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COMPOUNDED LUBRICATING OIL

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

This is a continuation-in-part of copending application Serial Number 89,370, filed April 23, 1949, now U. S. Patent 2,613,205, issued on October 7, 1952.

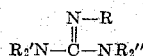
The art of metallic detergents for lubricating oil compositions adapted for use in internal combustion engines is well known to those versed in this field and has resulted in substantial improvements in lubricants. These detergents are particularly useful in lubricating oil compositions which are employed in internal combustion engines used in the operations of automobiles, aircraft and similar vehicles, including diesel engines, to 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, in accordance with the present invention, that if the reaction product of a phosphorus sulfide with an essentially hydrocarbon product is neutralized with guanidine or any of its derivatives as hereinafter defined or with any other compound containing a guanyl radical, the product so formed is very stable at the temperatures of engine operation and serves the purpose of a good detergent and anti-oxidant. When incorporated in mineral lubricating oil which is used in an internal combustion engine, and because it contains no metal, it is free from the objectionable feature of leaving a metallic deposit or ash. These compounds are effective not only when added directly to the crankcase lubricant but also when added to the engine fuel, since in the operation of the engine it will work its way from the combustion chamber into the crankcase and there blend with the lubricant.

Guanidine and guanidine derivatives may be employed as the basic reagents for neutralizing the titratable acidity of the phosphorus sulfide-hydrocarbon reaction product. The free base

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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 R, R', and R'' 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. R, R' and R'' 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 R, R' and R'' 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 triarylalkyl guanidines. Also highly preferred classes of substituted guanidines include the monoalkyl, mononaphthenyl, and mono-arylalkyl guanidines; unsymmetrical dialkyl, dinaphthenyl, and diarylalkyl guanidines. Somewhat less preferable but still useful classes are the symmetrical dialkyl, dinaphthenyl, and diarylalkyl guanidines, and the mono-, di-, and tri-aryl guanidines. Still other substituted guanidines may be used, such as biguanide, dicyandiamide, and dicyandiamidine.

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

Guanidine
α-Methylguanidine
α-Ethylguanidine

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α -Hexylguanidine
 α -Heptylguanidine
 α -Phenylethylguanidine
 α -Benzylguanidine
 α -Cyclohexylguanidine
 α -Decylguanidine
 α -Hexadecylguanidine
 α -Octadecylguanidine
 α -Phenylguanidine
 α,α -Dimethylguanidine
 α,α -Diethylguanidine
 α,α -Diisamylguanidine
 α,α -Dihexylguanidine
 α,α -Diheptylguanidine
 α,α -Diphenylethylguanidine
 α,α -Dibenzylguanidine
 α,α -Dicyclohexylguanidine
 α,α -Didecylguanidine
 α,α -Dihexadecylguanidine
 α,α -Diocadecylguanidine
 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 sulfide of phosphorus which is employed in the reaction with hydrocarbon material may be P_2S_3 , P_2S_5 , P_4S_3 , P_4S_7 or other phosphorus sulfide, and is preferably phosphorus pentasulfide, P_2S_5 .

The hydrocarbon material which may be reacted with a phosphorus sulfide in the first step of the production of additives of the present invention may be paraffins, olefins or olefin polymers, diolefins, acetylenes, aromatics or alkyl aromatics, cyclic aliphatics, petroleum fractions, such as lubricating oil fractions, petrolatums, waxes, cracked cycle stocks, or condensation products of petroleum fractions, solvent extracts of petroleum fractions, etc.

Essentially paraffinic hydrocarbons such as bright stock residuums, lubricating oil distillates, petrolatums or paraffin waxes may be employed. There may also be employed products obtained by condensing any of the foregoing hydrocarbons, usually through first halogenating the hydrocarbon, with aromatic hydrocarbons in the presence of anhydrous inorganic halides, such as aluminum chloride, zinc chloride, boron fluoride, and the like.

As examples of monoolefins may be mentioned isobutylene, acrolein, decene, dodecene, cetene (C_{16}), octadecene (C_{18}), cerotene (C_{26}), melene (C_{30}), olefinic extracts from gasoline or gasoline itself, 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 H_2 , by the dehydration of alcohols, etc.

