

UNITED STATES PATENT OFFICE

2,636,858

MINERAL OIL ADDITIVE

Robert H. Jones, Irvington, N. Y., and Leonard E. Moody, Cranford, N. J., assignors to Standard Oil Development Company, a corporation of Delaware

No Drawing. Application June 7, 1951,
Serial No. 230,418

10 Claims. (Cl. 252—32.7)

1

This invention relates to mineral oil compositions and particularly to lubricants containing a detergent additive.

The art of metallic detergents for lubricating oil compositions adapted for use in internal combustion engines is well known to have resulted in substantial improvements in lubricants. These detergents are particularly useful in lubricating oil compositions which are employed in internal combustion engines used in the operations of automobiles, aircraft and similar vehicles, including diesel engines, and improve their operation by preventing or retarding corrosion, piston ring sticking, cylinder wear, and carbon and varnish formation. However, when metallic detergents are used in lubricating compositions where oil consumption is high and engine conditions are severe, such as in aircraft engines, or where such concentrations of metallic detergents are used to maintain engine cleanliness under conditions where high deposit fuels of cracked or high sulfur nature are used, such as in automobile and diesel operation, the ash content from the metallic detergent accumulates in the combustion chamber and causes pre-ignition, detonation, spark plug fouling, valve burning, and ultimate destruction of the engine.

It has been found that a good detergent and anti-oxidant can be prepared by first reacting a hydrocarbon with a sulfide of phosphorus, which forms an acidic product, and then further reacting this product with a nitrogen base. This product is particularly useful in reducing varnish formation and ring sticking in the operation of internal combustion engines, and has the further advantage that it does not leave a metallic deposit or ash. However, this additive, when used alone, is not effective in reducing the tendency of the lubricating oil to cause corrosion of the bronze valve guide of an automotive engine, and in fact this bronze corrosion is actually increased by the presence of the additive.

It has been found, in accordance with the present invention, that if the additive described above is employed in combination with a zinc dithiocarbamate having organic groups which provide oil solubility, the bronze corrosion is markedly reduced. This effect is synergistic and results from a cooperative action of the two ingredients, the nature of which is not known, since the zinc dithiocarbamate alone increases the bronze corrosion. The synergistic effect between the two ingredients of the additive also results in reducing the tendency of a lubricating oil to form coke at very high temperatures. This is

2

a factor of importance in the operation of aviation engines.

The portion of the additive of the present invention which is formed by reacting a sulfide of phosphorus with a hydrocarbon and further reacting the product with a nitrogen base may be referred to in this specification as Ingredient A. In forming this ingredient the sulfide of phosphorus is reacted with an aliphatic hydrocarbon at a temperature of about 200° to about 600° F., and preferably from about 300° to 550° F., using from about 1 to about 10, preferably about 2 to about 5, molecular proportions of hydrocarbon to one molecular proportion of the sulfide of phosphorus in the reaction. It is advantageous to maintain a non-oxidizing atmosphere such as an atmosphere of nitrogen above the reaction mixture. Usually it is desirable to use an amount of the phosphorus sulfide that will completely react with the hydrocarbon so that no further purification becomes necessary. In the case of monoolefin polymers the preferred ratio is one molecular proportion of the phosphorus sulfide to 2 to 5 molecular proportions of polymer. In such a case the reaction is continued until all or substantially all of the phosphorus sulfide has reacted. The reaction time is not critical, and the time required to cause the maximum amount of phosphorus sulfide to react will vary greatly with the temperature. A reaction time of 2 to 10 hours is frequently necessary. If desired, the reaction product may be further treated by blowing with steam, alcohol, ammonia, or an amine at an elevated temperature, say about 200 to 600° F., to improve the odor.

The sulfide of phosphorus which is employed in the reaction described above may be P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 or other phosphorus sulfide or mixtures of sulfides, and is preferably phosphorus pentasulfide (P_2S_5) on account of its availability.

The hydrocarbon materials which may be reacted with the phosphorus sulfide may be paraffins, olefins, or olefin polymers, diolefins, acetylenes, petroleum fractions, such as lubricating oil fractions, bright stock residuums, petrolatums, waxes, cracked cycle stocks, or condensation products of petroleum fractions, solvent extracts of petroleum fractions, also aromatic hydrocarbons, such as benzene, alkylated benzenes, aromatic hydrocarbons derived from or contained in petroleum oils, and the like.

