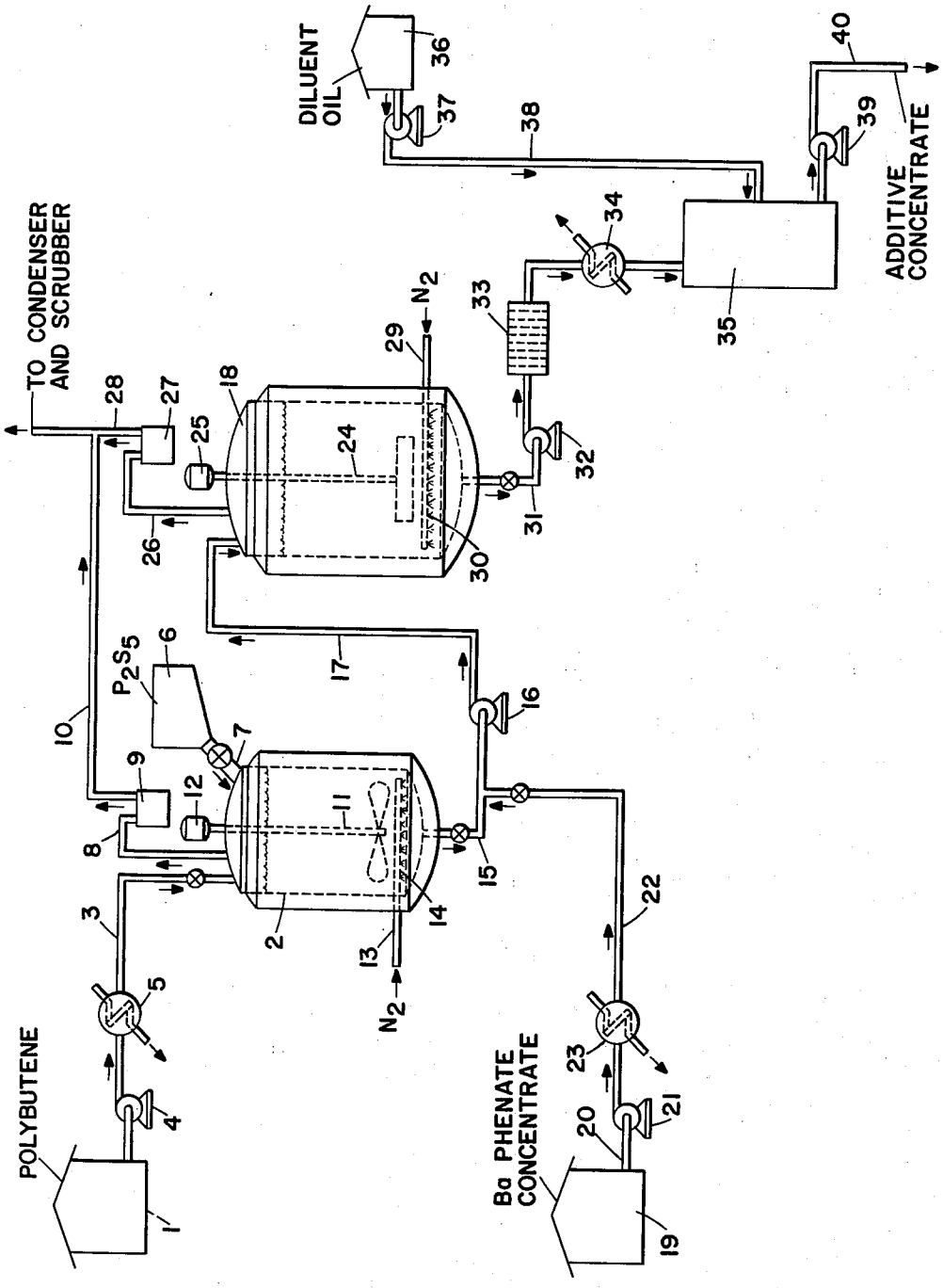
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PHOSPHOSULFURIZED DETERGENT-INHIBITOR ADDITIVE

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Carroll L. Knapp, Jr. Inventors
Stephen L. Wythe

By L. A. Strimbeck Attorney

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PHOSPHOSULFURIZED DETERGENT-INHIBITOR ADDITIVE

Carroll L. Knapp, Jr., Cranford, and Stephen L. Wythe, Westfield, N.J., assignors to Esso Research and Engineering Company, a corporation of Delaware

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1 Claim. (Cl. 252—32.7)

This invention is concerned with an improved lubricating oil detergent-inhibitor additive, with marketable concentrates and finished lubricating compositions containing the additive, and with a new process for manufacturing this detergent-inhibitor additive.

This application is a continuation-in-part of S.N. 448,366, "Improved Detergent-Inhibitor Additive for Lubricating Oils," filed August 6, 1954, and abandoned February 22, 1958.

During the past 15 years, rapid improvements have been made in lubricating oils used in internal combustion automotive engines through the use of detergent-inhibitor additives. Such additives enable the oil to keep various parts of the engine free of varnish, sludge, and coke-like deposits, and help reduce engine wear. The engines are, consequently, much better lubricated and their useful life is extended.

The detergent-inhibitors used in the past have been designed primarily for high temperature operation. Because of the trend in recent years to more powerful cars, there has been an increasing need for a detergent capable of handling the sludge formed under low temperature stop-and-go driving conditions. Under normal city or suburban operation, the engines of the newer cars are operating under what are, for them, light load conditions most of the time. Some of the larger cars operate principally on the idle system of the carburetor in this low-speed driving. The resulting rich mixtures and low engine temperatures accelerate sludge build-up markedly. For these newer types of engines, it is a major requirement of a lubricating oil that it be effective upnder conditions of both high and low temperature operation.

Phosphosulfurized hydrocarbons have been found to give excellent performance in both low and high temperature service—imparting oxidation resistance and detergency. In themselves, phosphosulfurized hydrocarbons are not useful, however, because they are extremely unstable and give off the obnoxious odor of hydrogen sulfide. Numerous attempts have been made in the past to stabilize such phosphosulfurized hydrocarbons, but quite often unsatisfactory results have been obtained. Neutralization or stabilization of phosphosulfurized materials with organic materials such as epoxides, olefins and alcohols, and with inorganic materials such as metal oxides or hydroxides, has resulted in unsatisfactory products. Either the problem of hydrogen sulfide evolution is not corrected or the phosphosulfurized hydrocarbon is caused to undergo some change such as sulfur loss that makes it much less effective as a detergent-inhibitor.

The present invention employs a detergent-inhibitor additive derived from a phosphosulfurized hydrocarbon. A suitable phosphosulfurized hydrocarbon is uniquely treated according to this invention with an oil-soluble, high alkalinity, organic neutralizing agent in such a manner that the detergent-inhibitor is effectively stabilized while still retaining its excellent sludge inhibiting and dispersing properties. Analytically this is observed in part by the fact that the sulfur content of the phosphosulfurized

hydrocarbon remains substantially unchanged during the neutralization step. The sulfur content of the product is within 95% of the sulfur content of the combined phosphosulfurized hydrocarbon and neutralizing agent reactants.

The preferred detergent-inhibitor additive of this invention is characterized also by the fact that the neutralizing agents used are in themselves effective oil additives. The organic neutralizing agents in the preferred embodiment, therefore, not only serve merely to stabilize the phosphosulfurized hydrocarbon, but also cooperate with it to produce a surprisingly effective detergent-inhibitor lubricating oil additive.

