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3,515,669

HIGH MOLECULAR WEIGHT CARBOXYLIC ACID ESTER STABILIZED METAL DISPERSIONS AND LUBRICANTS AND FUELS CONTAINING THE SAME

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19 Claims

ABSTRACT OF THE DISCLOSURE

Process for preparing Group I and/or Group II metal
dispersions in essentially inert diluents by contacting a
Group I or Group II basically reacting metal compound
with an acidic material in the presence of a stabilizing
agent and promoted. A typical process comprises carbon-
ating a mixture of barium hydroxide monohydrate, heptyl
phenol, and the reaction product of polyisobutenyl-sub-
stituted-succinic anhydride and pentaerythritol or an al-
kylene polyamine. The metal-containing dispersions thus
produced are useful as additives for fuels and lubricants.

This invention relates to a novel process for solubilizing
or dispersing basic metal compounds in liquid media.
Particularly, the invention relates to a process for pre-
paring stable dispersions of basic metal compounds in an
organic liquid medium. The novel compositions produced
by the process as well as lubricants and fuels contain-
ing these compositions also form part of the present in-
ventive concept.

It is well-known that stable dispersions of basic metals
are used extensively as detergents and corrosion inhibitors
in lubricating compositions, particularly as additives for
internal combustion engine lubricants. These solutions
have also been found useful as petroleum-distillate fuel
additives. For example, the presence of a basic metal in
a diesel fuel inhibits the formation of black exhaust smoke
upon combustion of the fuel in operating diesel engines.
Basic metal-containing compositions and uses therefor are
described, for example, in U.S. Pats. 2,616,905; 2,723,234;
2,777,874; 2,781,403; 3,031,284; 3,256,186; 3,312,618; and
3,342,733. The use of basic metal-containing compositions
as smoke suppressants in diesel fuels is disclosed in
German Auslegeschrift 1,243,915.

The metal-containing dispersions produced by the pro-
cess of the present invention are particularly useful as addi-
tives for lubricating compositions. For example, the prod-
ucts function effectively as dispersants and detergents in
lubricating oil compositions for internal combustion en-
gines. However, like the above-described metal contain-
ing products of the prior art, they are also useful as
anti-screensclogging agents in petroleum distillate fuels
(e.g., gasoline, kerosene, fuel oils, etc.) and smoke sup-
pressants in diesel fuels.

In accord with the foregoing, it is a principle of this
invention to provide a process for incorporating metal
compounds into organic liquid media.

Another object is to provide a process for preparing
stable metal-containing dispersions particularly useful as
additives for fuels and lubricants.

A further object is to provide novel metal-containing
compositions.

An additional object is to provide lubricant and fuel
compositions containing dispersed metal compounds there-
in.

These and other objects of the invention can be achieved
by the process comprising the steps of contacting an acidic
material with at least one basically reacting Group I

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or Group II metal compound in the presence of (A)
at least one promoter selected from the class consisting
of phenols, alcohols, and lower nitroalkanes, and (B)
at least one stabilizing agent selected from the class con-
sisting of the esters, amides, imides, and amidine deriva-
tives of organic acids wherein the acids are characterized
by a substantially saturated hydrocarbon portion having
at least about fifty aliphatic carbon atoms. The process
is normally conducted in the presence of a substantially
inert, essentially nonpolar organic liquid diluent. The novel
compositions produced by this process can then be in-
corporated in fuels and lubricants to provide the lubri-
cant and fuel compositions contemplated by this inven-
tion.

The acidic materials used in the present process are
preferably inorganic acids or inorganic acidic gases. How-
ever, the lower aliphatic carboxylic acids can also be
utilized, particularly lower alkanolic acids and especially
acetic formic acids. Suitable inorganic acids include strong
or weak acids such as hydrochloric acid, sulfuric acid,
nitric acid, phosphoric acid, and carbonic acid. The in-
organic acidic gases would generally be anhydrides of the
inorganic acids or "acid anhydride gas" such as CO₂.
Other suitable inorganic acidic materials include HCl,
SO₂, SO₃, air (due to the CO₂ content), NO₂, H₂S, N₂O₂,
PCl₃, ClO₂H₂Fe, SOCl₂, BF₃, CS₂, COS, H₂CrO₄, etc. For
reasons of economy, effectiveness and availability, the
preferred acidic materials are inorganic gases selected
from the class comprising CO₂, SO₂, and H₂S. Gaseous
carbon dioxide is the most preferred acidic material. Mate-
rials which are capable of producing the acidic reactants
in situ may also be used. For example, urea, carbamates,
and ammonium carbonates can be employed as acidic
materials since they produce CO₂ in situ under the con-
ditions of the process.