As examples of monoolefins may be mentioned isobutylene, decene, dodecene, centene (C_{10}), octadecene (C_{18}), cerotene (C_{28}), melene (C_{30}), olefinic extracts from gasoline or gasoline it-

self, cracked cycle stocks and polymers thereof, resin oils from crude oil, hydrocarbon coal resins, cracked waxes, dehydrohalogenated chlorinated waxes, and any mixed high molecular weight alkenes obtained by cracking petroleum oils. A preferred class of olefins are those having at least 20 carbon atoms per molecule, of which from about 12 to about 18 carbon atoms, and preferably at least 15 carbon atoms, are in a long chain. Such olefins may be obtained by the dehydrogenation of paraffin waxes, by the dehydrohalogenation of long chain alkyl halides, by the synthesis of hydrocarbons from CO and H₂, by the dehydration of alcohols, etc.

Another class of suitable olefinic materials are the monoolefin polymers, in which the molecular weight ranges from 100 to 50,000, preferably from about 250 to about 10,000. These polymers may be obtained by the polymerization of low molecular weight monoolefinic hydrocarbons, such as ethylene, propylene, butylene, isobutylene, normal and isoamylenes, or hexenes, or by the copolymerization of any combination of the above monoolefinic materials.

Diolefins which may be employed include well known materials such as butadiene, isoprene, chloroprene, cyclopentadiene, 2,3-di-methylbutadiene, pentadiene-1,3, hexadiene-2,4, and the like. Acetylene and substituted acetylenes may similarly be employed.

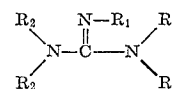
Another class of unsaturated hydrocarbon materials which may be advantageously employed in the preparation of the additives of this invention are high molecular weight copolymers of low molecular weight monoolefins and diolefins. The copolymer is prepared by controlled copolymerization of a low molecular weight olefin and a non-aromatic hydrocarbon showing the general formula C_nH_{2n-x}, in which x is 2 or a multiple of 2, in the presence of a catalyst of the Friedel-Crafts or peroxide type. The low molecular weight olefin is preferably an isoolefin or a tertiary base olefin, preferably one having less than 7 carbon atoms per molecule. Examples of such olefins are isobutylene, 2-methylbutene-1, 2-ethylbutene-1, secondary and tertiary base amylenes, hexylenes, and the like. Examples of the non-aromatic hydrocarbons of the above formula which can be used are the conjugated diolefins listed in the preceding paragraph, diolefins such as 1,4-hexadiene, in which the double bond is not conjugated, as well as the acetylenes. The copolymerization is preferably carried out in the presence of aluminum chloride, boron fluoride, or benzoyl peroxide, and the copolymer is preferably one having a molecular weight of about 1,000 to 30,000.

Another type of hydrocarbon material which may be similarly employed is a resin-like oil which has a molecular weight of from about 1,000 to 2,000 or higher, obtained preferably from a paraffinic oil which has been dewaxed and which is then treated with a liquified normally gaseous hydrocarbon, e. g., propane, to precipitate a heavy propane-insoluble fraction. The latter is a substantially wax-free and asphalt-free product having a Saybolt viscosity at 210° F. of about 1,000 to about 4,000 seconds or more.

Since the additives of the present invention are to be dissolved in mineral oils, the hydrocarbons which are reacted with a sulfide of phosphorus will be chosen with a view to provide a product which is soluble in the oil base or which has such marginal solubility that it can be plasticized with a high molecular weight alcohol, ester, or other plasticizer.

The reaction product of the sulfide of phosphorus and hydrocarbon possess titratable acidity, and this acidity may be reduced or completely neutralized by reacting the product with a metallic or non-metallic base. For the purposes of the present invention the non-metallic bases, specifically the nitrogen bases, are preferred, since the additives formed from them do not leave an inorganic residue. The bases which may be employed include ammonia and any of the organic nitrogen bases, such as amines and amine derivatives, guanidines and their derivatives, morpholine, pyridine, quinoline, and like substances.