The detergent-inhibitor additive of this invention is best characterized or described, not only by its ultimate physical inspections, but also by the nature of the starting or raw materials and the manufacturing process. In each of these three areas—ingredients, process, and product inspections—there are certain material features or conditions that must be met in order to obtain a satisfactory ultimate product.

The hydrocarbon base stock used to form the phosphosulfurized hydrocarbon is primarily characterized by its molecular weight, or alternatively by viscosity or boiling range. Materials of too low molecular weight result in unsatisfactory products, and those too high are difficult to process. Suitable hydrocarbon base stocks are those that result in materials that are completely oil-soluble after phosphosulfurization. By oil-soluble is meant that at 70° F. 2 wt. percent of the material is completely soluble in hexane. The preferred hydrocarbon starting materials used in this invention are heavy petroleum fractions, distillates or residua, and polybutenes, the polybutenes being particularly preferred although they are somewhat more expensive.

The neutralizing agent used to treat the phosphosulfurized hydrocarbon must be an oil-soluble, high alkalinity, metals-containing, organic material. "Oil-soluble" is defined above. By "high alkalinity" is meant that the material contains an excess of the metal component over that normally required to obtain a neutral product. The ratio of equivalents of metal to equivalents of organic acids is greater than 1.5, and can be greater than 2.0. Suitable organic neutralizing agents include the alkyl phenates, alkyl phenate sulfides, and sulfonates.

The phosphosulfurization conditions are not too important although the phosphosulfurized intermediate product should meet certain specifications. The neutralization of the phosphosulfurized hydrocarbon is an important step. The proportions of ingredients are carefully controlled, as are the temperature and water content of the neutralization reaction mixture. Care is taken to avoid the presence of any material amounts of water. It is important in this invention that the water content of the neutralization reaction mixture not exceed at any time 0.5 weight percent. This in part contributes to the retention of sulfur in the neutralized product. The maintenance of substantially anhydrous conditions is permitted by the use of oil-soluble neutralizing agents. In the past it has been customary to prepare neutralized phosphosulfurized materials using neutralizing agents that require water, alcohol or high dilution to accomplish neutralization, and this often resulted in a two-phase system and sulfur loss.

Detergent-inhibitor additives of the type of this invention are customarily marketed as oil concentrates containing 20 to 100% of the detergent-inhibitor additive in a suitable dispersing oil. The odor of such concentrates greatly affects their marketability. It is an important feature of this invention that suitable odor-free concentrates are obtained, such as a saleable product is achieved. Another important feature of the concentrate product is its physical stability. It has been found

many times in the past, when attempting to prepare a neutralized phosphosulfurized hydrocarbon, that a concentrate of the additive will gel or precipitate materials. These two features of the concentrate product of this invention can be characterized by the fact that 10 wt. percent of the concentrate in a lubricating oil base stock has a rating of less than 2.0 in the hydrogen sulfide stability test, after being held at 130° F. for 6 hours, and remains essentially unchanged in viscosity and appearance without the formation of sediment after this temperature treatment. It will be appreciated by those skilled in the art that an additive concentrate containing a phosphosulfurized material that meets these stringent requirements is one admirably suited for commercial sales.

The concentrate product of this invention can also contain other materials such as polymeric viscosity index improvers, dyes and extreme pressure agents. Such concentrates can contain 20 to 100% of active ingredients.

Finished lubricants based upon the detergent-inhibitor additive of this invention are characterized not only by excellent physical stability, but also by surprising performance. In addition to being essentially free from odors and change in physical characteristics upon storage, the improved lubricants of this invention impart a high degree of sludge dispersancy under both high and low temperatures of engine operation and, in fact, have been found to inhibit the formation of sludge. They also greatly inhibit the formation of varnish on engine surfaces in use, and markedly reduce engine wear. Higher molecular weight versions of the detergent-inhibitor additive of this invention, especially those derived from the polybutenes, also materially improve the viscosity index of the lubricating oil composition.

A subsidiary feature of this invention is the surprising finding that it is particularly advantageous to use the heavy metal di-organo dithiophosphates in combination with neutralized phosphosulfurized hydrocarbon, especially when preparing marketable multi-purpose additive concentrates. The metal salts, particularly the zinc salts, of dialkyl dithiophosphates are well known additives useful for imparting oxidation resistance and extreme pressure properties to lubricants. These dithiophosphates, which are the divalent heavy metal salts of phosphorus pentasulfide treated hydroxy compounds, have the propensity for undesirably evolving hydrogen sulfide. By combining these dialkyl dithiophosphate salts with the neutralized phosphosulfurized hydrocarbon of this invention to form additive concentrate "packages," stable, odor-free concentrates and finished lubricants are obtained. The surprising feature is that the use of dialkyl dithiophosphate salts permits the use of a lesser amount of neutralizing agent in preparing the neutralized phosphosulfurized hydrocarbon such that if the neutralized phosphosulfurized hydrocarbon were used alone, it would be of borderline quality from the standpoint of odor. The reason why it is possible to combine two materials that have the propensity to evolve hydrogen sulfide and obtain a stable product is not known at this time. One particular advantage of this combination that will be recognized by those skilled in the art is that it permits the use of a greater proportion, with respect to the organic neutralizing agent, of the phosphosulfurized hydrocarbon in the lubricant, which is desirable because of the phosphosulfurized hydrocarbon's low temperature sludge handling ability. The dialkyl dithiophosphate heavy metal salts, which in many instances are to be used in the finished lubricant anyway, in unexpectedly taking over a portion of the stabilizing function of the neutralizing agent, gives a result heretofore unappreciated.

When used in combination, the dialkyl dithiophosphates will usually be present in an amount in the range of 10 to 90% of the weight of the neutralized phosphosulfurized hydrocarbon in the composition, whether in a concentrate or in a finished lubricant. The oil-soluble dialkyl dithiophosphates having 1 to 12 carbon atoms in the alkyl groups, whether alike or different, straight or branched chain, are preferred. Other di-organo dithiophosphates are useful, such as those derived from alkyl hydroxy benzenes, cyclic alcohols, polymers containing functional hydroxy groups and the like, so long as they have satisfactory oil solubility. The organic groups can, of course, be substituted as with chloro, nitroso, amino, etc. groups.

While primarily intended for use in automotive engine lubricants, the neutralized phosphosulfurized hydrocarbon of this invention is useful in amounts in the range of 0.01 to 10 wt. percent in other oleaginous materials to impart dispersancy, oxidation resistance, extreme pressure properties, etc. Thus this additive can be used in fuel oils and jet fuels to disperse sludge and haze precursors and to impart oxidation resistance; in gear lubricants and automatic transmission fluids to inhibit varnish or sludge formation and to impart extreme pressure properties; and in synthetic ester lubricants to inhibit oxidative deterioration and to disperse sludge.

This invention will become clear from the following examples and description, during which the drawing attached to and forming a part of this specification will be discussed.

The drawing illustrates a preferred process for the manufacturing of a detergent-inhibitor additive according to the teachings of this invention.