Promoters useful according to the present process are
phenols, alcohols, and nitroalkanes. The phenolic pro-
moters include a variety of alkylated hydroxy-substituted
benzene and naphthalenes. A particularly useful class of
phenols are the mono- and di-alkylated phenols in which
each alkyl substituent contains from about six to about
two hundred carbon atoms, and preferably from six to
twenty carbon atoms. Illustrative phenolic promoters are
the heptylphenols, octylphenols, dodecylphenols, nonyl-
phenols, polypropylene (M.W. of 150)-substituted phenol,
polyisobutene (M.W. of 1200)-substituted phenols, cyclo-
hexylphenols and behenylphenols. The alcoholic promoters
are primarily the mono- and polyhydric alkanols having
from one to about twelve carbon atoms such as methanol,
ethanol, amyl alcohol, octanol, isopropanol, ethylene gly-
col, and the like. The particularly preferred alcoholic pro-
moters are the lower monohydric alkanols having up to
about seven carbon atoms. The nitroalkanes are the lower
nitroalkanes such as the nitropropanes, the nitropentanes,
and nitroheptanes. The preferred nitroalkane promoter
are 1- and 2-nitropropane. Mixtures of these various pro-
moters are also contemplated by the present invention.
This would include mixtures of phenolic promoters, alco-
hols, and nitroalkanes or a mixture of a nitroalkane and
one or more alcohols, or a mixture of alcohols and
phenols, or a mixture of nitroalkanes and alcohols. When
dispersions of calcium are being prepared, the promoter
advantageously includes a nitroalkane, preferably a nitro-
propane.

Basically reacting Group I or Group II metal com-
pounds can be sulfides, hydrosulfides, amides, or alcohol-
ates derived from alcohols having from about one to
about thirty carbon atoms. However, the preferred metal
compounds are the oxides, hydroxides, and lower alkox-
ides, the latter being derived from lower alkanols con-
taining up to about seven carbon atoms. The alkaline earth

metal oxides, hydroxides, and hydrates thereof are the preferred metal compounds. Specific basically reacting methal compounds include barium oxide, barium hydroxide monohydrate, lithium oxide, lithium hydroxide, sodium hydroxide, calcium oxide, calcium hydroxide, barium methoxide, calcium ethoxide, strontium isopropoxide, and the like.

The acids from which the stabilizing agents are derived correspond to the general formula $(R)(COOH)_n$ where n is a positive whole number having a value of one to six, preferably 1 or 2, and R is a mono- to hexavalent (depending on the value of n) substantially saturated aliphatic hydrocarbon radical having at least about fifty aliphatic carbon atoms. The variable R may contain pendant aryl groups or substantially inert polar groups. However, the polar groups should not be present in sufficiently large numbers to alter the substantially hydrocarbon character of the substituent. Exemplary polar groups include halo, carbonyl, oxy($-O-$), formyl, nitro, thio($-S-$) etc. The upper limit on the number of polar groups is about 10% by weight based on the total weight of the hydrocarbon portion of the substituent. The hydrocarbon substituent should contain no more than about 5% olefinic linkages based on the total number of carbon-to-carbon covalent linkages present in the substituent. Preferably, the number of olefinic linkages will not exceed about 2% of the total covalent linkages.

The source of the hydrocarbon substituent, R , on the acid includes principally the high molecular weight substantially saturated petroleum fractions and substantially saturated olefin polymers, particularly polymers of mono-olefins having from 2 to 30 carbon atoms. The especially useful polymers are the polymers of 1-mono-olefins such as ethylene, propene, 1-butene, isobutene, 1-hexene, 1-octene, 2-methyl-1-heptene, 3-cyclohexyl-1-butene, and 2-methyl-5-propyl-1-hexene. Polymers of medial olefins, i.e., olefins in which the olefinic linkage is not at the terminal position, likewise are useful. They are illustrated by 2-butene, 3-butene, and 4-octene. The preferred substituent is derived from polymerized isobutylene or propene.