A highly preferred group of basic substances which may be employed in neutralizing the phosphorus sulfide-hydrocarbon product comprises guanidine and its derivatives. The free base guanidine and its derivatives may be used as well as basic acting salts of such bases, by which is meant salts of acids whose strength, measured on a pH scale, is less than that of the acidic phosphorus sulfide-hydrocarbon product. Such basic acting salts are, for example, the carbonates of guanidine and its derivatives. Alternatively, the final products may be formed by double decomposition of a salt of guanidine or guanidine derivative, e. g., guanidine hydrochloride or sulfate, with a metal salt of the phosphorus sulfide-hydrocarbon reaction product. Although guanidine and its salts are preferred, substituted guanidines may be used. Broadly, the guanidine type basic compounds which may be reacted in accordance with the present invention may be defined by the formula



in which R₁, R₂, and R₃ represent hydrogen or hydrocarbon groups containing 1 to 20 carbon atoms, e. g., straight chain alkyl groups, such as methyl, ethyl, propyl, butyl, also higher straight and branched chain alkyl groups, such as octyl, isooctyl, 2-ethylhexyl, decyl, dodecyl, tetradecyl, cetyl and stearyl radicals. R₁, R₂ and R₃ may also represent cycloalkyl, arylalkyl, aryl or alkyl-aryl groups, for example, methylcyclohexyl, phenylethyl, phenyl, cresyl, and tert.-butylphenyl groups. It will be understood that R₁, R₂ and R₃ can be the same or different atoms or groups in the same molecule. However, in the case of a substituted guanidine it is most preferable to employ symmetrically tri-substituted compounds, and alkyl and cycloalkyl groups are the more preferred types of substituting groups. These include the symmetrical trialkyl, trinaphthenyl, and triaryl-alkyl guanidines. Also highly preferred classes of substituted guanidines include the monoalkyl, mononaphthenyl, and monoaralkyl guanidines; unsymmetrical dialkyl, dinaphthenyl and diaryl-alkyl guanidines. Somewhat less preferable but still useful classes are the symmetrical dialkyl, dinaphthenyl, and diaryl alkyl guanidines and the mono-, di-, and triaryl guanidines. Still other substituted guanidines may be used, such as bi-guanide, dicyandiamide, and dicyandiamidine.

Specific examples of basic acting compounds illustrating the above-described types are the following:

Guanidine
α-Methylguanidine
α-Ethylguanidine
α-Hexylguanidine

5

α -Heptylguanidine
 α -Phenylethylguanidine
 α -Benzylguanidine
 α -Cyclohexylguanidine
 α -Decylguanidine
 α -Hexadecylguanidine
 α -Octadecylguanidine
 α -Phenylguanidine
 α,α -Dimethylguanidine
 α,α -Diethylguanidine
 α,α -Diisopropylguanidine
 α,α -Diethylguanidine
 α,α -Diheptylguanidine
 α,α -Diphenylethylguanidine
 α,α -Dibenzylguanidine
 α,α -Dicyclohexylguanidine
 α,α -Didecylguanidine
 α,α -Dihexadecylguanidine
 α,α -Dioctadecylguanidine
 α,α -Diphenylguanidine

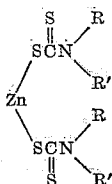
The α,γ -substituted guanidines corresponding to the above-listed α,α -substituted compounds.

The following symmetrical tri-substituted guanidines:

Trimethylguanidine
 Triethylguanidine
 Trioctadecylguanidine
 Tricyclohexylguanidine
 Tribenzylguanidine
 Triphenylguanidine
 Carbonates of any of the above-listed compounds.

