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3,511,780

OIL-SOLUBLE ASHLESS DISPERSANT- DETERGENT-INHIBITORS

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U.S. Cl. 252—32.7 16 Claims

ABSTRACT OF THE DISCLOSURE

An additive that is useful as a sludge dispersant, anti-
wear agent, antioxidant, and inhibitor of harmful deposit
formation in hydrocarbon compositions of the class of
gasolines, fuel oils, heating oils and lubricants is pre-
pared by condensing an alkenyl succinic anhydride with
an aliphatic polyamine or with an aliphatic polyamine
and a carboxylic acid, followed by further reaction of
the condensation product with a phosphosulfurized hydro-
carbon and with a dialkyl dithiophosphoric acid. The al-
kenyl succinic anhydride has an alkenyl group totaling
from about 40 to about 250 carbon atoms, as for exam-
ple the reaction product of 800 molecular weight poly-
isobutylene and maleic anhydride. Examples of the ali-
phatic polyamines include diethylene triamine and tetra-
ethylene pentamine. The carboxylic acid contains from
about 1 to 30 carbon atoms in an aliphatic hydrocarbon
chain and is preferably acetic acid. The phosphosulfurized
hydrocarbon is exemplified by P_2S_5 -treated polyisobutyl-
ene. Particularly suitable dialkyl dithiophosphoric acids
are derived from C_3 to C_{16} monohydric aliphatic al-
cohols, including mixed alcohols, such as a mixture of
isobutyl alcohol and amyl alcohol. The additive can be
used with conventional additives such as zinc dialkyl-
thiophosphate.

This application is a continuation-in-part of applica-
tion Ser. No. 284,842, filed June 3, 1963, and abandoned
subsequent to the filing of the present application.

The present invention relates to improved oil-soluble
additives that are useful as sludge dispersants and as
inhibitors of harmful deposit formation in hydrocarbon
oil compositions of the class of gasolines, fuel oils, heat-
ing oils and lubricants. The additives also possess anti-
oxidant and antiwear properties in such compositions
and can be prepared by reaction of alkenylsuccinic an-
hydrides with polyamines followed by further treatment
of the products of that reaction with phosphosulfurized
hydrocarbons, or by reaction of alkenylsuccinic anhy-
drides with polyamines and carboxylic acids followed by
reaction with phosphosulfurized hydrocarbons.

Lubricants for modern high compression piston type
internal combustion engines are required to have high
detergency, efficient sludge dispersing action, and high
oxidation resistance in order that those engines will be
kept free of varnish, sludge and coke-like deposits. In
other words, a heavy duty detergent type lubricating oil
must be employed in such engines in order to maintain
a high degree of engine cleanliness and thus promote
engine life.

In the past, the majority of detergents, sludge dis-
persants and antioxidant materials that have been devel-
oped for use in lubricating oils for internal combustion
engines have been metallic derivatives, particularly al-
kaline earth metal sulfonates, alkaline earth metal salts

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of alkyl phenol sulfides, colloidal dispersions of metallic
carbonates (particularly alkaline earth metal carbonates),
and the like. While in general additives of these types have
proved to be quite satisfactory in their function as sludge
dispersants and detergents, in many instances the ash
content of these additives has presented a disadvantage
in that the ash tends to accumulate in the combustion
chamber of the engine and there causes pre-ignition,
spark plug fouling, valve burning and similar undesirable
conditions. For this reason, an effective dispersant that
is ash-free is preferable over an ash-forming detergent
additive such as an alkaline earth metal salt of the types
mentioned above. Ash-free dispersants are also of ad-
vantage in fuel oil compositions and diesel fuels.

It has now been found in accordance with the present
invention that a particularly effective ash-free mineral-
oil-soluble detergent and dispersant having antioxidant
and antiwear properties can be prepared by treating the
condensation product of an alkenylsuccinic anhydride
and a polyamine, or of an alkenylsuccinic anhydride, a
polyamine, and a carboxylic acid, with an acidic reac-
tion product of a phosphorus sulfide with a hydrocarbon
and, in a modification, by treatment also with a dialkyl-
dithiophosphoric acid.

The preparation of reaction products of high molecular
weight alkenylsuccinic anhydrides with various polyamine
compounds is taught in U.S. Pat. 3,024,195 and 3,024,237
and also in British Pat. 922,831. The teaching in the
U.S. patents referred to is that alkenylsuccinic anhydrides
having alkenyl radicals derived from hydrocarbons of
400 to 3000 molecular weight can be reacted with amine
derivatives of piperazine. The British patent referred to
teaches that alkenylsuccinic anhydrides, as for example
a polyisobutenylsuccinic anhydride, can be reacted with
polyamines such as tetraethylene pentamine, diethylene
triamine, triethylene tetramine, and the like.