For convenience, the pertinent factors influencing the character of the product of this invention are summarized in Table I presented hereinafter. Suitable hydrocarbon raw materials have viscosities above 100 SSU at 210° F. and can be solids at this temperature. They can have boiling points above 400° F. at 10 mm. Hg abs. ranging upward to their decomposition temperature at this pressure. Hydrocarbons having a viscosity in the range of 1000 to 50,000 SSU at 210° F. are particularly preferred. Preferably, materials that are predominantly paraffinic are used, i.e., they contain over 80% of alkyl hydrocarbons and less than 5% of the carbon atoms are in aromatic rings. While many hydrocarbon sources can be used, preferred sources are heavy petroleum fractions including extracted residua and the polyolefins, e.g., polybutene polymers.

When petroleum fractions are used, they preferably meet the following inspections:

Viscosity, SSU at 210° F.	140–250
Viscosity index	70–110
Metals content, wt. percent	<0.2
API gravity, °	20–27

The polybutenes used should meet the following inspections:

Viscosity, SSU at 210° F.	1500–200,000
Flash, ° F.	>300

While the broad range above can be used, the polybutenes preferably have a molecular weight distribution such that 80 wt. percent of the material has a molecular weight in the narrower range of 700 to 100,000.

Phosphorus pentasulfide is used to form the phosphosulfurized hydrocarbon. While not critical, it should meet the following inspections:

Melting point, ° F.	270–280
Phosphorus, wt. percent	27.5–29.0
Sulfur, wt. percent	71.0–73.0

The oil-soluble, high alkalinity, metals-containing, organic compounds used to stabilize the phosphosulfurized hydrocarbons are, preferably, those known to the prior art. While several heavy di-valent metals such as zinc

and magnesium are useful, the metal component is preferably calcium and/or barium. It is preferred for the purpose of this invention to use calcium or barium alkyl phenates, alkyl phenate sulfides, sulfonates, or mixtures thereof, although equivalent calcium or barium compounds can be used.

Suitable metal alkyl phenols useful in this invention are known to the art, e.g., see U.S. 2,197,833. The alkyl phenols or equivalent alkylated aryl hydroxides used contain one or more alkyl groups, each of which can have in the range of 1 to 30, preferably 8 to 20 carbon atoms per alkyl radical. The alkyl phenols can contain more than one ring structure, and more than one hydroxy group, although alkylated monohydroxy benzenes are preferred. The total molecular weight of the alkyl phenols used is in the range of 200 to 700. The alkyl phenols can be synthesized by simple alkylation of cresol or naphthol with olefins. A suitable product can be prepared, for example, by alkylating phenol with polmeric materials obtained as by-products in the manfacture of butyl alcohol from petroleum refinery butenes. These polymeric materials consist essentially of normal butene, a small percentage of isobutene and other olefins, and give alkylated phenols having branched chain alkyl groups of 16 to 24 carbon atoms.

The alkyl phenol sulfides used are the thioethers and polysulfides of the above alkyl phenols. The sulfides comprise two or more of the alkyl phenol groups joined by one or more di-valent sulfur atoms, e.g., di (2,4-ditertiary amyl phenol) mono-sulfide. Preferably the alkyl phenol sulfides used contain in the range of 2.5 to 4.0 weight percent sulfur. Suitable alkyl phenol sulfides are known to the art, e.g., see U.S. 2,362,289 and 2,461,335.

The alkyl phenols can be converted to phenol sulfides, for example, by reaction with sulfur dichloride to produce essentially phenol monosulfides having thioether linkages. Sulfur monochloride can be used to produce essentially alkyl phenol disulfides.

The sulfonates used are also well known in the art. The sulfonic acids can be obtained through the sulfonation of either synthetic or natural hydrocarbons. The preferred sulfonic acids have molecular weights in the range of 300 to 700 (as the sodium soap). The synthetic acids preferably have molecular weights in the narrower range of 400 to 600. The acids can contain more than one sulfonyl group in the molecule. Suitable sulfonic acids are produced by sulfonating alkyl aromatic hydrocarbons such as didodecyl benzene. They can also be obtained by treatment of lubricating oil base stocks with concentrated or fuming sulfuric acid in a conventional manner to produce oil-soluble "mahogany" acids.

The alkyl phenols, the alkyl phenol sulfides, and the sulfonic acids are neutralized with an excess, usually at least 5% excess, of the calcium or barium base or mixtures thereof to obtain the desired high alkalinity materials. The sulfonates can, however, be first neutralized with a base of another metal, especially the alkali metals, and the desired alkaline earth material can then be obtained from these salts by reaction with the calcium or barium basic materials.

In forming the high alkalinity materials, according to one embodiment of this invention, mixtures of the alkyl phenols, alkyl phenol sulfides, sulfonic acids or their alkali metal salts are coneutralized to obtain unusually high alkalinity complexes. Thus a mixture of phenate sulfides and sulfonates can be obtained by blending a neutral sulfonate, e.g., sodium sulfonate, with an alkyl phenol and treating the blend with an excess of the metal neutralizing agent, e.g., calcium oxide. Preferably, the neutralization of the phenols or sulfonic acids is carried out in the presence of an oil diluent.

To obtain the desired high alkalinity product, particularly in the case of the phenates, it is desirable to use during neutralization such aids as CO_2 and water treatment. The amount of metal retained by the product is higher and the product is usually more stable.

The formation of high alkalinity alkyl phenates, alkyl phenate sulfides, and sulfonates of the requisite oil solubility and basicity as above described is well known to the art and need not be further described.

It is important in this inveniton to use the proper amount of the oil-soluble, high alkalinity, metals-containing, organic compound to stabilize the phosphosulfurized hydrocarbon. To assure proper stabilization, the weight of the high alkalinity, metals-containing, organic material times its alkaline neutralization number to a pH of 4 should exceed the weight of the phosphosulfurized hydrocarbon times its saponification number. The alkaline neutralization number is the amount of acid expressed as equivalent milligrams of potassium hydroxide which is required to react with one gram of the high alkalinity material to produce a pH of 4. The saponification number is the milligrams of potassium hydroxide necessary to saponify one gram of the phosphosulfurized hydrocarbon. For example, if it is dsired to stabilize 100 grams of a phosphosulfurized hydrocarbon having a saponification number of 20, it is necessary to use at least 200 grams of the high alkalinity organic material when it has a neutralization number of 10.

With reference to the drawing, the process for manufacturing the improved detergent-inhibitor additive of this invention will be described.

The hydrocarbon starting material, e.g., polybutene, is admitted from storage zone **1** to reactor **2** by line **3** and pump **4**. A heat exchanger **5** can be used to give some preheat to the polybutene. The phosphorus pentasulfide is admitted to reaction zone **2** from zone **6** by line **7**. It is preferred to add the phosphorus pentasulfide at one time with continuous addition of the polybutene.

Reaction zone **2** is preferably a glass-lined reactor and is also preferably jacketed so that the contents can be heated. For example, reactor **2** is a 2,000 gallon Pfaudler glass-lined, jacketed kettle. The reactor is provided with a vent line **8** which ends in a knockout drum **9**, from which gases are vented by line **10**. Preferably the contents of reactor **2** are agitated by an agitator **11**, driven by a motor **12**. It is preferred to supply a stripping gas, e.g., nitrogen, to the reactor by line **13** and distributing arrangement **14** to provide an inert reaction atmosphere and assist in removing hydrogen sulfide and other odor bodies.

The conditions of phosphosulfurization are not too critical although they should preferably be within the range specified in Table I. The product obtained by the phosphosulfurization step should meet the inspections given in the table. At no time during the reaction does the water content of the mixture exceed 0.5 weight percent, as excessive amounts of water cause sulfur loss.