The neutralizing reaction, in which the nitrogen base is reacted with the phosphorus sulfide-hydrocarbon product, may be carried out, preferably in a non-oxidizing atmosphere, by contacting the phosphorus sulfide-hydrocarbon reaction product either as such or dissolved in a suitable solvent such as naphtha, with a basic compound, preferably at a temperature of about 100 to 400° F. It is desirable to employ at least enough of the basic compound to neutralize the titratable acidity of the phosphorus sulfide-hydrocarbon product. In practice a somewhat greater amount of basic compound is generally employed, since this can be reacted in proportions greater than that required for neutralization. When the basic compound is added in the form of a carbonate, the completion of the reaction is indicated by a cessation of carbon dioxide evolution. It has been found that somewhat superior products are formed when a water soluble basic compound, e. g., guanidine carbonate, is dissolved in or mixed with water when contacted with the phosphorus sulfide-hydrocarbon reaction product. In the case of guanidine carbonate it is preferable to employ a mixture of the salt and water containing 30 to 70% by weight of the salt.

The second ingredient of the compounded additive of the present invention may be referred to as Ingredient B and is a zinc salt of a dithiocarbamic acid having organic groups of sufficient chain length to provide oil solubility. More specifically, this ingredient may be defined as a compound of the formula



6

wherein R, and R' may each represent hydrogen or a hydrocarbon radical, at least one of them being a radical. The hydrocarbon radicals may be aliphatic, cycloaliphatic or aromatic, but at least one aliphatic or cycloaliphatic hydrocarbon radical must be attached to each nitrogen atom, and there should be a total of at least six carbon atoms in the two groups attached to the nitrogen. The more preferred compounds are the zinc dialkyl or dicycloalkyl dithiocarbamates. The following are typical compounds suitable for use as Ingredient B:

Zinc di-n-butylidithiocarbamate
 Zinc diisobutylidithiocarbamate
 Zinc di-n-amylidithiocarbamate
 Zinc di-n-octylidithiocarbamate
 Zinc di-tert.-octylidithiocarbamate
 Zinc mono-n-hexylidithiocarbamate
 Zinc n-butylphenylidithiocarbamate
 Zinc dicyclohexylidithiocarbamate
 Zinc di-n-butenylidithiocarbamate
 Zinc di-wax-alkylidithiocarbamate

The amount of Ingredient A in the combined additive of the present invention is equal to and preferably somewhat greater than that of Ingredient B on a weight basis; and in general the proportion of Ingredient A is from 1 to 20 parts by weight to one part by weight of Ingredient B. When the combined additive is employed in a mineral lubricating oil, it is preferably added in concentrations of about 0.1 to about 20% by weight and more generally concentrations of 1.0 to 6.0% are employed. The proportions giving the best results will vary somewhat according to the nature of the ingredients of the additive and the specific purpose which the lubricant is to serve in a given case. For commercial purposes, it is convenient to prepare concentrated oil solutions in which the amount of the combined additive in the composition ranges from 20 to 50% by weight, and to transport and store them in such form. In preparing a lubricating oil composition for use as a crankcase lubricant, the additive concentrate is merely blended in the base oil in the required amount.

Below are given a description of the preparation of an additive of the type described above as well as laboratory and engine tests of the properties of lubricating oils containing the same. It is to be understood that these examples are given as illustrations of the present invention and are not to be construed as limiting the scope thereof in any way.

EXAMPLE 1

Preparation of P_2S_5 -bright stock-guanidine

665 gals. of phenol extracted Mid-Continent bright stock was charged to a reactor and heated to 250° F., nitrogen being blown through the charge and vigorous mechanical agitation maintained during the entire heating period. 25 cc. of a silicone polymer was added to prevent foaming. 485 lbs. of P_2S_5 was added over a fifteen minute period and the entire mixture was heated to 430–460° F. for about two hours, soaked at about 400° F. for three hours, and then filtered through Hi-flow (a filter aid). 3,865 lbs. of this product was charged to a reactor and heated to 170° F., nitrogen blowing and mechanical agitation being maintained during the entire heating period. A solution of 387 lbs. of guanidine carbonate and 752 lbs. of water was prepared by heating the two components to 180–250° F. This solution was

then poured into the reactor and the temperature raised to 300° F. over a period of six hours and held at 310–330° F. for three hours additional. The product was filtered through Hi-flow.