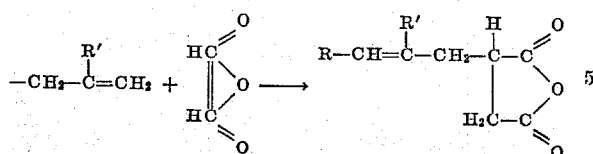
The preparation of reaction products of alkenylsuc-
cinic anhydrides with carboxylic acids and alkylene poly-
amines is disclosed and claimed in copending application
Ser. No. 241,174 of Norman Tunkel et al., filed Nov.
30, 1962, now abandoned. Briefly, such reaction products
can be prepared by the reaction of about 0.5 to 1.5 mole
proportions of a C_1 to C_{30} carboxylic acid, about 1
molar proportion of an alkylene polyamine, and about
0.5 to 3.0, e.g. 1.0 to 1.5 molar proportions of an
alkenylsuccinic anhydride (or its corresponding acid)
wherein the alkenyl group contains in the range of from
about 40 to about 250 carbon atoms, the reaction being
effected by heating all the reactants together until an
oil-soluble product is obtained, or by first reacting said
 C_1 to C_{30} carboxylic acid and said polyamine followed
by further reaction with said alkenylsuccinic anhydride,
or by first reacting said alkenylsuccinic anhydride and
said polyamine followed by further reaction with said
 C_1 to C_{30} carboxylic acid.

In the present invention, reaction products of the above
types are further reacted with an acidic organic compound
containing phosphorus and sulfur, more specifically with
a phosphosulfurized hydrocarbon. In particular, the re-
action products of the above type that are thus employed
in the present invention are those that contain sufficient
residual amino nitrogen to react with the acidic groups
of the phosphosulfurized hydrocarbon, as will be more
apparent in the ensuing description.

The preparation of an alkenylsuccinic anhydride is well
known in the art and simply involves reacting maleic an-
hydride with an organic compound having an olefinic
linkage. Generally, about equal molar proportions of
maleic anhydride and the olefinic material are merely
heated together, although the present invention is not
limited by any particular mode of preparation of the al-

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alkenylsuccinic anhydride. The reaction involved is illustrated by the following equation:

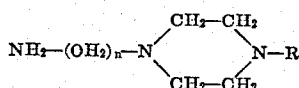


In the above equation R and R' can be hydrogen or hydrocarbon radicals but at least one of them must be a hydrocarbon group. The hydrocarbon radicals may be substituted, as for example chlorinated or sulfated, or they may be unsubstituted, and they will include aliphatic, acyclic and aromatic radicals. Preferably, the total number of carbon atoms in R and R' combined is within the range of from about 40 to 250, more preferably within the range of from about 50 to about 120. Particularly desirable for use in this invention because of low cost and ready availability are alkenyl groups obtained by polymerization of a C₂ to C₅ monoolefin wherein the polymer has a molecular weight within the range of from about 600 to about 3000. Especially useful products are obtained when the molecular weight range is from about 800 to about 1200. As specific examples, an alkenyl group may be derived from polypropylene or polyisobutylene.

The aliphatic polyamine that is employed in preparing the reaction products of the present invention may be an alkylene polyamine fitting the following general formula:



wherein *n* is 2 to 3 and *m* is a number from 0 to 10. Specific compounds coming within the formula include diethylene triamine, tetraethylene pentamine, dipropylene amine, octaethylene nonamine, and tetrapropylene pentamine. N,N-di-(2-aminoethyl)ethylene diamine may also be used. Other aliphatic polyamino compounds that may be used are the N-aminoalkyl piperazines of the formula



wherein *n* is a number 1 to 3, and R is hydrogen or an alkyl radical containing 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine, and N,N'-di-(2-aminoethyl) piperazine.

The use of mixtures of alkylene polyamines, mixtures of N-aminoalkyl piperazines, and mixtures of the alkylene polyamines with the N-aminoalkyl piperazines is also contemplated.

When preparing reaction products of the alkenylsuccinic anhydrides with the alkylene polyamines and/or the N-aminoalkyl piperazines, equimolar proportions of the alkenylsuccinic anhydride and the nitrogen-containing material can be employed, or an excess of the anhydride or the nitrogen compound can be used. Similarly, when preparing the reaction product of an alkenylsuccinic anhydride, a polyamine and a carboxylic acid, equimolar proportions of the three reactants can be used. However, variation in these relative proportions can be made, for example 1 to 3, e.g. 1.0 to 1.5 moles of the anhydride to 1.0 to 1.5 moles of the carboxylic acid can be used with 1 mole of polyamine.

The carboxylic acid component of the reaction mixture, when such is used, comprises a carboxylic acid of from 1 to 30 carbon atoms in an aliphatic hydrocarbon chain, which can be either branched or straight chain and either saturated or unsaturated. Both monocarboxylic acids and dicarboxylic acids are included. More generally, carboxylic acids having from 1 to 18 carbon atoms are used, including acetic acid, fumaric acid, adipic acid, sebacic acid, oleic acid, linoleic acid and stearic acid. Acetic acid is particularly preferred.