Also useful are the interpolymers of the foregoing olefins with other and/or with other interpolymizable olefinic substances such as aromatic olefins, cyclic olefins, polyolefins. Such interpolymers include, for example, those prepared by polymerizing isobutene with styrene; isobutene with butadiene; propene with isopropene; ethylene with piperylene; isobutene with chloroprene; isobutene with p-methyl-styrene; 1-hexene with 1,3-hexadiene; 1-octene with 1-hexene; 1-heptene with 1-pentene; 3-methyl-1-butene with 1-octene; 3,3-dimethyl-1-pentene with 1-hexene; isobutene with styrene and piperylene; etc.

The relative proportions of the mono-olefins to the other monomers in the interpolymers influence the stability and oil-solubility of the final products derived from such interpolymers. Thus, for reasons of oil-solubility and stability and the interpolymers contemplated for use in this invention should be substantially aliphatic and substantially saturated, i.e., they should contain at least about 80%, preferably at least about 95%, on a weight basis, of units derived from aliphatic mono-olefins.

Specific examples of such interpolymers include the copolymer of 95% of isobutene and 5% of styrene; the terpolymer of 98% of isobutene with 1% of piperylene and 1% of chloroprene; the terpolymer of 95% of isobutene with 2% of 1-butene and 3% of 1-hexene; the terpolymer of 80% of isobutene with 10% of 1-pentene and 10% of 1-octene; the copolymer of 80% of 1-hexene and 20% of 1-heptene; the terpolymer of 90% of isobutene with 2% of cyclohexene and 8% of propene; and the copolymer of 80% of ethylene and 20% of propene. The percentages refer to the percent by weight of total interpolymers.

Another source of hydrocarbon substituents are saturated aliphatic hydrocarbons, e.g., highly refined high

molecular weight white oils or synthetic alkanes such as are obtained by hydrogenation of the high molecular weight olefin polymers illustrated above or other high molecular weight olefinic substances.

Olefin polymers having molecular weights from about 700 to about 10,000 are the preferred source of the substituent with those having molecular weights of about 700 to 5000 being especially preferred.

The stabilizing agents are the esters, amides, imides, and amidines derived from the above-described carboxylic acids and the appropriate hydroxy compound or amine, respectively. As mentioned before, acid-producing equivalents such as anhydrides, halides, lower alkyl esters, and the like can be used in lieu of the acid per se in preparing these stabilizing agents. The indicated derivatives of mono- and dicarboxylic acids are preferred. The acid and acid-producing compounds necessary for preparing the stabilizing agents are known in the prior art. The stabilizing agents themselves are also known or can be prepared through conventional processes.

Substituted succinic acid derivatives constitute the most preferred class of stabilizing agents. Substituted succinic acid producing compounds are readily prepared by reacting maleic anhydride with a suitable olefin polymer or chlorinated hydrocarbon of the types described hereinabove. The reaction involves merely heating the two reactants at a temperature of about 100° to 200° C. The product of such a reaction is a succinic anhydride having a large hydrocarbon substituent. The hydrocarbon substituent may contain olefinic linkages. These may be converted, if desired, to saturated paraffin linkages by hydrogenation. The anhydride may be hydrolyzed by treatment with water or steam to the corresponding acid and the acid converted to the corresponding halide. It will be noted in this regard that the anhydride is equivalent to the acids and the acid halides insofar as their utility in the preparation of the dispersants of this invention. In fact, the anhydride is often more reactive than the acid and is often preferred.

In lieu of the olefins or chlorinated hydrocarbons, other hydrocarbons containing an activating polar substituent, i.e., a substituent which is capable of activating the hydrocarbon molecule in respect to reaction with maleic acid or maleic anhydride, may be used in the above-illustrated reaction for preparing the substituted succinic acids. Such polar substituents are exemplified by sulfide, disulfide, nitro, mercaptan, halo, carbonyl, or formyl radicals. Examples of such polar-substituted hydrocarbons include polypropylene sulfide, di-polyisobutene disulfide, nitrated mineral oil, di-polyethylene sulfide, brominated polyethylene, etc. Another useful method for preparing succinic acids and anhydrides involves the reaction of itaconic acid with a high molecular weight olefin or a polar-substituted hydrocarbon at a temperature usually within the range of from about 100°-200° C.