Upon completion of the phosphosulfurization reaction, the phosphosulfurized hydrocarbon is transferred by line **15**, pump **16**, and line **17** to the neutralization reaction vessel **18**.

The order of mixing of the phosphosulfurized hydrocarbon and the neutralizing agent is not critical. The oil-soluble, high alkalinity, metals-containing, organic material used to stabilize the phosphosulfurized hydrocarbon can be added directly to vessel **18**, or, as shown, can be gradually admixed with the phosphosulfurized hydrocarbon as it is transferred to the neutralization vessel **18**. For example, a barium phenate concentrate is supplied from reservoir **19** via line **20**, pump **21** and line **22**. It can be preheated via heat exchanger **23** in line **22** if desired. Alternatively, all of the cold neutralizing agent can be first added to vessel **18** followed by addition of the hot phosphosulfurized hydrocarbon which will bring the temperature up to that desired.

Vessel **18** can be of any suitable corrosion resistant material. For example, vessel **18** is a 5,000 gallon stainless steel vessel, insulated to permit adiabatic reaction conditions.

The contents of vessel **18** are preferably agitated as by

turbine agitator **24**, driven by motor **25**. The vessel is vented as by line **26**, which terminates in knockout drum **27**. Gases are vented from the knockout drum by line **28** and commingled with the gases in line **10**. The vented gases, if desired, can be dried as by condensing, scrubbed to remove hydrogen sulfide, and then reused in the process.

To maintain the requisite low water content in vessel **18** and to remove the small amount of H_2S and other odor bodies, it is preferred to strip the contents of the vessel during the neutralization and heat soaking reaction with an inert gas, e.g., nitrogen, which can be supplied by line **29** ending in a suitable distributing arrangement **30**.

As will be demonstrated in the examples, it is important that the temperature of neutralization be in the range of 150° to 600° F., preferably 280° to 450° F. This assures the proper reaction between the phosphosulfurized hydrocarbon and the high alkalinity organic neutralizing agent, and also the higher preferred temperature assures that the requisite substantially anhydrous conditions be maintained. The time of treatment will depend somewhat upon the size of the batch being treated. It is much preferred, however, to maintain the ingredients at a temperature above 280° F. for at least a half hour. Termination of the neutralization and heat soaking reaction can be conveniently determined by testing the product for stability against hydrogen sulfide evolution.

The stabilized phosphosulfurized hydrocarbon is removed from vessel **18** by line **31** upon completion of the reaction. It is pumped by pump **32** through a filter **33** and cooler **34** to a storage tank **35**. The filter, such as a plate and frame filter, removes essentially completely all inorganic salts from the stabilized phosphosulfurized hydrocarbon or detergent-inhibitor additive.

If desired, a diluent oil, such as a solvent extract, can be supplied to storage tank **35** from reservoir **36** via pump **37** and line **38** to obtain an additive concentrate. The additive concentrate can be then withdrawn from tank **35** via pump **39** and line **40** as needed. As mentioned previously, the oil concentrate so obtained is a very remarkable product, considering its nature, because of its clear and bright appearance, stability, and freedom from obnoxious odors.

The following table summarizes the pertinent conditions and features of the product and process of this invention, and gives the inspections that the product must meet in order to be satisfactory.

TABLE I.—PERTINENT FACTORS INFLUENCING CHARACTER OF PRODUCT

Reactants	Range	Preferred
P_2S_5:		
Wt. Percent S	70 to 75	71.0 to 73.
Wt. Percent P	27 to 30	27.5 to 29.
Organic Material	Nil	Nil.
Melting Point, ° F	260 to 290	270 to 280.
Hydrocarbon		Polybutene.
Staudinger Mol. Wt	500 to 200,000	700 to 100,000.
Vis., @ 210° F., SSU	100 to 100,000	1,000 to 50,000.
Boiling Pt., ° F., 10 mm. Hg		Above 400.
Sulfonic Acid (as 40-60% active ingredient concentrate in oil):		
Mol. Wt. (as Na Soap)	200 to 900	300 to 700.
Wt. Percent S	2 to 6	2.5 to 4.5.
Neut. No., Mg. KOH/gr	25 to 200	50 to 80.
Alkyl Phenol:		
Mol. Wt	200 to 700	300 to 500.
No. Arom. Rings/Molecule	1 to 3	1.
Alkyl group(s)—Total carbon atoms ea.	1 to 30	8 to 20.
Alkyl Phenol Sulfide (as 30-50% active ingredient concentrate in oil) (Alkyl phenol precursor has inspections as above):		
Wt. Percent S	2 to 6	2.5 to 4.0.
Wt. Percent Metal, as Ba	5 to 15	10.0 to 14.0.
Phosphosulfurized Hydrocarbon (PSHC):		
Appearance	Bright, clear	Do.
Water Content, Wt. Percent	Less than 0.5	Do.
Sapon. No., to pH of 4	30 to 120	60 to 90.
Wt. Percent P	1 to 10	2.5 to 4.5.
Wt. Percent S	3 to 15	4 to 8.
Sol. of 2 wt. percent in hexane at 70° F.	Complete	Do.
High Alkalinity Organic Material (as 30-60% oil concentrate):		
Sol. of 2 wt. percent in hexane at 70° F.	Complete	Do.
Neut. No. to pH of 4, Mg. KOH/gr.	10 to 150	50 to 100.
Equiv. metals/equiv. organics	Greater than 1.5	Greater than 2.
Vis. @ 210° F., SSU	100 to 1,000	200 to 400.
Metals Content, Wt. Percent	5 to 30	10 to 20.
Stripping Gas:		
Water, p.p.m.	Less than 100	Do.
Percent free Oxygen	Less than 0.5	Do.
Reaction Conditions:		
Phosphosulfurization—		
Wt. Percent P_2S_5 on hydrocarbon.	2 to 20	8 to 18.
Temp., ° F	150 to 600	275 to 500.
Time, hrs	0.5 to 15	0.5 to 10.
Diluents, contaminants, etc., Wt. Percent.	Less than 2	Do.
Water present, Wt. Percent.	Less than 0.5	Do.
Forming High Alkalinity Material—		
Equiv. Oxide or Hydroxide/Equiv. of Organic Acid (excl. CO_2).	1 to 20	1.5 to 5.
Temp., ° C		60 to 220.
Time, Hrs		1 to 5.
Neutralization of PSHC—		
Temp., ° F	150 to 600	280 to 450.
Time, Hrs	0.5 to 10	0.5 to 6.
Water present during reaction, Wt. Percent.	Less than 0.5	Do.
Equiv. Alkaline Material/Equiv. of Saponifiable Material in PSHC.	1 to 20	1 to 3.
Stripping during Neutralization—		
S.c.f. inert gas/bbl./hr	0 to 10	0.2 to 3.
Temp., ° F	200 to 400	325 to 375.
Time, Hrs	¼ to 10	3 to 6.
Detergent Inhibitor, Additive Inspections—		
Wt. Percent P		0.5 to 2.5.
Wt. Percent combined S		2 to 6.
Wt. Percent Metal, as Barium.		5 to 15.
Gravity, ° API		0 to 10.
H_2S Test Rating (10 Wt. Percent conc. 6 hrs. @ 130° F.).		0 to 2.
Neut. No., Mg. KOH/gr		0 to 10.
ASTM color (5 Wt. Percent in white oil).		2 to 5.
Vis. @ 210° F., SSU		1,000 to 3,000.