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While the reactants, i.e. the alkenylsuccinic anhydride and the polyamino compound (and, when used, the C₁ to C₃₀ carboxylic acid), upon simple mixing will interact to some extent to form salts, the products will generally be oil-insoluble. However, upon heating (e.g. to about 200–250° F.) the reaction mixture will become mineral-oil-soluble, and upon continued heating condensation reactions will begin to take place with the evolution of water. The evolved water can be readily removed by blowing nitrogen or other inert gas through the reaction mixture during the course of the reaction. The reaction may be carried out by heating the reactants for about 1 to 30 hours at 200 to 400° F., e.g. 250 to 350° F. Preferred reaction conditions include heating for 6 to 20 hours at 275 to 300° F.

Preformed alkenylsuccinic anhydride can be used, or the alkenylsuccinic anhydride can be made by first reacting the olefinic material with the maleic anhydride to form the alkenylsuccinic anhydride, thereafter adding the polyamino compound to the hot alkenylsuccinic anhydride, and then preferably further heating to form a condensation product. Similar procedures are used in the case of the 3-component reaction involving a polyamino compound, an alkenylsuccinic anhydride and a carboxylic acid. Preferably, a light mineral oil is added to the reaction mixture as a diluent after the formation of the alkenylsuccinic anhydride and before the addition of the polyamino compound or the polyamine plus fatty acid. An antifoaming agent such as a polysilicone can be added to the reaction mixture in order to prevent foaming during the addition of the amine.

In accordance with the present invention the reaction product of the alkenylsuccinic anhydride with a polyamino compound as hereinbefore described, or of the alkenylsuccinic anhydride with such a polyamino compound and a carboxylic acid, is further reacted with a phosphosulfurized hydrocarbon and it may be additionally reacted with a dialkylthiophosphoric acid. To facilitate the ensuing discussion, these two types of reactants may be referred to as organic thio-acids of phosphorus.

For convenience, the reaction product of the alkenylsuccinic anhydride with a polyamino compound or with a polyamino compound and a carboxylic acid will be referred to as the amine-containing intermediate. As previously stated, the amine-containing intermediate must have sufficient amino nitrogen remaining so that reaction with the acidic groups of the organic thio-acid of phosphorus is possible.

The amine-containing intermediate may be reacted with varying amounts of the phosphosulfurized hydrocarbon or with mixtures consisting of at least 15 wt. percent of phosphosulfurized hydrocarbon with 85 wt. percent or less of dialkylthiophosphoric acid, in amounts sufficient to give partial or complete neutralization of the amine portion of the amine-containing intermediate. Since the potency of the amine-containing intermediate is related, in part, to its basicity, the ratio of amine to organic thio-acid of phosphorus is limited in practice by the balance of the several functions of this additive. That is, if all the amine functions are neutralized by stoichiometric amounts of organic thio-acids the antioxidant and antiwear properties of the additive are maximized at the expense of detergency or deposit control. Most advantageously, ratios of amine to thio-acid are chosen so that dispersancy, antiwear and antioxidant potency are optimized. Generally if at least one amino group per mole of amine-containing intermediate is left unreacted, this optimization can be accomplished.

As little as 0.01 mole of the organic thio-acid of phosphorus may be reacted with 1 mole of the amine-containing intermediate. The maximum number of moles of the organic acid that can thus be reacted will depend on the number of amino nitrogen groups that are still available for neutralization in the intermediate, but normally complete neutralization of all of the amino groups is not desired. Generally, for each mole of amine-containing

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intermediate, in the range of about 0.01 to 0.2 mole of phosphosulfurized hydrocarbon will be sufficient to impart antiwear and antioxidant properties, although higher ratios of the reactant may be used, as already discussed. For the purpose of ascertaining the molar equivalent of the phosphosulfurized hydrocarbon, it is assumed that all of the phosphorus in that material is available as a monobasic acid. Reaction may be effected merely by mixing the reactants together and heating the mixture for from 1 to 30, e.g. 1 to 6 hours, or more usually from 2 to 5 hours at a temperature in the range of from about 100° F. to about 400° F., e.g. 100 to 250° F., or more generally from about 150° F. to about 225° F. The reaction may be aided by blowing a stream of inert gas through the mixture during the heating period.