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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-dimethylbutadiene, pentadiene-1,3, hexadiene-2,4, terpenes 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 amylene, 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 class of hydrocarbons which may be employed in a similar manner are aromatic hydrocarbons, such as benzene, naphthalene, anthracene, toluene, xylene, diphenyl, and the like, as well as aromatic hydrocarbons having alkyl substituents and aliphatic hydrocarbons having aryl substituents.

A still further class of hydrocarbons which may be employed in the reaction with sulfides of phosphorus are condensation products of halogenated aliphatic hydrocarbons with an aromatic compound, produced by condensation in the presence of aluminum chloride or other Friedel-Crafts type catalyst. The halogenated aliphatic hydrocarbon is preferably a halogenated long chain paraffin hydrocarbon having more than 8 carbon atoms, such as paraffin wax, petrolatum, ozocerite wax, etc. High viscosity paraffin oils, particularly heavy residual oil which has been treated with chemicals or extracted with propane or other solvents for the removal of asphalts, may be employed. The aromatic constituent may be naphthalene, fluorene, phenanthrene, anthracene, coal tar residues, and the like.

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

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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.

Another class of essentially hydrocarbon materials which may be similarly employed are sulfurized hydrocarbons, produced by the reaction of hydrocarbons with elemental sulfur. Any of the hydrocarbons described above may be sulfurized to produce suitable products, but the mono-olefin polymers are the most suitable. The sulfur is introduced by heating the hydrocarbon with elemental sulfur at a temperature of from about 250° F. to about 450° F. and preferably from about 350° F. to about 375° F. The sulfur may similarly be introduced after the hydrocarbon has been reacted with the phosphorus sulfide and even after the phosphorus sulfide-hydrocarbon product has been reacted with a guanidine compound. Products sulfurized by any of these methods are within the scope of the present invention.

The additive employed in the present invention is the neutralized reaction product obtained by reacting one or more of the herein described hydrocarbons with a phosphorus sulfide, preferably phosphorus pentasulfide. The phosphorus sulfide-hydrocarbon reaction product may be readily obtained by reacting the phosphorus sulfide with the hydrocarbon at a temperature of about 200° F. to about 600° F., and preferably from about 300° F. to about 550° F., using from about 1 to about 10, preferably about 2 to about 5, molecular proportions of hydrocarbon to 1 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 sulfide of phosphorus to two to five molecular proportions of polymer. In such 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 of about 200° F. to about 600° F. to improve the odor thereof.

The neutralized phosphorus sulfide-hydrocarbon reaction product may then be prepared by reacting the above phosphorus sulfide-hydrocarbon reaction product with the organic basic compound, such as guanidine or guanidine derivative of the type described above. This reaction 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 the basic compound, preferably at a temperature of about 100° F. 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 the basic compound can be reacted in proportions greater than that required for the neutralization of the titratable acidity. When the basic compound is added in the form of a carbonate, the com-

pletion 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.

Since the additives of the present invention are to be dissolved in mineral oils, the hydrocarbons which are reacted with a sulfide of phosphorus and the guanyl compounds 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 plasticizers.

When additives of the present invention are employed in mineral lubricating oils, they are preferably added in proportions of about 0.001 to about 10.0% and preferably 1.0 to 6.0%. The proportions giving the best results will vary somewhat according to the nature 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 additive in the composition ranges from 25% 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 with the base oil in the required amount.

In certain cases it may be found that the effect of adding compounds of the type described above to a lubricating oil will be to increase the detergent effect of the oil without sufficiently providing oxidation resisting characteristics. In such a case it is advantageous to add to the lubricant, in addition to the additives of the present invention, a substance containing sulfur and/or phosphorus. Elemental sulfur may be used for this purpose or an organic sulfur compound, particularly an organic sulfur compound capable of being decomposed to give free sulfur at a temperature to which the lubricant is subjected during use. Examples of such organic sulfur compounds are sulfurized mineral oils, terpenes, olefins, and diolefins, sulfurized animal and vegetable oils, sulfurized isobutylene polymer, etc.