When the reaction products of this invention are employed as additives in lubricating oils, they are preferably used in an amount in the range of 0.1 to 10% by weight, and preferably about 1.0 to 6.0% by weight. The proportions giving the best results will vary somewhat according to the nature of the additive and the intended use of the lubricant.

The lubricating oil base stocks used in the compositions of this invention can be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic, or mixed base crudes, or, if desired, various blended oils can be employed as well as residuals, particularly those from which asphaltic constituents have been carefully removed. The oils can be refined by conventional methods using acid, alkali and/or clay or other agents such as aluminum chloride, or they can 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 oils can be employed. Synthetic lubricating oils having a viscosity in the range of 70 to 400 SSU at 100° F. are also satisfactory. Examples of synthetic oils are: the ester of C_{13} Oxo alcohol with octanoic acid, di-2-ethylhexyl sebacate, C_{13} Oxo acid diester of tetraethylene glycol, the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid, the ester formed by contacting three moles of the monomethyl ether of ethylene glycol with one mole of phosphorus oxychloride, the polymer of chlorotrifluoroethylene containing twelve recurring units of chlorotrifluoroethylene, methyl polysiloxanes, the ester formed by reacting one mole of sulfur oxychloride with two moles of the methylether of ethylene glycol, the carbonate

formed by reacting C_8 Oxo alcohol with ethyl carbonate to form a half ester and reacting this half ester with tetraethylene glycol, and Fischer-Tropsch synthetic oils. For special applications, animal, vegetable or fish oils, or their hydrogenated or voltolized products, can also be employed alone or 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. Because one advantage of additives is that their use 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 esentials must, of course, be observed. The oil must possess the viscosity and volatility characteristics known to be required for the service contemplated. 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 34 to 400 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. In certain types of diesel engines and in gasoline engines, oils having viscosity indices above 100 are used.

Other agents can also be used in the oil composition, such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, thickeners, viscosity index improvers, oiliness agents, resins, rubber, olefin polymers, voltolized fats, voltolized mineral oils, and/or voltolized waxes, colloidal solids such as graphite or zinc oxide, and metallic or other soaps, sludge dispersers and antioxidants. Solvents and assisting agents, such as esters, ketones, alcohols, aldehydes, halogenated or nitrated compounds, and the like can also be employed.

In addition to being employed in lubricants, the additive of the present invention can also be used in motor fuels, hydraulic fluids, gear lubricants, greases, torque converter fluids, cutting oils, flushing oils, turbine oils or transformer oils, industrial oils, process oils and generally as detergents in oleaginous or hydrocarbon products.

Examples

The following examples further illustrate this invention. In the following descriptions, the intermediate products are first described, followed by descriptions of the final neutralized product. Illustrations showing the effectiveness of stabilization are first presented, followed by illusttrations of the engine performance of the additives of this invention. The examples are chosen to outline the material features of the invention.

The intermediates

I. PHOSPHOSULFURIZED COMPONENTS

Intermediate 1.—150 pounds of a deasphlted, dewaxed Panhandle residuum were heated to 100° F., and 15 pounds of phosphorus pentasulfide were added over a fifteen minute period. The residuum had a viscosity index of 95, a viscosity of 165 SSU at 210° F., and a gravity of 24.8° API. The mixture was then heated with stirring for about ten hours at 450° F., while being blown with a stream of nitrogen. The product was cooled to 250° F. and filtered. It had the following inspections:

Phosphorus, wt. percent	2.46
Sulfur, wt. percent	4.35
Neut. No. to pH of 4	29.8
Sapon. No.	72.45
Water	Nil

Intermediate 2.—Ninety pounds of a polybutene having an average molecular weight of about 1100 were reacted with nine pounds of phosphorus pentasulfide for ten hours at 425° F., with stirring and nitrogen blowing. All of the phosphorus pentasulfide had reacted and the product did not require filtration. In the examples below, Intermediate 2 was used with varying amounts of diluent oil. It had the following inspections:

Phosphorus, wt. percent	2.5
Sulfur, wt. percent	4.3
Neut. No. to pH of 4	26.4
Sapon. No. to pH of 4	65.8

Intermediate 3.—This material was similar to that in the example above, except that a greater amount of phosphorus pentasulfide was used.

Ninety pounds of the above 1100 molecular weight polybutene were reacted with 13.5 pounds of phosphorus pentasulfide at 425° F. for four hours. During the reaction, the mixture was stirred and blown with nitrogen. The product required no filtration and had the following inspections:

Phosphorus, wt. percent	3.4
Sulfur, wt. percent	6.1
Neut. No. to pH of 4	38.0
Sapon. No. to pH of 4	88.0
Vis. @ 210° F., SSU	20,400

II. HIGH ALKALINITY NEUTRALIZING AGENTS

The above acidic phosphosulfurized hydrocarbons were reacted with a number of oil-soluble alkaline agents whose properties are described below.

Intermediate A.—This is a commercially available lube oil additive marketed by the Enjay Company and known as Paranox 47.

It is an oil solution of an alkyl phenol sulfide neutralized with an excess of barium hydroxide and CO_2 treated. The product contains an excess of equivalents of barium over equivalents of acidic hydroxy functions in the phenol sulfide. It has the following inspections:

Barium, wt. percent	12.0–12.8
Sulfur, wt. percent	2.8–3.3
Neut. No. to pH of 4	73.0–93.0
pH	11

Intermediate B.—This product is an alkaline material containing calcium phenol sulfide, sulfonates and excess barium.

520 grams of a solution of a neutral calcium petroleum sulfonate having a molecular weight of 832 in a solvent extracted diluent oil (solution contained 1.44 wt. percent calcium, 2.0 wt. percent sulfur), 712 grams of a solution of (diisobutyl) phenol sulfide in a solvent extracted diluent oil (solution contained 5.62% sulfur and had a saponification number of 100.9), 560 grams of water and 208 grams of a solvent extracted mineral oil were heated together with stirring to 146° F. Then 668 grams of barium hydroxide pentahydrate were added slowly and the mixture heated to 212° F. and held there for three hours. The temperature was then raised to 302° F. and held there an additional half hour. The heating was discontinued and after the temperature fell to 250° F., the mixture was filtered through a heated Büchner funnel using Hi-Flo filter aid and suction. The resultant solution of the high alkalinity metal compound had a barium content of about 13.83% and a neutralization number of about 90.5.

Intermediate C.—15,400 grams of a solution containing about 33.9% of a neutral barium petroleum sulfonate having a molecular weight of 995 in a solvent extracted diluent oil were placed in a stainless steel pot together with about 3315 grams of a solution of diisobutylphenol sulfide (similar to that employed in Intermediate B) and 4655 grams of water, and the mixture was stirred and heated to 146° F. Then 4130 grams of barium hydroxide pentahydrate were added over a three minute period. The mixture was heated with stirring

to 212° F. and held there for one hour, then heated to 302° F. and held there for an additional half hour. The mixture was then cooled and filtered through a heated Buchner funnel using suction and Hi-Flo filter aid. Its inspections were:

Sulfur, wt. percent	2.4
Barium, wt. percent	12.2
Vis. @ 210° F., SSU	142.0
Initial pH	12.8
Neut. No. to pH of 4	67.5
Spec. Grav. @ 77° F	1.062

Intermediate D.—This was a commercially available high barium content sulfonate sold by the Bryton Chemical Company. It is made by overneutralizing a synthetic sulfonic acid having an average molecular weight of about 475 with barium hydroxide. The sulfonate had the following inspections:

Barium, wt. percent	16.49
Sulfur, wt. percent	3.10
Neut. No. to pH of 4	61.53
Initial pH	8.95

Intermediate E.—This product was an alkaline barium alkyl phenate.

