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REACTION PRODUCT OF AN ALIPHATIC AMIDE AND A PHOSPHORUS SULFIDE AND LUBRICANTS CONTAINING THE SAME

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12 Claims. (Cl. 252—32.7)

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This invention relates to compositions suitable as additives for an internal combustion engine lubricating oil comprising reaction products of a phosphorus sulfide with an aliphatic amide, and to a motor oil containing such an additive. The oils comprising such reaction products are suitable for use particularly under the conditions encountered in an internal combustion engine in which the lubricant is in close contact with metallic surfaces, metal compounds and high temperature gases and where corrosiveness is undesirable.

The objects achieved in accordance with the invention include the provision of a composition which is useful as an additive, and which, when added to lubricating oils, will markedly inhibit the very objectionable deposition of lacquer, acid and sludge formation, corrosion and other types of deterioration which tend to occur under operating conditions; the provision of lubricating oils containing such an addition agent; and other objects which will be apparent as embodiments are disclosed hereinafter.

In accordance with the invention, it has been found that a phosphorus sulfide may be reacted with an aliphatic amide, such as one containing at least 12 carbon atoms in the molecule, at an elevated temperature, and the resulting reaction product will have good solubility in lubricating oil. These reaction products have highly advantageous properties as additives for lubricants. They improve the corrosion, lacquer, sludge, viscosity increase, and the like characteristics of lubricating oils. Derivatives obtained from these sulfide-amide derived products, e. g., metal derivatives, also have these desired properties.

The sulfide-amide reaction temperature conditions vary somewhat with the amide used. The temperature should be elevated enough to give a reaction product which is soluble in lubricating oil but should not be so high as to decompose the reaction products, or the reaction product should be subsequently subjected to the elevated temperature. In general, the temperature will be in the range of about 250° to 600° F., preferably about 275° to 500° F. at atmospheric pressure. Economy of heat suggests that a temperature higher than that necessary to carry out the reaction will be wasteful.

The reaction time varies somewhat with the amide and the temperature and falls within the general range of from 1 minute to about 6 hours, desirably from about ¼ to about ¾ hour and preferably about ½ hour. The reaction is usually complete in four hours or less time. The

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reaction time is a function of the temperature, the amount of the sulfide that is to react, the subdivision of the sulfide, rate of stirring, etc. The reaction is somewhat exothermic and on a commercial scale the heat evolved thereby may be used to maintain the temperature. The ingredients may be added in increments if this is desirable for temperature control or for other reasons.

The reactions may be carried out in the presence or absence of air, or in an atmosphere of a non-deleterious gas, such as H_2S or nitrogen.

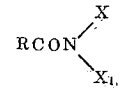
The sulfide-amide reaction may be carried out with direct admixture of the reactants, or by their admixture in the presence of a diluent which may or may not be subsequently removed. A volatile inert solvent, such as a saturated hydrocarbon boiling in the desired temperature range, may be used as a diluent which is to be subsequently removed. If a volatile solvent is used, it may be selected so as to have a boiling point that will assist in controlling the temperature if the reaction is carried out under reflux conditions. Alternatively, a heavier oil such as white oil, or a lubricating oil of about the same properties as that to which the new composition is to be added, may be used as a diluent which is not to be removed. In a commercial embodiment of the invention, a diluent probably would not be used unless it is a mineral oil, and a diluent is not necessary.

The pentasulfide is preferred although other phosphorus sulfides or mixtures of sulfides may be employed. Phosphorus pentasulfide is most economic and readily available and for this reason is used in the illustrative examples.

The amide or mixture of amides may be reacted with the phosphorus sulfides in ratios of about 0.1 to 1.0 mol of sulfide per mol of amide. Even small amounts show a significant improvement. Generally, about 0.5 to about 1.0 mol of the sulfide is the usual range that will be used.