The stabilizing agents prepared from the reaction of polyolefin-substituted succinic acid or anhydride and mono- or polyamines, particularly polyalkylene polyamines having up to about 10 amino nitrogens, are especially suitable. The reaction products generally comprise a mixture of amides, imides, and/or amidines. The reaction products of polyisobutene-substituted succinic anhydride and polyethylene polyamines containing up to about ten amino nitrogens are excellent stabilizing agents. These anhydride-amine products are disclosed in 3,018,250; 3,024,195; 3,172,892; 3,216,936; 3,219,666; and 3,272,746. Included within this group of dispersants are those products prepared by post-treating the reaction product of the amine and substituted succinic anhydride with carbon disulfide, a boron compound, an alkyl nitrite, urea, thiourea, guanidine, alkylene oxide, and the like as disclosed in 3,200,107; 3,256,185; 3,087,936; 3,254,025; 3,281,428; 3,278,550; 3,312,619; and British specification 1,053,577. Half-amide half-metal salt and half-ester, half-metal salt derivatives of hydrocarbon sub-

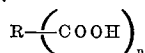
stituted succinic acids are also useful stabilizing agents. The products are disclosed in 3,163,603 and applicant's co-pending application Ser. No. 567,052.

The esters of the above acids are also very useful stabilizing agents. These esters are prepared by reacting the acid or anhydride with a mono- or polyhydric hydroxy compound such as an alcohol or phenol according to standard procedures for preparing esters of carboxylic acids. Typical esters of this type are disclosed in British specification 981,850, U.S. Pat. 3,311,558, and applicant's co-pending application Ser. No. 567,052 filed July 22, 1966. The preferred esters are the esters of the polyolefin-substituted succinic acids or anhydrides and polyhydric aliphatic alcohols containing 2 to 10 hydroxy groups and up to about 40 aliphatic carbon atoms. Such alcohols include ethylene glycol, glycerol, sorbitol, pentaerythritol, polyethylene glycol, diethanol amine, triethanolamine, N,N'-di(hydroxyethyl)-ethylene diamine, and the like. If the alcohol reactant contains reactive amino hydrogens (or if an amine reactant contains reactive hydroxyl groups), a mixture comprising the reaction products of the substituted succinic acid reactant and both the hydroxyl and amino functional groups is possible. Such reaction products can include half-ester, half-amides, esters, amides, and imides. See U.S. Pat. 3,324,033.

Suitable monocarboxylic acid derivatives and methods for their preparation are disclosed in detail in British patent specification 1,075,121, U.S. Pats. 3,272,746; 3,340,281; 3,341,542; and 3,342,733.

The foregoing copending application, patents and foreign specifications are incorporated herein by reference for their disclosure of (1) the requisite acids or acid producing compounds such as acid halides, acid anhydrides, and the like useful in producing the stabilizing agents, (2) processes for preparing esters, amides, imides, and amidines from these acid producing compounds, and (3) actual examples of suitable esters, amides, etc., which can be satisfactorily employed as stabilizing agents in the present invention.

A convenient method for preparing the acylated nitrogen stabilizing agents from



comprises reacting the acid or an acid-producing compound characterized by at least one



group wherein X is selected from the class consisting of halogen, hydroxy, hydrocarbonoxy, and acyloxy radicals, with at least about one-half an equivalent of a nitrogen-containing compound characterized by the presence within its structure of at least one group of the formula



The above process is generally carried out by heating a mixture of the acid-producing and nitrogen-containing reactants at a temperature above about 80° C., preferably within the range of about 100° C. to about 250° C. The use of a solvent such as benzene, toluene, naphtha, mineral oil, xylene, n-hexane, or the like often desirable in the above process to facilitate the control of the reaction temperature.

The relative ratio of the acid-producing compounds to the nitrogen-containing reactants in the above process are such that at least about one-half of a stoichiometrically equivalent amount of a nitrogen-containing reactant is used for each equivalent of the acid-producing compound. It should be noted that the equivalent weight of the nitrogen-containing reactant is based upon the number of the nitrogen-containing radicals,



Similarly, the equivalent weight of the acid-producing compound is based upon a number of acid radicals of the formula



where X is as previously defined. Thus, ethylenediamine has two equivalents per mole; amino guanidine has four equivalents per mole; and a succinic acid or ester has two equivalents per mole.