680 grams of an alkylated phenol (predominantly a wide cut nonyl phenol from the alkylation of phenol with tripropylene) were dissolved in 1058 grams of a phenol extracted solvent dewaxed paraffinic oil (vis. @ 100° F. of 150 SSU) and 885 grams of barium hydroxide pentahydrate were then slowly added over a period of an hour. The reaction took 2½ hours at an average temperature of 250° F. During the last hour, the mixture was kept saturated with CO_2. A total of 2390 grams of material was recovered. A 58.3 weight percent solution of the raw product in light kerosine, designated Intermedaite E, was then prepared. The raw product contained 3.0 volume percent solids. The kerosine solution was filtered and had the following inspections:

	Percent
Sulfated ash	18.0
Carbonate ion	2.7

III. BASE STOCKS USED IN OIL BLENDS

In the ensuing examples, the additives were dissolved in a variety of base stocks for purposes of bench and engine tests. These base stocks are listed below:

Base stock 1.—This consisted of 89.8 weight percent of a solvent extracted and dewaxed petroleum distillate 7.5 weight percent of an oil solution containing 20% by weight of a polyisobutylene V.I. improver having a molecular weight of 18,000, and 2.7 weight percent of a polymethacrylate ester of C_9 alcohols. Base stock 1 had a Saybolt viscosity of 157.4 seconds at 100° F., and 49.7 seconds at 210° F.

Base stock 2.—This was a blend of 81.9 volume percent of a neutral oil having a viscosity of about 330 SSU at 100° F. and a viscosity index of about 103, and 18.1 volume percent of a bright stock having a viscosity of about 150 SSU at 210° F. and a viscosity index of about 100. The neutral was a MEK dewaxed, phenol treated, clay contacted oil derived from a Panhandle crude. The bright stock was a propane deasphalted and dewaxed, phenol and clay treated residua. Base stock 2 had a viscosity of 478.3 SSU at 100° F. and a viscosity index of 101.4.

Stability tests

The examples below illustrate combinations of alkaline and phosphosulfurized intermediates according to this invention that are stable against hydrogen sulfide evolution. This property is measured by the hydrogen sulfide stability test.

IV. HYDROGEN SULFIDE STABILITY TEST

The hydrogen sulfide stability of an additive is tested by mixing a given amount of the phosphosulfurized hydrocarbon in a lubricating oil base stock. 800 ccs. of this blend are then heated in a one-quart, narrow-neck bottle for a specified time at 130° F. (unless specified otherwise). After this, a piece of filter paper, moistened with a saturated lead acetate solution, is placed over the mouth of the bottle for a period of five minutes. The lead sulfide stain obtained is rated for its intensity. A rating of 10 is a dark stain with a trace of sulfur overlay. A rating of 10+ is a stain with considerable sulfur overlay. A rating of 0 means that essentially no stain was obtained.

V. EXAMPLES 1 THROUGH 11

Example 1.—This example shows the importance of the ratios of ingredients used to form the neutralized phosphosulfurized hydrocarbon, and the effect of temperature.

Blends of Intermediate 1 and Intermediate B were heated with stirring and nitrogen blowing in the concentrations and at the temperatures indicated in Table II. Lubricating oil compositions were then prepared and evaluated in the hydrogen sulfide stability test.

Five or ten weight percent of the product was admixed with Base stock 1, and the products were tested for hydrogen sulfide stability after heating for six hours at 130° F. They were then blown with nitrogen and stored for ten days at room temperature and again rated. The products were then further heated for six hours at 130° F. and again rated. The results are presented in Table II.

TABLE II

Formulation	Grams of Intermed. 1	Grams of Intermed. B	Temp., ° F.	Wt. percent Product Blended in Oil	Rating after 6 hrs. @ 130° F.	Rating after 10 days @ Rm. Temp.	Rating after Storage and heating 6 hrs. @ 130° F.
1	100	100	150	5	9	1.5	7
2	100	100	200	5	8	1.0	7
3	100	100	250	5	10	0.5	6
4	1,000	1,000	280	10	1.5	----------	----------
5	100	100	300	5	1.5	----------	2
6	100	50	300	5	8	0.75	5
7	100	75	300	5	7	0	3

A comparison of Formulations 1 through 5 indicates the effect of reaction temperature and the effectiveness of stabilization. It can be seen that while a temperature above 150° F. gives some improvement if maintained for a sufficient length of time, a temperature of at least about 280° F. is most desirable in order to obtain the best degree of stabilization. Also, the high temperature results in a more economic processing time. A comparison of Formulations 5 through 7 indicates the effect of the relative proportions of the materials and the effectiveness of stabilization. It can be seen, as shown by Formulation 5, that the weight of the oil-soluble high alkalinity organic compound (Intermediate B) times its Neutralization number to a pH of 4 (100×90.5) must be greater than the weight of the phosphosulfurized hydrocarbon times its saponification number (100×72.5) in order to obtain a satisfactory product.

Example 2.—Intermediate 1 was reacted with an equal part by weight of Intermediate A at a temperature of 310° F. for four hours with nitrogen stripping. A blend was then prepared, designated Formulation 8, which consisted of 10% by weight of the reaction product and 90% by weight of lubricating oil Base stock 1. 800 ccs. of Formulation 8, after standing ten days at room temperature, were then exposed to a strip of paper impregnated with lead acetate. No stain at all was produced.

Example 3.—This was substantially the same type of additive as in Example 2.

1,000 grams of Intermediate 1 were reacted with 1,000 grams of Intermediate A at 280° F. for six hours. Four weight percent of this reaction product was blended with 96 weight percent of Base stock 2 to give Formulation 9. In the hydrogen sulfide stability test, Formulation 9 rated 0 after six hours at 130° F.

Example 4.—100 grams of Intermediate 2, 50 grams of a solvent refined naphthenic 28.9° API gravity diluent oil (Diluent oil 1) and 150 grams of Intermediate A were heated together at 250–270° F. for three hours, and then at 320° F. for two hours with nitrogen blowing. Sixteen weight percent of this reaction mixture was then blended with 84 weight percent of Base stock 1 to give Formulation 10. Formulation 10 had an H_2S demerit in the hydrogen sulfide stability test of only 4, even after prolonged heating for 24 hours, and on further storage for 40 days at room temperature gave a stability rating of 0, the solution apparently absorbing hydrogen sulfide.

Example 5.—119 grams of Intermediate 2, 119 grams of Diluent oil 1, and 238 grams of Intermediate B were heated at 280° F. for 7.5 hours. Formulation 11 was then prepared by mixing 20 weight percent of the reaction product with 80 weight percent of Base stock 1. Formulation 11, when evaluated in the H_2S stability test, gave a rating of 0.5 after one hour, and 1.0 after four hours of heating at 130° F.