Below are given detailed descriptions of preparations of examples of lubricating oil additives described above as well as engine tests in which an oil containing the additives was used as the lubricant. 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

202 grams (0.8 mol) of octadecene was dissolved in an equal weight of a conventionally refined Coastal distillate oil in a three-necked round bottomed flask equipped with a stirrer, solids addition flask, nitrogen inlet tube, and condenser. The temperature of the mixture was raised to 125° C. and 44 grams (0.2 mol) of phosphorus pentasulfide was added over a period of one hour. The temperature was then raised to 144° C. and maintained at this point for two hours, stirring being continued. The entire reaction was conducted in an atmosphere of nitrogen. The hot solution was filtered to remove a small amount of tarry material.

90 grams of the concentrate of the P_2S_5 treated octadecene prepared as described above was placed in a beaker and heated to 125° C. 11 grams of guanidine carbonate was added over a period of two hours with vigorous stirring. Three drops of silicone fluid was added to minimize foaming during this operation. After the guanidine carbonate was added the temperature was raised to 144° C. and then retained at this point for two hours, after which the solution was filtered.

Example 2

A guanidine product in the form of a concentrate was prepared in the manner and from the materials described in Example 1, except that in the step of neutralization with guanidine carbonate 88 grams of the concentrate of P_2S_5 -octadecene product was treated with a mixture of 5 grams of guanidine carbonate and 1 gram of water.

Example 3

Reactions were carried out as in Example 2, except that a mixture of 5 grams of guanidine carbonate and 7 grams of water was used in the neutralization reaction.

Example 4

1200 grams of polyisobutylene of a molecular weight of about 1200 was placed in a three-liter, three-necked round bottom flask and heated to 300° F. 125 grams of phosphorus pentasulfide was added and the temperature raised to 400° F. over a two-hour period, and heating was continued at this temperature for three more hours with stirring. The mixture was blown with nitrogen for another five hours at 400° F. and then filtered. 200 grams of the phosphorus pentasulfide-treated polyisobutylene thus prepared was dissolved in 200 g. of a solvent extracted Mid-Continent distillate oil of 150 seconds (Saybolt) at 100° F. and treated with 25 g. of guanidine carbonate dissolved in 35 g. of water at 130° C. for three hours and filtered.

Example 5

152.5 grams of polyethylene of molecular weight of about 400 was placed in a reaction flask as in Example 4 and heated to 300° F. 30 grams of phosphorus pentasulfide was added and the temperature raised to 400° F. and held at this point for 6½ hours, after which the reaction mixture was filtered. The product was diluted with 150 grams of a solvent extracted Mid-Continent distillate oil of 150 seconds (Saybolt) viscosity at 100° F. 200 grams of this solution was treated at 300° F. with 40 grams of guanidine carbonate dissolved in 100 grams of water and the mixture stirred at this temperature for 3½ hours and filtered.

Example 6

150 grams of polybutene-1 having a viscosity of 135 seconds (Saybolt) at 210° F. was placed in a reaction flask and 40 grams of phosphorus pentasulfide added at 300° F. This mixture was then heated at 400° F. for 6½ hours with stirring and filtered. The product was diluted with 150 grams of the solvent oil employed in Example 5. 278 grams of this solution was treated with 20 grams of guanidine carbonate dissolved in 50 grams of water and the mixture heated at 350° F. for 4½ hours and filtered.

Example 7

(a) The hydrocarbon material used in this

preparation was a lubricating oil bright stock derived from a Panhandle crude and having, before treatment, a viscosity of 150 seconds (Saybolt) at 210° F. This was submitted to propane deasphalting, propane dewaxing, and to phenol, sulfuric acid, and clay treatments. 138 lbs. of this material was placed in an 18 gallon enameled reactor equipped with a "strip" electric heater and a Lightning twin propeller mixer, and heated to 200-250° F. At this temperature 13.8 lbs. of powdered P_2S_5 was added slowly. The reactor was vented to a scrubber to remove the evolved H_2S , nitrogen was introduced at the bottom of the reactor, and stirring was maintained at a speed sufficiently rapid to prevent the P_2S_5 from settling out. After the P_2S_5 had been added, the mixture was heated to 400° F. and stirred at this temperature for 7 hours. The mixture was then filtered through Hy-flo (a filter aid).

