ethylene Amines" in "Encyclopedia of Chemical Technology," Kirk and Othmer, volume 5, pages 898–905, Interscience Publishers, New York (1950). Such compounds are prepared most conveniently by the reaction of ethylene dichloride with ammonia. This process results in the production of somewhat complex mixtures of ethylene amines including cyclic condensation products such as piperazines. These mixtures are useful in the process of this invention. On the other hand, satisfactory products may also be obtained by using pure ethylene amines. For reasons of economy as well as effectiveness as a dispersant, an especially useful ethylene amine is a mixture of ethylene amines prepared by the reaction of ethylene chloride and ammonia. The latter amine has a composition similar to that of tetra-ethylene pentamine and is available in commerce under the trade name of "Polyamine H."

Other polyamines quite suitable for the purposes of this invention include alkylene polyamines such as: 1,3-propylene diamine, 1,4-butylamine diamine, propylene polyamines in which the amino groups are attached to the 1- and 3-carbon atoms, butylene polyamine in which the amino groups are attached to the 1- and 4-carbon atoms, and the C-alkyl substituted derivatives of these and other such alkylene polyamines.

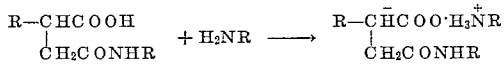
It has been noted that at least one-half of the chemical equivalent of the alkylene polyamine per equivalent of substituted succinic anhydride must be used in the process to produce a satisfactory product with respect to dispersant properties; and, generally, it is preferred to use these reactants in equivalent amounts. Amounts up

to 2.0 chemical equivalent (per equivalent of substituted succinic anhydride) have been used with success; although, there appears to be no advantage derived upon the use of more than this amount. The chemical equivalency of the alkylene polyamine reaction is based upon the nitrogen content, i.e., one having four nitrogens per molecule has four equivalents per mole.

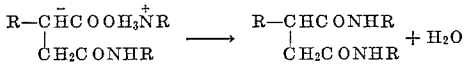
The reaction of the process involves acylation and the resulting by-product is water. The reaction conditions are such that this water is removed as it is formed. Presumably, the first principal reaction that occurs, following salt formation, is the formation of a half amide as follows:



followed then by salt formation:

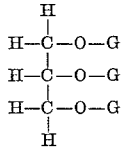


and involving final dehydration of this salt to form the product:

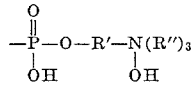


The first two of these reactions appear to take place spontaneously (when a substituted succinic anhydride is used) on mixing; but, the third requires heating. Temperatures within the range of 80° C. to about 200° C. are satisfactory; and, within this range, it is preferred to use a reaction temperature of from about 100° C. to about 160° C. A useful method of carrying out this step is to add some toluene to the reaction mixture and to remove the water by azeotropic distillation. As mentioned before, there is also some imide formation in this reaction.

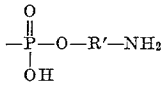
The phosphatides useful in this invention are phosphorus-containing lipides such as lecithin or cephalin. Phosphatides which are especially useful are the ones having the structural formula



wherein G is selected from the class consisting of fatty acyl radicals, phosphorus containing radicals having the structural grouping



and phosphorus containing radicals having the structural grouping



wherein R′ is a lower alkylene radical having from 1 to about 10 carbon atoms and R″ is a lower alkyl radical having from 1 to 4 carbon atoms, and at least one of the G radicals is a said phosphorus-containing radical. The fatty acyl radicals are for the most part those derived from fatty acids having from 8 to 30 carbon atoms in the fatty radicals, e.g., octanic acid, stearic acid, oleic acid, palmitic acid, behenic acid, myristic acid, and eleostearic acid. Especially desirable radicals are those derived from commercial fatty compounds such as soybean oil, cotton seed oil, peanut oil, corn oil, coffee bean oil, castor seed oil and rapeseed oil.

Soybean lecithin is the most desirable phosphatide, both from the commercial and economical standpoint. It contains roughly two-thirds phosphatide and one-third glyceride oil with a phosphorus content of about 2.2% and a nitrogen content of about 0.9% on a dry basis, with the moisture content only about 1%. Soybean lecithin is described in detail in Encyclopedia of Chemical Technology, Kirk and Othmer, volume 8, pages 309–326 (1952).

The lubricating oil base in which the additives of this invention are useful is generally a mineral oil having a viscosity range from about 40 S.U.S. at 100° F. to about 200 S.U.S. at 210° F. However, oils of animals, vegetable or mineral origin may be used in applications where one of the three groups is preferred. Also, synthetic oils can be used when preferred, e.g., jet engine lubricants where a polyester oil such as didodecyl adipate or di-2-ethylhexyl sebacate is often preferred. Other synthetic oils which may be used are polymerized polyisobutene, polymerized propylene, polymerized cracked paraffin waxes, dioctyl adipate, dioctyl sebacate, etc. But, generally a mineral lubricating oil is preferred due to commercial and economical feasibility.

The combination of component (A), an acylated amine, and component (B), a phosphatide, is notably effective in the suspension of elemental sulfur in a lubricating oil. By this invention, sulfur can be maintained in suspension in an oil for a period of time in excess of one month at temperatures down to 0° F.

The manner in which the above components can be blended to give the desired additive combination is as follows: add component (A) to component (B); then to this mixture, add diluent mineral oil and stir the resulting combination for about 10 minutes at a temperature of about 60° C. The final lubricating oil blend can be prepared by the following procedure: mix one part of the above additive combination with 98 parts of the base lubricating oil, to the resulting solution add 1 part of flowers of sulfur and agitate the resulting mixture at about 125° C. for about 15 minutes. It is recommended that a true "flowered" sulfur be used because of its larger surface area and the resulting ease with which it can be dispersed in the lubricating oil. The effective suspension of elemental sulfur in a lubricating oil can be shown by testing the following blend examples:

Example A

A "blank" is prepared by mixing 1 part of elemental sulfur with 99 parts of mineral oil at about 125° C. for about 10 minutes.