The preparation of phosphosulfurized hydrocarbons is well known in the art and is described for example in U.S. Pat. 2,875,188. Thus the phosphosulfurized hydrocarbons may be prepared by reaction of a sulfide of phosphorus such as P_2S_5 with a suitable hydrocarbon material such as a heavy petroleum fraction, a polyolefin, or a terpene such as alpha-pinene. The heavy petroleum fractions that may be employed include distillates or residua containing less than 5% of aromatics and having viscosities at 210° F. in the range of about 140 to 250 SUS. The preferred hydrocarbons are polyolefins having Staudinger molecular weights in the range of from about 500 to about 200,000 and containing from 2 to 6 carbon atoms per olefin monomer. Particularly preferred are the polyisobutenes having Staudinger molecular weights in the range of from about 700 to about 100,000. The phosphosulfurized hydrocarbon can be prepared by reacting the hydrocarbon with from about 5 to 30 wt. percent of a sulfide of phosphorus, preferably with from about 10 to 20 wt. percent of phosphorus pentasulfide under anhydrous conditions at temperatures of from about 150 to about 600° F. for from about one-half to about 15 hours.

The preparation of dialkyldithiophosphoric acids is also well known and involves the reaction of aliphatic alcohols with P_2S_5 . Normally, about 4 moles of an aliphatic alcohol, or more usually a mixture of alcohols, is treated with 1 mole of phosphorus pentasulfide. Reaction temperatures are normally in the range of from about 100° to about 250° F. and reaction times may range from about 1 to about 6 hours.

Dialkyldithiophosphoric acids that are particularly suited for use in the present invention are those derived from C_3 to C_{18} monohydric aliphatic alcohols and include not only those derived from the simple alcohols and mixtures thereof, such as isopropyl, normal butyl, isobutyl, methylisobutyl carbinyl, n-decyl, and so on, but also those derived from mixed alcohols such as the C_8 or C_{13} alcohols that are obtained by reacting olefins with carbon monoxide and hydrogen and subsequent hydrogenation of the resultant aldehydes. Mixed alcohols in the C_8 - C_{18} range, consisting chiefly of lauryl alcohols, obtained by the hydrogenation of coconut oil, e.g. those sold under the trade name "Lorol," can also be employed in preparing the dialkyldithiophosphoric acids. Other alcohols obtained from the hydrogenation of natural fats and oils may also be used.

Suitable mixed dialkyldithiophosphoric acids include those prepared from isobutyl alcohol and mixed primary amyl alcohols; from isopropyl alcohol and C_8 oxo alcohols, from a mixture of mixed amyl alcohols and technical lauryl alcohol (e.g. Lorol); from a mixture of isopropyl alcohol, methylisobutyl carbinol and C_8 oxo alcohols; and others.

The invention will be further understood by the following examples.

EXAMPLE 1

A mixture of 180 pounds (0.180 pound mole) of polyisobutylene of about 800 molecular weight and 22.5 lbs. (0.230 pound mole) of maleic anhydride was heated for 24 hours at 450° F. under a nitrogen blanket to form

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polyisobutenylsuccinic anhydride. The product was found to have a saponification number of 86.6 mg. KOH/gm. of reaction mixture. A light mineral lubricating oil having a viscosity of 150 SUS at 100° F. was added as a diluent in sufficient quantity to result in a solution containing 75 wt. percent of the polyisobutenylsuccinic anhydride. Then 30 p.p.m. of Dow Corning 60,000 cs. polymethyl silicone was added as an antifoamant. Next, 17.22 lbs. (0.091 pound mole) of tetraethylene pentamine and 5.46 lbs. (0.091 pound mole) of acetic acid were added. The reaction mixture was then heated at 300° F. for 10.5 hours while nitrogen was blown through it until no more water came off. The reaction product concentrate, after filtration, contained 2.22 wt. percent nitrogen based on the total product, i.e. the actual reaction product and oil diluent.

EXAMPLE 2

A phosphosulfurized hydrocarbon was prepared by reacting 100 parts by weight of polyisobutylene having an average Staudinger molecular weight of about 940 with 15 parts by weight of phosphorus pentasulfide for about 8 hours at temperatures in the range of 425-450° F. During the reaction the mixture was stirred and blown with nitrogen. The resulting phosphosulfurized polyisobutylene analyzed about 3.5 wt. percent of phosphorus and about 6.6 wt. percent of sulfur. Its viscosity at 210° F. was about 20,000 SUS. For convenience in handling in subsequent reactions, the product was diluted with a light mineral oil to form a 70 wt. percent concentrate.

EXAMPLE 3

Mixed dialkyldithiophosphoric acids were prepared by reacting a mixture of 35 wt. percent of primary amyl alcohols and 65 wt. percent of isobutyl alcohol with phosphorus pentasulfide using a mole ratio of alcohol to P_2S_5 of 4 to 1. The reaction was conducted at about 170° F. for a period of about 4 hours until a specific gravity of about 1.05 was attained, measured at 78° F. The reaction product was then stripped of hydrogen sulfide with the aid of a stream of nitrogen, the product being cooled to about 90 to 100° F., and the product was then filtered.