(b) The reactor which was used in (a) was thoroughly cleaned and 49 lbs. of the P_2S_5 -bright stock reaction product (prepared as in (a)) was introduced. This was then neutralized with 4.9 lbs. of guanidine carbonate in the form of a mixture with 9.95 lbs. of water. This mixture was heated to complete the solution of the salt and was added to the reactor while still hot, the temperature of the P_2S_5 -bright stock product being 120-140° F. The mixture was vigorously stirred and blown with nitrogen, and the evolved H_2S was vented to a scrubber. The mixture was then heated to 350-370° F. over a 4 to 5 hour period to drive off the water. As the temperature was raised, the material became quite viscous until at approximately 250° F. the material had a grease-like gel structure. This gel broke after heating at approximately 350° F. for one hour. The heating was continued until a sample of the material which had been cooled to room temperature was still fluid. The final product was filtered through Poly-cel, and contained not more than 0.5% of water.

Example 8

A preparation was carried out as in Example 7, using the same bright stock material, except that 70 lbs. of the bright stock and 7.8 lbs. of P_2S_5 were employed in the first step, and in the neutralization step 33 lbs. of P_2S_5 -bright stock product and 3.3 lbs. of guanidine carbonate dissolved in 6.6 lbs. of water were employed.

Example 9

A further preparation was carried out, using the same materials and method as in Example 7, except that in the first step 87 lbs. of bright stock and 8.7 lbs. of P_2S_5 were employed, and the reaction product was filtered through Poly-cel instead of Hy-flo. In the neutralization of this product 67 lbs. of reaction product and 6.7 lbs. of guanidine carbonate dissolved in 13.4 lbs. of water were employed.

Example 10

The guanidine products prepared by the methods of Examples 1 to 7 and 9 were blended in a lubricating oil base consisting of a solvent extracted Coastal naphthenic oil of 60 seconds viscosity (Saybolt) at 210° F. The blends contained 4 weight per cent of the products (or about 2 wt. per cent of active ingredients except in Examples 7 and 9 where the active ingredient content is not known). The blends were submitted to a standard twenty-hour Lauson engine test, which was conducted by operating the Lauson engine at 1800 R. P. M. for 20 hours with a 1.5

indicated kilowatt load, 300° F. oil temperature and 295° F. jacket temperature. A different engine, but of the same type, was employed in testing the products of Examples 7 and 9. A similar test was applied to the unblended base oil. The oils were rated by the demerit system, wherein a perfectly clean surface is given a rating of 0, while a rating of 10 is given to the worst condition which could be expected of that surface. The results are shown in the following table:

Oil Composition	Hydrocarbon Reacted with P ₂ S ₅	Concentration of Guanidine Carbonate in Aqueous Solution	Piston Skirt Varnish Demerit
Base oil			3.8
Base oil+4% product of Example 1	Octadecene	Solid salt	0.8
Base oil+4% product of Example 2	do	83%	0.4
Base oil+4% product of Example 3	do	42%	0.0
Base oil+4% product of Example 4	Polyisobutene	42%	0.8
Base oil+4% product of Example 5	Polyethylene	29+	1.4
Base oil+4% product of Example 6	Polybutene-1	29%	1.4
Base oil			4.5
Base oil+4% product of Example 7	Bright stock	33½%	0.25
Base oil+4% product of Example 9	do	33½%	0.25

These results show the excellent detergency characteristics of the guanidine products and also show that the use of aqueous solutions of guanidine carbonate gives an improved product over the use of solid guanidine carbonate. The mechanism by which the use of water gives an improved product is not definitely known. However, it is apparently related to the effect of water or steam in causing a decrease in the sulfur content below the theoretical value.