A large variety of aliphatic amides are suitable. The aliphatic amides having at least 12 carbon atoms in a molecule are preferred. The preferred amides are those which contain either an amido hydrogen (a hydrogen directly connected to the nitrogen), or an olefinic double bond, or both. The choice may be controlled by the desired lubricant, solubility characteristics of the primary sulfide-amide or the final derivative product. The amide should not be so highly unsaturated or conjugated as to give reaction products which are not oil dispersible. Di-amides and compounds containing several amide groups

may be used. Typical amides are those which correspond to a carboxylic acid having from 12 to about 20 carbon atoms in the molecule obtainable from natural products, such as dodecanoyl amide, tetradecanoyl amide, octadecanoyl amide, eicosanoyl-amide and the corresponding unsaturated amides containing one or more olefinic double bonds in the molecule. The amides may contain a lower aliphatic substituent for one or both of the amido hydrogens in many instances. These may be represented by the formula



where R is an aliphatic hydrocarbon radical and X and X_1 are hydrogen and/or a lower aliphatic substituent, such as methyl, ethyl up to amyl. The amide stock used may be a mixture of amides of different molecular weight or different degrees of unsaturation. It need not be pure and amounts of other amides may be present provided that the above amides form the major or essential components. An inherent property of such amides is their freedom from sulfurized radicals.

The process is preferably conducted so that the yield is very high and appreciable amounts of oil insoluble products are not formed. Generally, the amount of sulfide is chosen so that it will all react at the temperature selected, and the reaction is continued until it is consumed.

The sulfide-amide reaction products may be utilized in the form of their metal derivatives. Mixed derivatives or mixtures of the derivatives may be employed. These derivatives are formed from agents capable of replacing an acid hydrogen atom. Although the formation of the above derivatives may not involve replacement of acid hydrogen, the materials used as agents fall into the class of materials capable of replacing or reacting with acid hydrogen.

The metal derivatives may be formed from one or more metal compounds, such as their sulfides, oxides, hydroxides, carbides and cyanamides. The preferred metals are group I, group II and group III metals of the periodic table, such as potassium, zinc, barium and aluminum.

In the preparation of the above type metal derivatives, the reaction step of forming the metal derivatives may be carried out at temperatures in the range of about 100° to about 350° F., a temperature in the range of about 180° to 280° F. being preferred.

From about 0.25 to about 6.0 equivalents of the metal compound may be used per mol. of the sulfide in the sulfide-amide reaction product, preferably about 1.0 to about 3.0 equivalents. An equivalent is the quotient of a mol. divided by the valence of the metal concerned.

It is beneficial to have water present in the reaction step of forming the metal derivative, and this may be introduced as water of crystallization, or as a hydrate of the metal compound, or it may be introduced separately. A plurality of metals may be used.

If the amount of the metal is small, the final product may be a mixture of the initial reaction product and the metal derivative.

The yield in the above reaction step is very high.

After this reaction step is complete, the reaction mass may be used directly as an additive, or preferably it is processed, e. g., centrifuged or filtered, to remove water and any traces of oil insoluble by-product substances. If an excess of the metal compound is used, the unreacted excess may be separated at this stage. If a solvent is used as a diluent, it may be removed by vacuum distillation at this stage.

These new compositions impart many desirable properties to lubricants to which they have been added. They act as detergents therein, and also as inhibitors of corrosion and lacquer and sludge formation.

The amount of the above described primary product or derivatives of sulfide-amide reaction products to be added to an oil will depend upon the characteristics of the oil and intended use. Some oils have more of a tendency to corrode metals, or to form acids, sludges and lacquer deposits than others, and such oils require larger quantities of the addition agent. Also, oils that are intended for higher temperatures require larger amounts of the additive. In general, for lubricating oils the range is from 0.25% to 10% by weight, but under some circumstances amounts as low as 0.01% show a significant improvement. As to an upper limit, it will be uneconomical to add more than is necessary to impart to the lubricant the desired properties. Generally, not over 50% would be used, although since the new materials are lubricants, even 100% thereof could be used. The products are substantially free from corrosive sulfur and in this respect are to be distinguished from gear lubricants.

The following examples of the preparation of new compositions in accordance with the invention and tables of results of tests of lubricants comprising some of such compositions will serve to illustrate and point out some advantages but in no wise to limit the scope of the invention as otherwise disclosed and claimed herein.

EXAMPLE 1

(*a*) 140 grams of commercial octadecane amide (analysis: 75% by weight of octadecanoyl-amide and 25% hexadecanoyl-amide), 55.5 grams of phosphorus pentasulfide and 420 grams of No. 225 Red Oil (a conventional acid treated Mid-Continent lubricating oil base stock of S. A. E. 20) were mixed and heated to 500° F. in an inert nitrogen atmosphere for 30 minutes with agitation. The reaction mass was filtered hot. No sludge was formed. The reaction product contained 1.4% phosphorus and 3.4% sulfur. This filtrate product was used as the Example 1 (*a*) additive in the test reported hereinafter.