The upper limit of the useful amount of the nitrogen-containing reactant appears to be about two moles for each equivalent of the acid-producing compound. Such amount is required, for instance, in the formation of products having predominantly amidine linkages. Beyond this limit, the excess amount of a nitrogen-containing reactant appears not to take part in the reaction and thus simply remains in the product apparently without any adverse effect. On the other hand, the lower limit of about one-half equivalent of a nitrogen-containing reactant used for each equivalent of the acid producing compound is based upon the stoichiometry for the formation of products having predominantly imide linkages. In most instances, the preferred amount of the nitrogen-containing reactant is approximately one equivalent for each equivalent of the acid-producing reactant.

The esters may be prepared by any one of several methods. A preferred method involves the reaction of a suitable alcohol or phenol with the acid producing compound, preferably the anhydride. The esterification is usually carried out at a temperature above about 100° C., preferable between 150° C. and 300° C.

The water formed as a by-product is removed by distillation as the esterification proceeds. A solvent may be used in the esterification reaction to facilitate mixing, temperature control, and the removal of water from the reaction mixture. Useful solvents include xylene, toluene, diphenyl ether, chloro benzene, and mineral oil.

The relative proportions of the acid reactant and the hydroxy reactants depend to a large measure upon the type of product desired, the number of hydroxyl groups present, and the number of carboxyl groups. For instance, the formation of a half-ester of a hydrocarbon-substituted succinic acid, i.e., one in which only one of the two carboxyl radicals is esterified, requires one mole of a monohydric alcohol for each mole of succinic acid reactant whereas the formation of a diester of a succinic acid involves the use of two moles of the monohydric alcohol for each mole of the acid. On the other hand, one mole of a hexahydric alcohol may combine with as many as six moles of a succinic acid to form an ester in which each of the six hydroxyl radicals of the alcohol is esterified with one of the two acid radicals of the succinic acid. For purpose of this invention, it has been found that esters obtained by the reaction of equimolar amounts of the reactant and hydroxy reactant are particularly useful.

In some instances, it is advantageous to carry out the esterification in the presence of a catalyst such as sulfuric acid, pyridine hydrochloride, hydrochloric acid, benzene sulfonic acid, p-toluene sulfonic acid, phosphoric acid, or any other known esterification catalyst. The amount of the catalyst in the reaction may be as little as 0.01% (by weight of the reaction mixture), more often from about 0.1% to about 5%.

The esters of this invention likewise may be obtained by the reaction of the acid with an epoxide or the acid anhydride with a mixture of an epoxide and water. This reaction is similar to one involving the acid or anhydride with a glycol. Epoxides which are commonly available for use in such reactions include, ethylene oxide, propylene oxide, styrene oxide, 1,2-butylene oxide, 2,3-butylene oxide, epichlorohydrin, cyclohexene oxide, 1,2-octylene oxide, epoxidized soybean oil, methyl ester of 9,10-epoxystearic acid, and butadiene monoepoxide. For the most

part, the epoxides are the alkylene oxides in which the alkylene radical has from two to about eight carbon atoms; or the epoxidized fatty acid esters in which the fatty acid radical has up to about thirty carbon atoms and the ester radical is derived from a lower alcohol having up to about eight carbon atoms.

The process of the present invention is normally conducted in the presence of a substantially inert, essentially nonpolar organic liquid diluent. Since the resulting products are particularly useful as additives for lubricating oil and fuel compositions, the diluent normally will be a liquid which is soluble in lubricating oils and fuels. For this reason, the diluent usually comprises a lubricating oil such as a synthetic lubricating oil or a mineral lubricating oil. However, other organic diluents can also be employed, either alone or in combination with each other or in combination with lubricating oil diluents. Suitable solvents include dialkyl ketones, alkyl aryl ketones, (e.g., dipropyl ketone, methyl butyl ketone, acetophenone) and ethers such as n-propylether, n-amylether, and isoamyl-ether.

Particularly useful diluents include the aliphatic and aromatic hydrocarbons and halohydrocarbons such as benzene, toluene, xylene, chlorobenzene; lower boiling petroleum distillates such as kerosene and the various naphthas, the normally liquid aliphatic hydrocarbons and halohydrocarbons such as hexane, heptane, hexene, chlorohexane, cyclopentane, cyclohexane, ethyl cyclohexane, and the like. These diluents which serve as the reaction medium are used alone or in combination with mineral oil or other natural or synthetic oils. When a combination of oil in one or more of the other solvents is used, the weight ratio of oil to the other solvent is generally 1:20 to 20:1. It is usually desirable for the lubricating oil to comprise at least about 50% by weight of the weight of diluent, especially if the product is to be used as a lubricant additive.