Example B

A blend containing a phosphatide and sulfur is prepared by adding 0.8 part of soybean lecithin and 1 part of elemental sulfur to 98.2 parts of mineral oil and agitating the resulting mixture for about 10 minutes at about 125° C.

Example C

An acylated amine is prepared by reacting at about 150° C., 1,000 parts of polyisobutylene substituted succinic anhydride (prepared by the reaction of a chlorinated polyisobutylene, having an average chlorine content of 4.3 weight percent and an average of about 71 carbon atoms, with maleic anhydride at about 200° C. and the resulting product has an acid number of 101) with 109 parts of an ethylene polyamine mixture having an average composition corresponding to that of tetraethylene pentamine. A blend containing an acylated amine and sulfur is prepared by adding 0.6 part of the acylated amine described above and 1 part of elemental sulfur to 98.4 parts of mineral oil and agitating the resulting mixture for about 10 minutes at about 125° C.

Example D

A blend containing an acylated amine, a phosphatide and sulfur is prepared by adding 0.4 part of an acylated

amine prepared as in Example C, 0.13 part of soybean lecithin, and 1 part of elemental sulfur to 98.47 parts of mineral oil and agitating the resulting mixture for about 10 minutes at about 125° C.

Example E

A blend containing an acylated amine, a phosphatide and sulfur is prepared by adding 0.18 part of an acylated amine prepared as in Example C, 0.5 part of soybean lecithin, and 1 part of elemental sulfur to 98.32 parts of mineral oil, and agitating the resulting mixture for about 10 minutes at about 125° C.

The above blends were each separated into three equal portions and a sulfur sedimentation test was run on each of these portions at temperatures of 0° F., 32°F., and room temperature; the appearance of each sample was noted after one week, two weeks, three weeks and four weeks. The following table shows the results and an overall rating of each blend example, with a lower number representing a more desirable result [the rating is based on 0 for C (clear sedimentation), 25 for Tr (trace of sedimentation), 50 for L (light sedimentation), 75 for M (medium sedimentation), and -00 for H (heavy sedimentation)]:

Time	Blend A			Blend B			Blend C			Blend D			Blend E		
	0° F.	32° F.	RT	0° F.	32° F.	RT	0° F.	32° F.	RT	0° F.	32° F.	RT	0° F.	32° F.	RT
1st wk	M	C	C	C	Tr	C	C	C	C	C	C	C	C	C	C
2nd wk	H	C	C	Tr	L	C	C	Tr	C	C	C	C	C	C	C
3rd wk	H	Tr	C	L	L	C	Tr	M	C	C	L	C	C	Tr	C
4th wk	H	Tr	Tr	L	L	C	Tr	M	C	C	L	C	C	Tr	C
Rating	450			300			225			100			50		

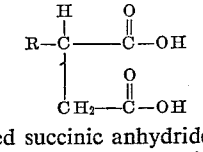
It will be noted that blends D and E, which contain the additive combination of this invention, show ratings of 100 and 50 respectively, whereas blends A, B, and C scored poorly, showing ratings of 450, 300, and 225 respectively.

The present invention is not to be considered as limited by any of the examples herein described which are presented merely for illustration.

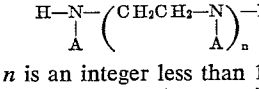
What is claimed is:

1. An oil-soluble additive composition consisting essentially of

(A) from about 5 to about 90% by weight of an oil-soluble acylated amine prepared by the process which comprises mixing one equivalent of a substituted succinic compound selected from the class consisting of substituted succinic acids having the structural formula



and substituted succinic anhydrides thereof in which R is a hydrocarbon radical containing from about 50 to about 7000 aliphatic carbon atoms, with from about 0.5 to about 2.0 equivalents of an ethylene polyamine having the structural formula



wherein *n* is an integer less than 10, and A is a radical selected from the class consisting of hydrocarbon, hydrogen, and aminohydrocarbon, and heating the resulting mixture at a temperature within the range of from about 80° C. to about 200° C. to effect acylation;

(B) from about 90 to about 5% by weight of a phosphatide selected from the class consisting of lecithin and cephalin; and

(C) from about 0.01 to about 48% by weight of a mineral oil.

2. The additive composition of claim 1 wherein the ethylene polyamine used in the preparation of component (A) is an ethylene polyamine mixture having a composition corresponding to that of tetraethylene pentamine.

3. The additive composition of claim 1 wherein the equivalent amount of ethylene polyamine used in the preparation of component (A) is about 1.

4. The additive composition of claim 1 wherein the R radical in the succinic acids used in the preparation of component (A) is a hydrocarbon radical derived from an olefin polymer.

5. The additive composition of claim 1 wherein the R radical in the succinic acids used in the preparation of component (A) is a radical derived from a polyisobutene having a molecular weight within the range from about 700 to about 100,000.

6. The additive composition of claim 1 wherein the phosphatide is soybean lecithin.

7. The additive composition of claim 1 wherein the proportions of components are as follows:

from about 35 to 45% by weight of component (A),

from about 8 to about 18% by weight of component (B), and

from about 38 to about 48% by weight of component (C).

8. A lubricating composition consisting essentially of a major proportion of a lubricating oil and from about 0.01 to about 10% by weight of the oil soluble lubricant additive combination described in claim 1 and from about 0.01 to about 5% by weight of elemental sulfur.

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