Example 11

A blend containing 4% by weight of the 50% concentrate of guanidine product prepared as described in Example 1 (2% of active ingredient) in a solvent extracted paraffinic type of mineral lubricating oil of SAE 30 viscosity grade and a sample of the unblended oil base were employed as the crankcase lubricant in 36 hour tests with a Chevrolet engine operated at 30 brake horsepower, 3150 R. P. M. speed, 280° F. oil temperature and 200° F. jacket temperature. The piston skirt varnish demerit was determined. The results are shown in the following table:

Lubricant	Varnish Demerit
Base oil	0.6
Base oil+4% product of Example 1	0.3

Example 12

Blends containing 4% each of the product of Example 1, and 6% each of the products of Examples 4, 7, and 8, in a solvent extracted paraffinic type mineral lubricating oil of SAE 30 viscosity grade and a sample of the unblended base oil were employed as the crankcase lubricant in tests with a Caterpillar diesel engine operated for 120 hours and 6 hours of break-in time for each test, at approximately 19.8 brake horsepower, 1000 R. P. M. speed, 145-150° F. oil-to-bearing temperature, and 175-180° F. water jacket temperature. After each test was completed, the ring

zone demerit rating was determined. The results are shown in the following table:

Lubricant	Ring Zone Demerit
Base oil	2.1
Base oil+4% product of Example 1	1.1
Base oil+6% product of Example 4	0.6
Base oil+6% product of Example 7	0.7
Base oil+6% product of Example 8	0.5

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, thiophosphates, phosphites and thiophosphites, metal salicylates, metal xanthates and thioxanthates, metal thiocarbamates, amines and amine derivatives, reaction products of metal phenates and sulfur, reaction products of metal phenates and phosphorus sulfides, metal phenol sulfonates and the like. Thus the additives of the present invention may be used in lubricating oils containing such other addition agents as barium tert.-octyl-phenol sulfide, calcium tert.-amylphenol sulfide, nickel oleate, barium octadecylate, calcium phenyl stearate, zinc diisopropyl salicylate, aluminum naphthenate, calcium cetyl phosphate, barium di-tert.-amylphenol sulfide, calcium petroleum sulfonate, zinc methylcyclohexyl thiophosphate, calcium dichlorostearate, etc. Other types of additives such as phenols and phenol sulfides may be employed.

The lubricating oil base stocks 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, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichlorodiethyl ether, nitrobenzene, crotonaldehyde, etc. Hydrogenated oils, white oils, or shale oil may be employed as well as synthetic oils, such as esters and polyethers as well as those 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. Also, for special applications, animal, vegetable or fish oils or their hydrogenated or voltolized products may be employed in admixture with mineral oils.

For the best results the base stock chosen should normally be that oil which without 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 or other oils, no strict rule can be laid down for the choice of the base stock. Certain essentials must of course be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. The oil must be a satisfactory solvent for the additive, although in some cases auxiliary solvent agents may be

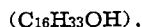
used. The lubricating oils, however they may have been produced, may vary considerably in viscosity and other properties depending upon the particular use for which they are desired, but they usually range from about 40 to 150 seconds Saybolt viscosity at 210° F. For the lubricating of certain low and medium speed diesel engines the general practice has often been to use a lubricating oil base stock prepared from naphthenic or aromatic crudes and having a Saybolt viscosity at 210° F. of 45 to 90 seconds and a viscosity index of 0 to 50. However, in certain types of diesel engine and other gasoline engine service, oils of higher viscosity index are often preferred, for example, up to 75 to 100, or even higher, viscosity index.

In addition to the material to be added according to the present invention, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, anti-oxidants, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like may also be employed.

Assisting agents which are particularly desirable as plasticizers and defoamers are the higher alcohols having 8 or more carbon atoms and preferably 12 to 20 carbon atoms. The alcohols may be saturated straight and branched chain aliphatic alcohols such as octyl alcohol



lauryl alcohol ($C_{12}H_{25}OH$), cetyl alcohol



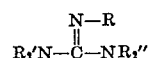
stearyl alcohol, sometimes referred to as octadecyl alcohol ($C_{18}H_{37}OH$), heptadecyl alcohol ($C_{17}H_{35}OH$), and the like; the corresponding olefinic alcohols such as oleyl alcohol; cyclic alcohols such as naphthenic alcohols; and aryl substituted alkyl alcohols, for instance, phenyl octyl alcohol, or octadecyl benzyl alcohol; or mixtures of these various alcohols, which may be pure or substantially pure synthetic alcohols. One may also use mixed naturally occurring alcohols such as those found in wool fat (which is known to contain a substantial percentage of alcohols having about 16 to 18 carbon atoms) and in sperm oil (which contains a high percentage of cetyl alcohol); and although it is preferable to isolate the alcohols from those materials, for some purposes wool fat, sperm oil or other natural products rich in alcohols may be used per se. Products prepared synthetically by chemical processes may also be used, such as alcohols prepared by the oxidation of petroleum hydrocarbons, e. g. paraffin wax, petrolatum, etc.