Example 6.—Fifty grams of Intermediate 2 were reacted with 100 grams of Intermediate D for six hours at 350° F. while dissolved in 150 grams of a solvent extracted mineral oil having a viscosity of 100 SSU at 210° F. The mixture was then cooled to 250° F. and filtered. 120 grams of the filtered product were dissolved in 680 grams of Base stock 1 to give Formulation 12. 800 ccs. of Formulation 12 gave a rating of 0 after one hour at 130° F. when tested in the hydrogen sulfide stability test.

Example 7.—2.3 parts by weight of Intermediate 2 were blended with 2.3 parts by weight of a solvent extracted diluent oil and 7.0 parts by weight of Intermediate C. The blend was heated at 300° F. for four hours with nitrogen blowing. 7.40 volume percent of the resulting product dissolved in Base stock 2 had an H_2S rating of 0.5 in the hydrogen sulfide stability test after six hours at 130° F.

Example 8.—One thousand grams of Intermediate A, 1000 grams of Intermediate D, 1000 grams of Intermediate 2 and 1000 grams of a solvent extracted diluent oil were reacted at 350° F. for five hours. Five weight percent of this product in base oil 1 gave a rating of 0.5 in the hydrogen sulfide stability test after four hours.

Example 9.—600 grams of Intermediate 3, 600 grams of a solvent extracted diluent oil and 585 grams of Intermediate E were heated for one hour at 275° F., with stirring and nitrogen blowing. The product had the following inspections:

Sulfur, wt. percent	2.2
Sulfated ash	11.4
Phosphorus	1.1
Sp. grav. @ 75° F.	0.967
Carbonate	2.3

Five weight percent in Base stock 2 rated 0 after two hours at 140° F. in the hydrogen sulfide stability test.

Example 10.—2530 grams of Intermediate D, 1265 grams of Intermediate 3, and 1265 grams of a solvent extracted diluent oil were reacted for 1½ hours at 275° F. 5.15 weight percent of the resulting product in Base stock 2 rated 0 in the hydrogen sulfide stability test after two hours at 130° F. The product had the following inspections:

Sulfur, wt. percent	3.05
Barium, wt. percent	7.39
Phosphorus, wt. percent	0.94

Example 11.—Nine parts by volume of the additive of Example 9 are mixed with one part of a zinc dialkyl dithiophosphate (Lubrizol–1060) and diluted with Base stock 2 to obtain a marketable odor-free concentrate containing 30 volume percent of active ingredient. The zinc dialkyl dithiophosphate can be obtained by reacting phosphorus pentasulfide with an alcohol mixture containing 30 weight percent isopropanol and 70 weight percent methyl isobutyl carbinol, and neutralizing the acid so obtained with zinc oxide.

VI. COMPARATIVE EXAMPLES

The effectiveness of the above stabilization technique can be seen from the following comparative examples.

Comparative Example 1.—Five weight percent of Intermediate 1 was blended in Base stock 1 without heating. 800 ccs. of this blend were allowed to stand for eight hours at room temperature in a one-quart bottle, and then tested for stability in the hydrogen sulfide stability test. A heavy black stain of lead sulfide was produced on the paper in a period of only five minutes. The blend was then heated for six hours at a temperature of 130° F. The blend then had a rating of 10+ in this test. This example illustrates the tendency of oil solutions of phosphosulfurized hydrocarbons to evolve hydrogen sulfide, and shows the importance of a treatment as proposed by this invention.

Comparative Example 2.—Five weight percent of the untreated solution of Intermediate 2 was blended with 95 weight percent of Base stock 1. This blend gave a demerit of 10+ after 24 hours of heating at 130° F. in the hydrogen sulfide stability test, and on further storage for forty days at room temperature gave a similar rating of 10+.

Comparative Example 3.—2.5 weight percent of Intermediate 2 was blended with 95 weight percent of Base stock 1. This composition gave a rating of 10 after one hour, and a rating of 10+++ after four hours of heating at 130° F. in the hydrogen sulfide stability test. Comparison of these Comparative Examples 2 and 3 to Examples 4 and 5 shows that the treatment of phosphosulfurized polybutenes according to this invention substantially improves the stability of lubricating oil compositions containing the phosphosulfurized material.

Comparative Example 4.—98 grams of Intermediate 2 were heated for four hours at 300° F. with 195 grams of a 40 weight percent solution of a neutral calcium sulfonate in oil. The neutral calcium sulfonate solution had the following inspections:

Calcium, wt. percent	1.81
Neut. No.	Less than 7

112 grams of this mixture were then combined with 688 grams of Base stock 1. This blend gave a rating of 10 in the hydrogen sulfide stability test after four hours.

Comparative Example 5.—As in Comparative Example 4, 96 grams of Intermediate 1 were blended with 192 grams of the neutral calcium sulfonate at room temperature for four hours, and then 110 grams of the mixture were combined with 690 grams of Base stock 1. The resultant 800 ccs. of the blend were rated for hydrogen sulfide stability, and a rating of 10+ was obtained after four hours.

Comparative Example 6.—78 grams of Intermediate 1 were heated for four hours at 300° F. with 156 grams of a 40 weight percent solution of a neutral barium sul-

fonate in oil. The barium sulfonate solution had the following inspections:

Sulfur, wt. percent	2.04
Barium, wt. percent	5.90

120 grams of the resulting product were then blended with 680 grams of Base stock 1 and tested for hydrogen sulfide stability. A rating of 10+ was obtained after four hours.

Comparative Example 7.—80 grams of Intermediate 1 were blended with 160 grams of the above neutral barium sulfonate and held for four hours at room temperature. 120 grams of this blend were then combined with 680 grams of Base stock 1 and tested for hydrogen sulfide stability. A rating of 10+ was obtained after four hours.

Comparison of Comparative Examples 4 through 7 with Example 1 shows the necessity of using high alkalinity materials, and that a reaction of the materials at a relatively high temperature is necessary in order to achieve stabilization.

Comparative Example 8.—100 grams of Intermediate 1 and 100 grams of Intermediate B were blended together at room temperature for three hours. 80 grams of this product were then combined with 720 grams of Base stock 1 and tested for hydrogen sulfide stability. A rating of 10 was obtained after four hours.

Effectiveness of products as detergent inhibitors

The effectiveness of the products of Examples 1 through 11 as detergent inhibitors is shown below in a variety of bench scale and engine tests. The following tests were used.

I. TEST METHODS

Caterpillar L-1 test.—This is a test designed to evaluate the sludge inhibiting and dispersancy qualities of an additive under high temperature operation. This is a standard test using a caterpillar single cylinder diesel test engine, CRC designation L-1-545. The fuel may contain either 0.4 or one weight percent sulfur. The test involves running a one-cylinder (5¾" bore times 8" stroke) diesel engine for 120 hours or more at 1800 r.p.m. with a 20 horsepower load. The engine is then rated for cleanliness by visual inspection.

Chevrolet L-4 test.—This is a standard test, CRC designation: L-4-545, used to determine corrosion inhibition effectiveness of additives. In this test a varnish demerit below about 1, and a bearing weight loss of about 0.150 gm. are considered good.

Low temperature sludge test.—This test is designed to evaluate the performance of an oil under low temperature stop-and-go driving conditions and in particular, its effectiveness in controlling sludge. A 1953 six-cylinder Chevrolet engine, attached to a dynamometer in a test stand, containing the oil is put through the following repeated cycles for a time in the range of 120 or more hours.