EXAMPLE 4

A mixture of 1200 parts by weight of the reaction product concentrate of Example 1, 133 parts by weight of the phosphosulfurized hydrocarbon concentrate of Example 2, and 256 parts by weight of the dialkyldithiophosphoric acids of Example 3, was heated at 212° F. for 1 hour, with a stream of nitrogen bubbling beneath the surface of the mixture. The product was a very viscous, oil-soluble material. It was diluted with 1589 parts by weight of solvent 150 neutral mineral oil, giving a 50 wt. percent additive concentrate, hereinafter referred to as "Additive A."

EXAMPLE 5

Using the procedure of Example 4, a mixture of 3700 parts by weight of the concentrate of Example 1 and 1245 parts by weight of the phosphosulfurized hydrocarbon concentrate of Example 2 was heated for 2 hours at 212° F., with nitrogen stripping. This additive concentrate is hereinafter referred to as "Additive B."

EXAMPLE 6

Using as the base oil a mineral lubricating oil having a viscosity of 325 SUS at 100° F. and a viscosity index of about 100, the following compositions were prepared:

Composition 1.—3.97 wt. percent of the "Additive A" concentrate of Example 4 and 96.03 wt. percent of the base oil.

Composition 2.—3.5 wt. percent of a commercial detergent inhibitor, 0.9 wt. percent of a zinc dialkyldithiophosphate antiwear additive, 95.6 wt. percent of the base oil.

Composition 3.—3.33 wt. percent of "Additive B" con-

trate of Example 5, 0.9 wt. percent of zinc dialkylphosphosphate antiwear additive, 95.57 wt. percent of base oil.

The commercial detergent inhibitor mentioned above is a mineral oil solution containing an additive prepared by reacting a mixture of a phosphosulfurized polybutylene and nonyl phenol with barium hydroxide trihydrate and blowing the reaction mixture with carbon dioxide. The approximate analysis of the concentrate is 27 wt. percent of phosphosulfurized polyisobutylene, 7 wt. percent nonyl phenol, 10.6 wt. percent barium oxide, 2.5 wt. percent carbon dioxide, and 48.2 wt. percent mineral oil.

The zinc dialkyldithiophosphate antiwear additive was an oil solution consisting of about 25 wt. percent of mineral lubricating oil and about 75 wt. percent of zinc di-*l*-dithiophosphate prepared by treating a mixture of butanol and mixed amyl alcohols with P_2S_5 followed by neutralizing with zinc oxide.

Each of the compositions 1 to 3 described above was used for sludge dispersing ability in the ER4-90 Ford sludging test. Prior experience has shown that this sludge test gives sludge deposits similar to those obtained in stop-and-go driving, such as would be experienced in cab operation. Briefly described, in this test a Ford 6-cylinder engine is run on a dynamometer stand through driving cycles consisting of a first cycle operating at 500 m. for 1½ hours, a second cycle operating at 2000 m. for 2 hours, and a third cycle also operating at 2000 m. for 2 hours but using slightly higher oil pressure and water jacket temperatures. The three cycles are repeated over and over again in sequence until the desired total test time has elapsed. Make-up oil is added as required so that the crankcase oil level is maintained at all times between about 3½ and 4 quarts. After a selected test time has elapsed, the engine is inspected by disassembling it sufficiently to permit visual examination of the rocker arm cover, the rocker arm assembly, the cylinder head, the push rod chamber, the push rod member cover, the crankshaft, the oil pan, and the oil screen. The oil screen is rated as "percent covered with sludge" and the other parts are visually rated for sludge deposition using a merit system in which a numerical rating of 10 represents a perfectly clean part and 0 a part covered with the maximum amount of sludge possible. The merit ratings are averaged to give an overall engine merit rating.

The results of the preceding ER4-90 test are summarized in Table I. From these results it will be seen that each of the compositions in which an additive of the present invention was employed, i.e. Compositions 1 and 3, gave better performance than the composition containing the commercial detergent additive, i.e. Composition 2.

TABLE I.—ER 4-90 ENGINE TEST RESULTS

Runs on test.....	Merit ratings		
	100	200	286
Composition 1.....	9.95	9.7	9.1
Composition 2.....	9.9	7.4	6.7
Composition 3.....	9.99	9.9	9.5

All screen ratings were zero, except for Composition 2 at 286 hours, in which case 10% of the screen was covered with sludge.

EXAMPLE 7

A composition was prepared consisting of 3.97 wt. percent of the "Additive A" concentrate of Example 4, 96.03 wt. percent of an SAE 10 grade mineral lubricating oil. This composition was subjected to the Volkswagen Valve Train Wear Test. In this test the Volkswagen engine is lubricated with the oil in question and the engine is run for a period of 100 hours using the following electronically controlled operating cycle, which is continuously repeated for the duration of the test:

- (a) Five minutes at about 600 r.p.m., no load
- (b) Ten minutes at about 1200 r.p.m., no load
- (c) Shut down for one minute

The oil temperature during the test is the temperature normally reached by the oil during engine operation; i.e. no attempt is made to hold the oil temperature at a controlled level.