The Red Oil may be omitted in this and other examples, because it acts merely as an inert diluent.

Similar preparations using 1½ times or twice the above amount of the phosphorus sulfide gave good yields, and no sludge, as will be seen from Examples 2 and 3.

(*b*) 197 grams of the above reaction product (*a*) was mixed with 31.4 grams of barium hydroxide octahydrate, and heated on a steam bath for two hours with agitation, and then blown with air at 250° F. for two hours. The reaction mass was then filtered hot. The filtrate product analyzed 7.0 weight percent ash.

(*c*) 197 grams of the above reaction product (*a*) was mixed with 11.2 grams of potassium hydroxide and 21.5 cc. water, and heated on a steam bath for two hours with agitation, and then blown with air at 250° F. for two hours. The reaction mass was then filtered hot. The filtrate product analyzed 5.38 weight percent ash.

In order to demonstrate the properties of the sulfide-amide reaction products in improving the characteristics of lubricating oils, a number of representative additives were incorporated into conventional lubricating oils. The lubricating oils containing these additives were tested according to laboratory test procedures for evaluating the service stability of oils as described in a paper by R. E. Burk, E. C. Hughes, W. E. Scovill and J. D. Bartleson presented at the Atlantic City Meeting of the American Chemical Society in September 1941, and in another paper by the same authors presented at the New York City Meeting of the American Chemical Society in September 1944, published in Industrial and Engineering Chemistry, Analytical Edition, vol. 17, No. 5, May 1945, pages 302–309. The latter paper also correlates the results of such laboratory tests with the so-called standardized "Chevrolet Engine Test."

Essentially the laboratory test equipment consists of a vertical thermostatically heated, large glass test tube, into which is placed a piece of steel tubing of about one third its length and of much smaller diameter. A piece of copper-lead bearing strip is suspended within and from the upper end of the steel tube by a copper pin, and an air inlet is provided for admitting air into the lower end of the steel tubes in such a way that in rising the air will cause the oil present to circulate. The test tube is filled with an amount of the oil to be tested which is at least sufficient to submerge the metals.

The ratios of surface active metals to the volume of oil in an internal combustion test engine are nearly quantitatively duplicated in the test equipment. In the "standard" test the temperature used is approximately the average temperature of the crankcase. The rate of air flow per volume of oil is adjusted to the same as the average for a test engine in operation. Of the catalytic effects, those due to iron are the most important. They are empirically duplicated by the addition of a soluble iron salt. Those due to lead-bromide are duplicated by its addition. In the "standard" test, 0.012% of iron salt is added; and in the "iron tolerance" test this is increased to 0.05%. The duration of the test is adjusted to that usually used in engine type tests. As is shown by the data in the papers referred to, the laboratory tests have been correlated with engine tests and the properties of the oil in an engine may be determined from the result of the laboratory tests.

The results given in the following table were obtained from tests using:

A 160 cubic centimeter sample of the lubricant composition
70 liters of air per hour
100 square centimeters of steel surface
4.4 square centimeters of copper-lead surface
1.0 square centimeter of copper surface
0.01% by weight of lead bromide powder
0.05% soluble iron calculated as Fe_2O_3 (ferric-2-ethyl hexoate in C. P. benzene)

The "iron tolerance" tests were run at 280° F. for thirty-six hours. The lacquer is deposited on the steel tube and is determined by difference in weight of the tube after washing with chloroform and drying to constant weight. The corrosion was determined by difference in weight of the metal pieces after scrubbing with chloroform. The used oil was sufficient to enable the determination of all of the usual oil tests, viz. isopentane insolubles, viscosity, acid number, etc.

The data in the following table shows the results obtained in testing the new additives by the tests described.

"Iron tolerance" tests on a conventional Mid-Continent acid treated heavy duty lubricating oil base stock (S. A. E. 30) and compositions containing this oil and sulfide-amide reaction products of the invention were run for several of the additives. The results given in the following table are representative.