Upon completion of the present process, solids are removed from the reaction mass by filtration or other conventional means, and the resulting reaction product, including the inert diluent, can be added directly to the lubricating oil or fuel composition in which it is to be employed. Optionally, readily removable diluents can be removed by conventional techniques such as distillation prior to incorporating the reaction mixture into the lubricant or fuel composition. As is apparent to those skilled in the art, the amount of diluent employed can be increased or decreased during formation of the dispersions or before adding to the fuel or lubricant to facilitate mixing, temperature control, or to meet some other particular requirement related to the ultimate use of the composition.

It is obvious that it may be desirable to use reflux conditions to retain diluent and/or promoter having a boiling point that is lower than that of the reaction temperature. The need for such conditions depends on the particular promoters and diluents, the amount of each present, the reaction temperature, the duration of the reaction, and the amount of metal to be dispersed in the reaction product.

The invention encompasses bringing the various reactants together in any order. However, the procedure found to produce the best overall results comprises forming an initial reaction mixture made up of at least one each of a basically reacting metal compound, promoter, stabilizing agent, and the diluent. The acidic material is then introduced into this initial mixture. During the course of the reaction, the acidic material and the basically reacting metal compound react to form a metal-containing reaction product which is dispersed in the reaction medium. The stabilizing agent prevents the metal-containing reaction product from precipitating, i.e., it "stabilizes" the dispersion.

This basic preferred order of reaction can be varied to produce the best results with given reactants under given conditions. Thus, the basically reacting metal com-

pound can be added in increments during the introduction of the acidic material. Moreover, additional stabilizing agent and/or diluent can be added during or after the process. The determination of an optimum order of reaction for given conditions is a matter of routine experimentation.

The basically reacting metal compound and the stabilizing agent normally are employed in amounts such that the ratio of equivalents of stabilizing agent to equivalents of Group I and/or Group II metal is about 1:0.1 to about 1:30 and preferably 1:0.5 to about 1:12. For purposes of determining this ratio, the number of equivalents in a stabilizing agent is the number of carboxylic acid functions present. For example, a polyisobutenyl substituted succinic methyl ester contains two carboxylic functions. Thus, it has two equivalents per molecule. The number of carboxyl functions present in the stabilizing agent is readily apparent from the amount of acid producing compound used in preparing the stabilizing agent. The number of equivalents in the basically reacting metal compound depends on its valence. Thus, calcium and barium have two equivalents per mole of metal.

The amount of acidic material employed depends upon the amount of metal to be dispersed in the reaction mixture. Theoretically, the ratio of equivalents of acidic material to equivalents of metal to be dispersed is 1:1. However, as a practical matter, utilization of the acidic material is not very efficient where inorganic acidic gases are used. Accordingly, the ratio of equivalents of acidic material to equivalents of metal to be dispersed ranges from the stoichiometric ratio of about 1:1 to a large excess, for example, about 1:10.

From the foregoing, it is apparent that the entire amount of basically reacting metal employed in the reaction mixture is not necessarily reacted with the acidic material and thereby dispersed. All that is required is that some acidic material be reacted with at least a portion of the basically reacting metal compound so that some metal compound is dispersed in the reaction mixture. Unreacted non-dispersed metal is normally removed from the reaction mixture upon completion by filtration or other convenient means.

The promoter will be present in the reaction mass in an amount such that the ratio of the number of equivalents of promoter to basic metal compound is about 0.05:1 to about 1:1 and preferably 0.1:1 to 0.5:1. The number of equivalents for a phenolic promoter depends upon the number of phenolic hydroxy groups present in the molecule. Thus one mole of heptyl phenol contains one equivalent of promoter. Similarly, the number of alcoholic hydroxyl groups in an alcohol corresponds to the number of equivalents per mole of alcohol. Ethylene glycol, accordingly contains two equivalents of promoter per mole. Likewise, the number of equivalents per mole of a nitroalkane corresponds to the number of nitro groups per mole.