The wear on each tappet is measured and the wear for the 8 tappets is averaged. The oil is considered to have failed the test if wear exceeds 10×10^{-4} inch on any tappet.

The test composition described above passed this test with an average wear of less than 1×10^{-4} inch and the wear did not exceed 1×10^{-4} inch on any individual tappet. In contrast to this, a multigrade 10W-30 motor oil containing 0.9 wt. percent of the commercial antiwear additive and about 3.5 wt. percent of a commercial detergent inhibitor similar to that described in Composition 2 of Example 6 gave an average wear of about 8×10^{-4} inch.

EXAMPLE 8

A composition similar to Composition 3 of Example 6 was prepared by simple mixing of 3.33 wt. percent of the "Additive B" concentrate of Example 5, 0.9 wt. percent of the zinc dialkyldithiophosphate concentrate used in the said Composition 3, and 95.57 wt. percent of an SAE 30 grade mineral lubricating oil. This composition was subjected to the industry-recognized General Motors MS Procedure, Sequence I through III, as described in the special technical publication, STP No. 315 of Technical Committee B of ASTM Committee D-2, dated Jan. 22, 1962. In this test the oil is run in an Oldsmobile engine in accordance with the outlined test procedure and various parts are then rated on a merit basis.

The test results obtained are given in Table II in comparison with similar results obtained on a General Motors reference oil identified as GMR6063. It will be seen that the composition of the present invention had a higher rating than the reference oil.

TABLE II

	Merit ratings	
	Test composition	Reference oil
Lifter rust.....	9.3	7.7
Engine rust.....	8.0	6.9
Avg. varnish.....	9.7	9.0
Avg. sludge.....	9.9	9.2

EXAMPLE 9

Polyisobutenylsuccinic anhydride of about 1000 molecular weight prepared in the manner of Example 1 is reacted with tetraethylene pentamine in the proportion of 2 moles of the anhydride to 1 mole of the pentamine, the two reactants being mixed together at about 160° F. and then heated to 275° F., the latter temperature being maintained for a period of about 6 hours while bubbling a stream of nitrogen beneath the liquid surface of the mixture. At the end of the 6 hours, sufficient solvent neutral mineral oil (150 SUS at 100° F.) is added to give a 75 wt. percent concentrate of reaction product.

A portion of the concentrate prepared as just described in a quantity of 2000 parts by weight is reacted with about 460 parts by weight of a 70 wt. percent concentrate of phosphosulfurized polyisobutylene prepared in the manner of Example 2 from polyisobutylene of about 780 molecular weight by reaction with 15 wt. percent of P_2S_5 . The reaction between the phosphosulfurized hydrocarbon and the alkenylsuccinic anhydride-polyamine condensation product (i.e. the amine-containing intermediate) is conducted for 90 minutes at 225° F. while blowing with nitrogen as described in Example 4. The molar ratio of phosphosulfurized hydrocarbon to amine-containing intermediate in this reaction is about 0.5 to 1.

EXAMPLE 10

To a heating oil comprising a mineral oil distillate having a boiling range of about 350° to 680° F. and derived from mixed cracked and straight run distillates is added 0.05 wt. percent of the product of Example 9 as a sludge dispersant, antioxidant and pump wear reducing agent.

EXAMPLE 11

About 0.006 wt. percent of the product of Example 5 is added to a leaded gasoline to serve as a carburetor detergent additive.

EXAMPLE 12

A compounded lubricant suitable for use as a crankcase oil is prepared by blending into a light mineral base oil having an added viscosity index improver to place it in the SAE 10W-30 viscosity class, 5 wt. percent of the "Additive A" concentrate of Example 5, 1 wt. percent of a high alkalinity (59 total base number) barium sulfonate derived from hydrocarbon sulfonic acids of about 440 molecular weight and 0.7 wt. percent of zinc dialkyldithiophosphates derived from mixed C₄ and C₅ alcohols.

EXAMPLE 13

An additive concentrate suitable for blending into a mineral lubricating oil composition to give combined sludge dispersing and antiwear properties is prepared by mixing together 80 parts by weight of the "Additive B" concentrate of Example 5, 20 parts by weight of a commercially available synthetic high alkalinity calcium sulfonate concentrate consisting of a 46 wt. percent concentrate in mineral oil of a calcium sulfonate prepared from alkylbenzene sulfonic acids of about 420 molecular weight, containing 11.4% calcium and having a total base number of 319, and 12 parts by weight of the zinc dialkyldithiophosphate concentrate described in Composition 2 of Example 6.