EXAMPLE 2

Bronze corrosion test

A laboratory bronze corrosion test was applied to oil blends containing the product of Example 1, with and without the further addition of zinc dibutyldithiocarbamate. The test was carried out by heating the oil sample to 650° F. in the presence of a quarter-section of a bronze aviation engine valve guide for a period of 17 hours, and the loss in weight of the valve guide section, after washing in cyanide solution, determined. Blends were made in three different aviation lubricating oils prepared from base stocks derived from different types of crude oils. The results obtained were as follows:

Test Oil	Weight Loss (mg./g. of valve guide)
Oil I.....	1.28
Oil I+3% product of Example 1.....	1.36
Oil I+6% product of Example 1.....	1.56
Oil I+0.75% zinc dibutyldithiocarbamate.....	1.60
Oil I+3% product of Example 1+0.5% zinc dibutyldithiocarbamate.....	0.38
Oil II.....	0.46
Oil II+6% product of Example 1.....	0.79
Oil II+3% product of Example 1+0.5% zinc dibutyldithiocarbamate.....	0.32
Oil III.....	0.58
Oil III+3% product of Example 1+0.5% zinc dibutyldithiocarbamate.....	0.55

perature at 500–520° F. At the end of the test the oil is poured from the cup which is then washed with naphtha and dried with air to a constant weight. The difference in the weight of the cup before and after the test is taken as the amount of coke deposit. In the data given below the designations "Oil I" and "Oil II" refer to the base oils described in Example 2. The results are as follows:

Test Oil	Coking Deposit (mg. of coke)
Oil I.....	56
Oil I+6% product of Example 1.....	52
Oil I+0.5% zinc dibutyldithiocarbamate.....	23
Oil I+3% product of Example 1+0.5% zinc dibutyldithiocarbamate.....	14
Oil II.....	21
Oil II+6% product of Example 1.....	47
Oil II+3% product of Example 1+0.5% zinc dibutyldithiocarbamate.....	12

EXAMPLE 4

Aviation C. F. R. engine test

Some of the oil blends of the type described in the preceding examples were evaluated in a C. F. R. engine test, which was conducted for a period of 100 hours, the C. F. R. engine being operated at 1800 R. P. M. and 4 brake horsepower. The oils were rated by a demerit system, wherein a perfectly clean surface is given a rating of zero while a rating of 10 is given to the worse condition which could be expected on that surface. Oils I, II and III are the same as in Example 2. The results are shown in the following table:

Test Oil	Duration of Test	Demerits			
		Over- all	Ring Zone	Piston Skirt Varnish	Rings Stuck
Oil I.....	Hours 50	2.7	6.7	3.6	2.5
Oil I+0.75% zinc dibutyldithiocarbamate.....	100	2.0	4.7	2.7	0.8
Oil II+6% product of Example 1.....	100	1.7	3.8	2.8	1.1
Oil II+3% of Example 1+0.5% zinc dibutyldithiocarbamate.....	100	1.5	3.6	2.5	0.0
Oil III+3% product of Example 1+0.5% zinc dibutyl dithiocarbamate.....	100	1.3	2.5	2.4	0.0

EXAMPLE 3

Coking test

An aluminum cup coking test was applied to oil blends of the type described in Example 2. The test is carried out by charging the test oil to a weighted aluminum cup which is heated with an electrical jacket and fitted with a stirrer placed 1/8" from the cup bottom. The stirrer is started and the oil temperature is raised to 550° F., when the stirrer is stopped for ten minutes. The stirrer is then operated for 10 minutes and stopped again for 10 minutes for a total of four 10-minute off cycles. During the test the oil temperature is kept at 550° F. and the jacket tem-

The products of the present invention may be employed not only in ordinary hydrocarbon lubricating oils but also in the "heavy duty" type of lubricating oils which have been compounded with such detergent type additives as metal soaps, metal petroleum sulfonates, metal phenates, metal alcoholates, metal alkyl phenol sulfides, metal organo phosphates, phosphites, thiophosphates, and thiophosphites, metal xanthates and thio-xanthates, metal thiocarbamates, and the like. Other types of additives, such as phenols and phenol sulfides, may also be present.

The lubricating oil base stock used in the compositions of this invention may be straight mineral lubricating oils or distillates derived from

paraffinic, naphthenic, asphaltic or mixed base crudes, or if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils may be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced by solvent extraction with solvents such as phenol, sulfur dioxide, etc. Hydrogenated oils or white oils may be employed as well as synthetic oils resembling petroleum oils, prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products.