Table I

Additive of Example No.	None	1(*a*)	1(*b*)	1(*c*)
Concentration of Additive in percent by weight	0	1.5	1.5	1.5
Lacquer Deposit (in milligrams)	39.4	0.9	5.5	1.0
Sludge (Isopentane insoluble in milligrams)	809	27.3	442	74.2
Corrosion (in milligrams) weight loss of Cu-Pb	6.4	5.5	0.9	−3.3
Acid Number	9.4	2.1	3.4	1.7
Viscosity Increase (SUS)	658	1	118	29

These data show the marked improvement imparted to the lubricating oil by the sulfide-amide reaction products of the invention. The very marked improvements in every indicated characteristic is particularly noteworthy since these are achieved with 1.5% of the additives in the oil.

EXAMPLE 2

(*a*) Example 1(*a*) was repeated except that the amount of phosporus pentasulfide employed was doubled.

(*b*) The reaction product of Example 2(*a*) was converted to the potassium derivative in accordance with the process described in connection with Example 1(*c*).

EXAMPLE 3

(*a*) Example 1(*a*) was repeated except that the amount of phosphorus pentasulfide was one and one half times as large.

(*b*) The barium derivative of Example 3(*a*) was formed as described in connection with Example 1(*b*).

(*c*) The potassium derivative of Example 3(*b*) was formed as described in connection with Example 1(*c*).

EXAMPLE 4

(*a*) 150 grams of the amide previously described in Example 1, 58.9 grams of phosphorus pentasulfide, and 460 grams of the No. 225 Red Oil were mixed and reacted for one-half hour at 300° F. The reaction product was filtered hot with a yield of 645 grams.

(*b*) The corresponding potassium derivative was formed by reacting 221 grams of the reaction product, 12 grams of potassium hydroxide, and 23.1 cc. of water for one hour and then blowing for one hour at 250° F. The product was filtered hot with a yield of 203 grams. The ash content was 2.26%.

EXAMPLE 5

(*a*) Example 4(*a*) was repeated except that the reaction temperature was 400° F.

(*b*) The potassium derivative of Example 5(*a*) was made following the procedure described in Example 4(*b*).

The oxidation test performance is shown in the following table in which each of the additives was used in a concentration of 1.5% in a heavy duty conventional acid-treated Mid-Continent stock (S. A. E. 30).

Table II

Additive of Example No.	2(a)	2(b)	3(a)	3(b)	3(c)	4(a)	4(b)	5(a)	5(b)
Lacquer (in mgs.)	0.5	0.9	0.0	1.9	0.0	0.4	4.5	0.5	0.4
Sludge (pentane insolubles in mgs.)	13.9	140.2	15.6	218.9	35.3	2.0	98.7	6.0	10.4
Corrosion of Cu-Pb (mgs.)	3.1	0.2	3.9	2.1	−0.7	0.4	0.5	−3.4	0.1
Acid Number	2.4	2.9	2.2	2.7	1.9	1.9	2.1	1.6	1.5
Viscosity Increase (SUS)	35.0	81.0	36.0	55.0	34.0	1.0	48.0	12.0	24.0

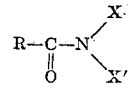
In order to prevent foaming of the oil containing a small proportion of the additive it is desirable in some cases to add a very small amount of tetra-amyl silicate, or an alkyl ortho carbonate, ortho formate or ortho acetate. 0.0003% of polyalkyl-silicone oil, or 0.001% of tetra-amyl silicate was found to prevent foaming upon bubbling of air through oil containing a few percent of the additive.

It will be obvious to one skilled in the art that sulfide-amide reaction products and similar products obtained by introducing phosphorus and/or sulfur into an amide as prepared according to different procedures but having substantially the same properties as those herein described, may be converted to derivatives or made up into lubricant compositions or both in accordance with the invention. The invention as claimed contemplates all such compositions except as do not come within the following claims.

The application describes the subject matter in my application, Ser. No. 682,292, filed July 9, 1946, now abandoned.

I claim:

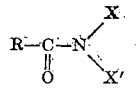
1. As a composition of matter, the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



where R is an aliphatic hydrocarbon radical and X and X′ are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce an oil dispersible reaction product suitable for addition to a motor oil to improve its resistance to deterioration during service.