For use as lubricating oil additives the reaction products of this invention may be incorporated in lubricating oil compositions in concentration ranges of from about 0.1 to about 10 wt. percent, and will ordinarily be used in concentrations of from about 0.1 to about 5 wt. percent. The lubricating oils to which the additives of the invention may be added include not only mineral lubricating oils but synthetic oils. The mineral lubricating oils may be of any preferred types, including those derived from the ordinary paraffinic, naphthenic, asphaltic, or mixed base mineral crude oil by suitable refining methods.

The additives of this invention may also be employed in middle distillate fuels for inhibiting the formation of sludge and sediment in such fuels. Concentration ranges of from about 0.002 to about 2 wt. percent, or more generally from about 0.005 to about 0.1 wt. percent, are employed. Petroleum distillate fuels boiling in the range of from about 300° F. to about 900° F. are contemplated. Typical of such fuels are No. 1 and No. 2 fuel oils that meet ASTM Specification D-396-48T, diesel fuels qualifying as Grades 1D, 2D and 4D of ASTM Specification D-975-51T, and various jet engine fuels.

The additives may also be employed in gasolines in concentrations ranging from about 0.001 to about 1.0 wt. percent as deposit preventing additives, carburetor detergents, and the like.

In either the fuel or lubricant compositions, other conventional additives may also be present including dyes, pour point depressants, antiwear agents, antioxidants such as phenyl- α -naphthylamine, tert. octylphenol sulfide, bis-phenols such as 4,4'-methylene bis(2,6-di tert. butylphenol), viscosity index improvers such as polymethacrylates, polyisobutylene, alkyl fumarate-vinyl acetate copolymers, and the like, as well as other dispersants. The latter may be of the conventional metal-containing type, including barium tert. octylphenol sulfide, calcium non-

including barium tert. octylphenol sulfide, calcium nonylphenol sulfide, or any of the sulfonate detergents of either the normal type or the well-known high alkalinity type, containing excess metal base over that required for simple neutralization of the sulfonic acids. Such sulfonates include barium or calcium petroleum sulfonates, calcium di-C₈ alkylbenzene sulfonate, barium di-C₉ alkylbenzene sulfonate, and calcium C₁₆ alkylbenzene sulfonate. The alkyl groups may be derived from simple olefin polymers, e.g. C₈ from diisobutylene, C₉ from tripropylene, and C₁₂ from tetraisobutylene.

As is apparent from the foregoing examples, it is within the contemplation of this invention to prepare additive concentrates in which the concentration of additive is greater than would normally be employed in a finished lubricant. These concentrates may contain in the range of from 20 to 80% of additive on an active ingredient basis, the balance being mineral oil. Such concentrates are convenient for handling the additive in the ultimate blending operation into a finished lubricating oil composition. The additive concentrates may be made up simply of an additive of the present invention in a suitable mineral oil medium or they may include other additives that are intended for use along with the additives of the invention in a finished lubricant. Thus if the additives are to be used in conjunction with conventional detergents, an additive concentrate can be prepared containing say 30 to 60 wt. percent of an additive of the invention and 5 to 20 wt. percent of a metal sulfonate, e.g. calcium petroleum sulfonate, or a metal alkylphenol sulfide, e.g. calcium nonylphenol sulfide, with the balance being a mineral lubricating oil. Alternatively 5 to 15 wt. percent of an antiwear agent such as a zinc dialkyldithiophosphate may also be present in the additive concentrate package.

The additives of this invention are particularly useful in lubricating oil compositions in conjunction with metal dialkyldithiophosphate antiwear additives as taught in the foregoing examples. Suitable metal dialkyldithiophosphates include the oil-soluble zinc, nickel, cadmium, and lead salts of dialkyldithiophosphoric acids derived by reaction of sulfides of phosphorus, particularly P₂S₅ with alcohols having in the range of from about 3 to about 20 carbon atoms, more usually in the range of from about 3 to 10 carbon atoms. Metal salts of any of the specific dialkyldithiophosphoric acids disclosed earlier in the specification may be employed. In lubricating oil compositions the metal dialkyldithiophosphates are normally employed in concentration ranges of from about 0.1 to about 3 wt. percent, depending upon the particular metal salt employed as well as its intended function, i.e. as an antioxidant and/or as a wear reducing agent.

It is also within the contemplation of this invention to prepare additive concentrates in which the reaction between the phosphosulfurized hydrocarbon and the amine-containing intermediate is conducted in the presence of a metal dialkyldithiophosphate. Proportions will vary somewhat, depending on relative molecular weights and other factors, but they may range from about 5 to 20 wt. percent of phosphosulfurized hydrocarbon, 5 to 20 parts by weight of metal dialkyldithiophosphate and 10 to 50 parts by weight of the amine-containing intermediate, together with sufficient mineral lubricating oil to give a concentrate of the desired active ingredient content. As a specific example, 44.4 wt. percent of the reaction product concentrate of Example 1, 13.7 wt. percent of the phosphosulfurized polyisobutylene of Example 2, 21.3 wt. percent of the zinc dialkyldithiophosphate concentrate employed in preparing Compositions 2 and 3 of Example 6, and 20.6 wt. percent of a light mineral lubricating oil of 150 SUS viscosity at 100° F. may be mixed together and heated at 210 to 215° F. for 2 to 3 hours, using nitrogen blowing.