For the best results the base stock chosen should normally be an oil which with the new additive present gives the optimum performance in the service contemplated. However, since one advantage of the additives is that their use also makes feasible the employment of less satisfactory mineral oils, no strict rule can be laid down for the choice of the base stock. The additives are normally sufficiently soluble in the base stock, but in some cases auxiliary solvent agents may be used. The lubricating oils will usually range from about 40 to 150 seconds (Saybolt) viscosity of 210° F. The viscosity index may range from 0 to 100 or even higher.

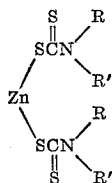
Other agents than those which have been mentioned may be present in the oil composition, such as dyes, pour point depressants, heat thickened fatty oils, sulfurized fatty oils, sludge dispersers, antioxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, and the like.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having preferably 8-20 carbon atoms, e. g. octyl alcohol, lauryl alcohol, stearyl alcohol, and the like.

In addition to being employed in lubricants, the additives of the present invention may also be used in other mineral oil products such as motor fuels, heating oils, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils, transformer oils, industrial oils, process oils, and the like, and generally as antioxidants in mineral oil products. They may also be used in gear lubricants, greases and other products containing mineral oils as ingredients.

What is claimed is:

1. A mineral oil containing about 0.1 to about 20% by weight of an additive consisting of (A) a product obtained by reacting a phosphorus sulfide with a hydrocarbon and neutralizing the acidic reaction product thus formed with a nitrogen base, and (B) a zinc dithiocarbamate of the formula

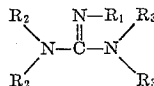


in which R and R' are members of the group consisting of hydrogen and hydrocarbon radicals,

at least one being a member of the group consisting of aliphatic and cycloaliphatic hydrocarbon radicals, the total number of carbon atoms in the two groups being at least 6, the ratios of the two ingredients of the additive being from 5 to 20 parts by weight of A to one part by weight of B.

2. A composition according to claim 1 in which the mineral oil is a lubricating oil fraction.

3. A composition according to claim 1 in which the nitrogen base is an organic base reacting compound selected from the group consisting of: (1) free bases of the composition



in which R₁, R₂ and R₃ are each members of the group consisting of hydrogen and hydrocarbon radicals containing 1 to 20 carbon atoms, and (2) basic reacting salts of the aforementioned free bases.

4. A composition according to claim 1 in which the zinc dithiocarbamate is a zinc dialkyldithiocarbamate having a total of at least 6 carbon atoms in the two alkyl groups.

5. A composition according to claim 3 in which the zinc dithiocarbamate is a zinc dialkyldithiocarbamate having a total of at least 6 carbon atoms in the two alkyl groups.

6. A composition according to claim 1 in which the basic reacting compound is guanidine carbonate.

7. A mineral lubricating oil containing about 0.1 to about 20% by weight of an additive consisting of (A) the product obtained by reacting phosphorus pentasulfide with a lubricating oil bright stock and neutralizing the product thus formed with guanidine carbonate, and (B) zinc dibutyldithiocarbamate, the ratios of the two ingredients of the additive being from 5 to 20 parts by weight of A to one part by weight of B.

8. A mineral lubricating oil containing about 3% by weight of the product obtained by reacting phosphorus pentasulfide with a lubricating oil bright stock and neutralizing the product thus formed with guanidine carbonate, and about 0.5% by weight of zinc dibutyldithiocarbamate.

9. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 1, the amount of said additive in the composition being 20-50% by weight.

10. A composition consisting essentially of a mineral lubricating oil and an additive as defined in claim 7, the amount of said product in the composition being 20-50% by weight.

ROBERT H. JONES.
LEONARD E. MOODY.

References Cited in the file of this patent UNITED STATES PATENTS

Number	Name	Date
2,316,090	Kelso	Apr. 6, 1943
2,409,686	McNab	Oct. 22, 1946
2,412,903	Miller et al.	Dec. 17, 1946
2,422,075	Bray	June 10, 1947
2,451,345	McNab et al.	Oct. 12, 1948