Cycle	R.p.m.	Jacket Water Outlet Temp., ° F.	Oil Sump Temp., ° F.	Intake Air, ° F.	Torque, lb. ft.	Brake, H.P.	Air/ Fuel Ratio	Exhaust Back Press., mm. Hg.	Cycle Duration, Hrs.
1	500	115±5	115±5	70	0	0	9.5/1	0	1½
2	2,000	160±5	175±5	70	105	40	11.5/1	1	2
3	2,000	180±5	215±5	70	105	40	11.5/1	1	2

The various parts of the engine are rated periodically for sludge on a demerit scale from 0 to 10, 0 being no deposits and 10 being the maximum deposits that the part is capable of holding. A rating of 2 or below after about 250 hours indicates that the test oil had fairly good detergency properties.

Oxidation and corrosion test.—An oil blend is heated at 365° F. and stirred with a weighed piece of copper-lead bearing while being blown with air. Small amounts of powdered iron and lead oxide are present in the oil throughout the test as catalysts. The number of hours required for the bearing to lose a given weight of metal is used as a measure of the oxidation stability of the oil.

II. RESULTS

Caterpillar L-1 tests.—The products above were evaluated in Caterpillar L-1 tests and compared against a typical commercial detergent of the barium alkyl phenol sulfide-calcium sulfonate type and against some of the intermediates. The tests are outlined in Table III.

TABLE III.—CATERPILLAR L-1 TEST

[Base stock 2, 1% sulfur feed]

Detergent Additive	Conc., Vol. percent	Test, Hours	Demerits		
			Ring Zone	R.Z. #1	T.G.F.,[2] percent
Intermediate 3	3.5	120	1.75	1.57	2.5
Intermediate C	6.35	120	0.47	0.10	
Example 7	7.40	120	0.08	0.01	
Example 7—Cont.	7.40	240	0.35	0.09	
Example 8	5.15	120	0.17	0.01	0
Example 9	5.15	120	0.41	0.02	8
Example 10	5.15	120	0.10	0.01	5
Conventional Additive [1]	8.0	120	0.51	0.12	
	8.0	240	1.03	0.53	

[1] 25 wt. percent of barium tertiary octyl phenol sulfide, 11.2 wt. percent of calcium sulfonate, and 63.8 wt. percent of a solvent extracted diluent mineral oil.
[2] Top groove fill.

The above table illustrates that the products of this invention (Examples 7, 8, 9, 10) are superior to either of the intermediates used (Intermediates 3, 6) or conventional additives in diesel engine performance.

Low temperature sludge performance.—An additive 1, similar to that of Example 8, was formulated into a finished lubricant, and tested in the Chevrolet engine low-temperature test. For comparison, a conventional oil formulation was also tested. Table IV gives the formulations, and Table V gives the results of the tests.

The additive of this invention was made by reacting 31.6 parts (on final product) of an 1100 average molecular weight polyisobutylene with 4.74 parts of phosphorus pentasulfide for about 8.5 hours at 425° F. while blowing with nitrogen. 36 parts of the phosphosulfurized hydrocarbon were then reacted with 32 parts of Intermediate A and 32 parts of Intermediate D for five hours at 350° F. while blowing with nitrogen. The neutralized material was then filtered. About 400 gallons of the additive were obtained.

The undiluted additive had the following inspections:

Barium, wt. percent	8.59
Phosphorus, wt. percent	1.28
Sulfur, wt. percent	4.18
Neut. No., Mg KOH/gm.	6.98
Sapon. No., Mg KOH/gm.	21.2
Vis., SUS @ 210° F.	2283
Flash point, ° F.	435
ASTM color, @ 5 vol. percent in white oil	4.5

TABLE IV

	Formula 20	Conventional Formula 20
Mineral oil—1 [a]	49.7	48.1
Mineral oil—2 [b]	39.1	37.9
V.I. Improver—1 [c]	2.6	3.0
V.I. Improver—2 [d]	5.0	5.0
Antioxidant [e]	0.7	1.0
Additive—1	2.9	
Conv. Additive [f]		5.0
Vis. @ 100° F., SUS	348.8	344.8
Vis. @ 210° F., SUS	67.4	66
Viscosity Index	140.5	139

[a] A phenol extracted and solvent dewaxed type of oil having the following inspections:

Gravity, ° API	29.5
Vis. @ 100° F., SSU	250
Viscosity index	100

[b] A phenol extracted and solvent dewaxed type of oil having the following inspections:

Gravity, ° API	33.1
Vis. @ 100° F., SSU	110
Viscosity index	100

[c] A polyisobutylene viscosity index improver having a molecular weight of 18,000.

[d] A polymethacrylate viscosity index improver—Acryloid 710.

[e] A zinc dialkyl (isopropyl/methylisobutyl carbinol) dithiophosphate sold by the Lubrizol Corporation under the name Lubrizol 1060.

[f] A mixture of 37.5 weight percent of a neutral calcium petroleum sulfonate and 62.5 percent of a phosphosulfurized barium alkyl phenol sulfide marketed by the Enjay Company under the name Paranox 62.

TABLE V.—CHEVROLET ENGINE LOW-TEMPERATURE SLUDGE TEST

	Over-all Engine Sludge Demerits after—			
	100 Hrs.	154 Hrs.	220 Hrs.	264 Hrs.
Formula 20	0.2	0.5	1.1	1.6
Formula 20 Repeat	0.5	0.8	1.3	1.6
Conv. Formula 20	0.8	1.1	1.9	2.3

While the conventional formulation gave good results in this test, the superiority of Formula 20 is clearly demonstrated.

Oxidation stability.—Four weight percent of the additive of Example 3 was dissolved in base stock 2 and evaluated in the Chevrolet L-4 test for 36 hours. This formulation gave a piston skirt varnish demerit of 0.9 and a copper-lead bearing weight loss of 0.032 gram. The base stock alone gives varnish demerits in excess of 2 and bearing weight loss in excess of 0.500 gram.

Five weight percent of the additive of Example 7 was dissolved in base stock 2 and tested in the oxidation and corrosion test. The base stock required 13 hours to reach 150 milligrams bearing weight loss, while the additive blend required 27 hours, excellent performance in this test.

The invention having been described, what is sought to be protected by Letters Patent is succinctly set forth in the following claim.

What is claimed is:

A method for preparing a concentrate of a detergent-inhibitor additive derived by stabilizing an oil-soluble phosphosulfurized hydrocarbon, normally evolving hydrogen sulfide, which comprises reacting said phosphosulfurized hydrocarbon, in the presence of a mineral oil diluent, with a stabilizing amount of a high alkalinity neutralizing agent at a temperature in the range of 150 to 600° F. for at least 0.5 hour under substantially anhydrous conditions, the weight of said neutralizing agent times its alkaline neutralization number to a pH of 4 being at least equal to the weight of said phosphosulfurized hydrocarbon times its saponification No., said neutralizing agent having been obtained by reacting, in the presence of carbon dioxide, an alkaline earth base in at least 5 weight percent excess with at least one compound selected from the group consisting of alkyl phenols, alkyl phenol sulfides, sulfonic acids and metal salts thereof such that the ratio of equivalents of metal to equivalents of organic acids is greater than 1.5, said concentrate containing more than 20 weight percent of the resulting stabilized additive in said mineral oil diluent.

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