The scope of this invention is to be determined by the

aims appended hereto and is not to be limited by the examples presented in the foregoing specification.

What is claimed is:

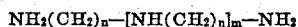
1. A method of preparing an oil-soluble additive for mineral oils which comprises reacting together at about 0 to 400° F. about 1 mole proportion of a condensation product, selected from the class consisting of:

(a) products obtained from the reaction at about 200 to 350° F. of about 0.5 to 3.0 molar proportions of alkenylsuccinic anhydride and about 1 molar proportion of aliphatic polyamine, and

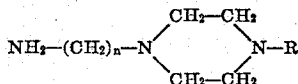
(b) products obtained from the reaction at about 200 to 350° F. of about 0.5 to 3.0 molar proportions of alkenylsuccinic anhydride, about 1 to 1.5 molar proportions of C₁ to C₃₀ carboxylic acid, and about 1 molar proportion of aliphatic polyamine,

with at least 0.01 molar proportion of phosphosulfurized hydrocarbon, and with at least 0.01 molar proportion of dialkyl dithiophosphoric acid, said alkenylsuccinic anhydride having an alkenyl group totaling in the range of from about 40 to 250 carbon atoms,

said aliphatic polyamine being selected from the class consisting of N,N-di-(2-aminoethyl) ethylene diamine, alkylene polyamines having the formula



wherein *n* is 2 to 3 and *m* is a number from 0 to 10, and N-aminoalkyl piperazines of the formula



wherein *n* is a number 1 to 3, and R is selected from a group consisting of hydrogen and aminoalkyl radicals containing 1 to 3 carbon atoms.

2. Method as defined by claim 1 wherein said dialkyl dithiophosphoric acid comprises mixed dialkyl dithiophosphoric acids derived from isobutyl alcohol and amyl alcohol.

3. Method as defined by claim 1 wherein said condensation product is a product obtained from 1 to 1.5 molar proportions of alkenylsuccinic anhydride and about 1 molar proportion of aliphatic polyamine.

4. Method as defined by claim 1 wherein said condensation product is a product obtained from 1 to 1.5 molar proportions of alkenylsuccinic anhydride, 1 to 1.5 molar proportions of C₁ to C₃₀ carboxylic acid and about 1 molar proportion of polyamine.

5. Method as defined by claim 1 wherein said alkenylsuccinic anhydride contains alkenyl groups derived from a polymer of a C₂ to C₅ monoolefin having a molecular weight in the range of from about 600 to about 3000.

6. Method as defined by claim 1 wherein said phosphosulfurized hydrocarbon is the product of treatment of polyisobutylene with P₂S₅.

7. Method as defined by claim 1 wherein said reac-

tion with phosphosulfurized hydrocarbon is conducted at 100 to 250° F.

8. Method as defined by claim 1 wherein said condensation product is the reaction product of tetraethylene pentamine and polyisobutenylsuccinic anhydride derived from polyisobutylene of molecular weight in the range of about 800 to 1200.

9. Method as defined by claim 1 wherein said condensation product is the reaction product of acetic acid, tetraethylene pentamine, and polyisobutenylsuccinic anhydride derived from polyisobutylene of molecular weight in the range of about 800 to 1200.

10. The product obtained by the method of claim 1.

11. Oil composition comprising a major proportion of a mineral oil selected from the class consisting of gasoline, middle distillate fuel, and lubricating oil and from 0.1 to 10 wt. percent of the additive defined by claim 1.

12. Lubricating oil composition comprising a major proportion of a mineral lubricating oil and from 0.1 to 10 wt. percent of the additive defined by claim 1.

13. Gasoline containing 0.001 to 1.0 wt. percent of the additive defined by claim 1.

14. A concentrate of an additive having sludge dispersancy, deposit inhibiting, antioxidant and antiwear properties, which comprises a mineral oil to which has been added in the range of 20 to 80 wt. percent of the product obtained by the method of claim 1.

15. A concentrate of an additive having sludge dispersancy, deposit inhibiting, antioxidant and antiwear properties, which comprises a mineral lubricating oil to which have been added in the range of 30 to 60 wt. percent of the product obtained by the method of claim 1 and in the range of 5 to 20 wt. percent of a conventional metal-containing lubricating oil additive.

16. An additive concentrate as defined by claim 15 including in the range of 5 to 15 wt. percent of a zinc dialkyl dithiophosphate.

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