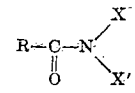
2. As a composition of matter, the reaction product of one mol of octadecane amide and an amount within the range of 0.1 to 1.0 mol of phosphorus pentasulfide, reacted at a temperature within the range of 250 to 600° F. to produce an oil dispersible reaction product suitable for addition to a motor oil to improve its resistance to deterioration during service.

3. As a composition of matter, a metal derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



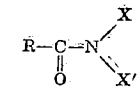
where R is an aliphatic hydrocarbon radical and X and X′ are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a compound of a metal selected from groups I, II and III of the periodic table at a temperature within the range of about 100 to about 350° F. to form a metal derivative which is suitable for addition to a motor oil to improve its resistance to deterioration during service.

4. As a composition of matter, the potassium derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



where R is an aliphatic hydrocarbon radical and X and X′ are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a potassium compound at a temperature within the range of about 100 to about 350° F. to form a potassium derivative which is suitable for addition to a motor oil to improve its resistance to deterioration during service.

5. As a composition of matter, the barium derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:

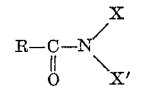


where R is an aliphatic hydrocarbon radical and X and X′ are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a barium compound at a temperature within the range of about 100 to about 350° F. to form a barium derivative which is suitable for addition to a motor oil to improve its resistance to deterioration during service.

6. As a composition of matter, the barium derivative of the reaction product of one mol of octadecane amide and about one-half mol of phosphorus pentasulfide, reacted at a temperature of about 500° F. to produce a reaction product which is reacted with a barium compound at a temperature within the range of about 100 to about 350° F. to form a barium derivative which is suitable for addition to a motor oil to improve its resistance to deterioration during service.

7. A lubricating composition comprising a major amount of mineral lubricating oil and a minor

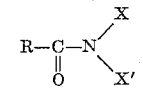
amount sufficient to inhibit the deterioration of said oil in service of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



where R is an aliphatic hydrocarbon radical and X and X' are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce an oil dispersible reaction product.

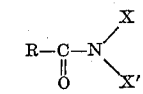
8. A lubricating composition comprising a major amount of mineral lubricating oil and a minor amount sufficient to inhibit the deterioration of said oil in service of the reaction product of one mol of octadecane amide and an amount within the range of 0.1 to 1.0 mol of phosphorus pentasulfide, reacted at a temperature within the range of 250 to 600° F. to produce an oil dispersible reaction product.

9. A lubricating composition comprising a major amount of mineral lubricating oil and a minor amount sufficient to inhibit the deterioration of said oil in service of the metal derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



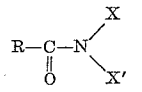
where R is an aliphatic hydrocarbon radical and X and X' are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a compound of a metal selected from groups I, II and III of the periodic table at a temperature within the range of about 100 to about 350° F. to form a metal derivative which is oil dispersible.

10. A lubricating composition comprising a major amount of mineral lubricating oil and a minor amount sufficient to inhibit the deterioration of said oil in service of the potassium derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



where R is an aliphatic hydrocarbon radical and X and X' are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a potassium compound at a temperature within the range of about 100 to about 350° F. to form a potassium derivative which is oil dispersible.

11. A lubricating composition comprising a major amount of mineral lubricating oil and a minor amount sufficient to inhibit the deterioration of said oil in service of the barium derivative of the reaction product of one mol of an aliphatic amide free of sulfurized radicals and having 12 to 20 carbon atoms in the molecule, said amide having the formula:



where R is an aliphatic hydrocarbon radical and X and X' are selected from the group consisting of hydrogen and alkyl radicals of up to about 5 carbon atoms, and an amount within the range of 0.1 to 1.0 mol of a phosphorus sulfide, said amide and sulfide being reacted at a temperature within the range of 250 to 600° F. to produce a reaction product which is reacted with a barium compound at a temperature within the range of about 100 to about 350° F. to form a barium derivative which is oil dispersible.

12. A lubricating composition comprising a major amount of mineral lubricating oil and a minor amount sufficient to inhibit the deterioration of said oil in service of the barium derivative of the reaction product of one mol of octadecane amide and about one-half mol of phosphorus pentasulfide, reacted at a temperature of about 500° F. to produce a reaction product which is reacted with a barium compound at a temperature within the range of about 100 to about 350° F. to form a barium derivative which is oil dispersible.

JOHN D. BARTLESON.

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The following references are of record in the file of this patent:

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