In addition to being employed in lubricants the additives of the present invention may also be used in motor fuels, hydraulic fluids, torque converter fluids, cutting oils, flushing oils, turbine oils or transformer oils, industrial oils, process oils and generally as anti-oxidants in mineral oil products. They may also be used in gear lubricants and greases. Since they are powerful surface active agents, they have practical use in dry cleaning fluids, mineral, spirit and aqueous paints, in flotation agents, and as dispersants for insecticides in aqueous and non-aqueous solu-

tions. They are also valuable anti-oxidants for natural and synthetic rubbers.

What is claimed is:

1. A mineral oil containing a detergent quantity of a product obtained by reacting one molecular proportion of a phosphorus sulfide with 1 to 10 molecular proportions of a hydrocarbon at about 200 to about 600° F. and treating the acidic reaction product at about 100 to about 400° F. with an amount sufficient to neutralize the titratable acidity of such reaction product of an organic basic reaction compound selected from the group consisting of: (1) free bases of the composition—



in which R, R' and R'' 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, said basic reacting salts being salts of acids whose strength, measured on a pH scale, is less than that of the said acidic reaction product.

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

3. A composition according to claim 2 in which R, R' and R'' of the formula each represent the same atom or group.

4. A composition according to claim 2 in which R, R' and R'' of the formula represent alkyl groups.

5. A composition according to claim 2 in which R, R' and R'' each represent hydrogen.

6. A composition according to claim 1 in which the compound employed to neutralize the phosphorus sulfide-hydrocarbon reaction product is guanidine carbonate.

7. A composition according to claim 1 in which the acidic reaction product is obtained by reacting phosphorus pentasulfide with a monoolefin.

8. A composition according to claim 7 in which the phosphorus pentasulfide-monoolefin reaction product is neutralized with guanidine carbonate.

9. A composition according to claim 7 in which the monoolefin is polyisobutylene.

10. A composition according to claim 8 in which the guanidine carbonate is contacted with the acidic product in the form of a mixture with water, said mixture containing 30-70% by weight, of guanidine carbonate.

11. A mineral lubricating oil containing a detergent quantity of a product obtained by reacting about one molecular proportion of phosphorus pentasulfide with two to five molecular proportions of polyisobutylene at a temperature of about 300 to about 550° F., and neutralizing the product thus obtained with guanidine carbonate.

12. A composition according to claim 11 in which the guanidine carbonate is employed in the form of a mixture with water, such mixture containing 30-70% by weight of guanidine carbonate.

13. A composition consisting essentially of a mineral lubricating oil and a product as defined in claim 1, the amount of said product in the composition being 25 to 50% by weight.

14. A composition consisting essentially of a mineral lubricating oil and a product as defined in claim 8, the amount of said product in the composition being 25 to 50% by weight.

15. A composition according to claim 1 in which the hydrocarbon which is reacted with a phos-

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phorus sulfide is a lubricating oil bright stock.

16. A mineral lubricating oil containing a detergent quantity of a product obtained by reacting about one molecular proportion of phosphorus pentasulfide with one to ten molecular proportions of a lubricating oil bright stock at a temperature of 200° to 600° F., and then treating the acidic reaction product at about 100-400° F. with an amount sufficient to neutralize the titratable acidity of such reaction product of guanidine carbonate.

17. A mineral lubricating oil containing a detergent quantity of a product obtained by heating a lubricating oil bright stock with one-tenth its weight of phosphorus pentasulfide at a temperature of about 400° F. for a period of

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about seven hours, then neutralizing the resulting reaction product at 120-140° F. with an aqueous solution of guanidine carbonate, and heating the final product at about 350-370° F. until the water content was not greater than about 0.5%.

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