As stated before, an organic diluent is normally employed in a process. Since the diluent is inactive, the amount present is not particularly critical. However, the diluent will ordinarily comprise from about 10% to about 90%, and preferably 30% to 70%, by weight of the reaction mixture based on the total weight of material in the reaction mixture exclusive of the acidic material.

The temperature at which the acidic material is contacted with the initial reaction mixture can vary from about 75° to about 300° C. The optimum temperature depends in a large measure upon the promoters employed. With phenolic promoters, the temperature usually ranges from about 80° C. to about 300° C. and preferably from about 100° C. to about 250° C. When an alcohol is employed as a promoter, the temperature usually will not exceed the reflux temperature of the reaction mixture and preferably will not exceed about 100° C. Temperatures of about 100° C. to about 125° C. are very useful when the promoter is a nitroalkane. The

optimum temperature for a mixture of promoters is readily ascertained using the suggested temperature ranges as guides.

The following examples demonstrate the preparation of typical stabilizing agents. It is to be understood that these examples are merely illustrative. In lieu of the products produced in Examples 1-4, other stabilizing agents disclosed in the hereinbefore discussed prior art can be utilized. Unless otherwise indicated, all percentages and parts express percent by weight and parts by weight.

EXAMPLE 1

(A) A reaction mixture comprising 196 parts by weight of mineral oil, 280 parts by weight of a polyisobutenyl (M.W. 1000)-substituted succinic anhydride (0.5 equivalent) and 15.4 parts of a commercial mixture of ethylene polyamine having an average composition corresponding to that of tetraethylene pentamine (0.375 equivalent) is mixed over a period of approximately fifteen minutes. The reaction mass is then heated to 150° C. over a five-hour period and subsequently blown with nitrogen at a rate of five parts per hour for five hours while maintaining a temperature of 150-155° C. to remove water. The material is then filtered producing 477 parts of product in oil solution.

(B) The procedure of Example 1(A) is repeated but the amount of amine is increased so that the ratio of equivalents of polyisobutenyl substituted succinic anhydride to ethylene polyamine mixture is 1:1.

(C) The procedure of Example 1(A) is repeated with the amount of amine being increased so that the ratio of equivalents of anhydride to amine is 1:1.5.

(D) The procedure of Example 1(A) is repeated except that the ratio of equivalents of anhydride to amine is 1:2.

EXAMPLE 2

A mixture of 1.0 equivalent of a mono-carboxylic acid (prepared by chlorinating a polyisobutene having a molecular weight of 750 to a product having a chlorine content of 3.6% by weight, converting the product to the corresponding nitrile by reaction with the equivalent amount of potassium cyanide in the presence of a catalytic amount of cuprous cyanide and hydrolyzing the resulting nitrile by treatment with a 50% excess of a dilute aqueous sulfuric acid at the reflux temperature) and 0.5 equivalent of ethylene diamine is mixed with twice its volume of xylene. The resulting mixture is heated at the reflux temperature until no more water is removed by distillation. The mixture is heated further and the xylene is removed by distillation under reduced pressure. The residue is the desired acylated nitrogen compound.

EXAMPLE 3

A methyl ester of a high molecular weight mono-carboxylic acid is prepared by heating an equimolar mixture of a chlorinated polyisobutene having a molecular weight of 1,000 and a chlorine content of 4.7% and methylmethacrylate at 140°-220° C. The resulting ester is then heated with a stoichiometrically equivalent amount of triethylene tetramine at 100°-200° C. to produce an acylated nitrogen compound useful as stabilizing agent in the process of the present invention. If desired, the intermediate methyl ester can be employed as a stabilizing agent.

EXAMPLE 4

(A) An ester of a polyisobutenyl succinic acid is prepared by forming a mixture of 340 parts mineral oil, 617 parts of polyisobutenyl substituted succinic anhydride and 75 parts of monopentaerythritol. This mixture is heated to about 190° C. over a three-hour period. The reaction mixture is subsequently blown with nitrogen at the rate of 10 parts per hour for 11 hours at 190°-200° C. to remove water. At this point an additional 113 parts of mineral oil are added and the mixture filtered. The filtra-

tion produces 1,110 parts of filtrate which is an oil solution of the desired ester.

(B) A substantially hydrocarbon-substituted succinic anhydride is prepared by chlorinating a polyisobutene having a molecular weight of 1000 to a chlorine content of 4.5% and then heating the chlorinated polyisobutene with 1.2 molar proportions of maleic anhydride at a temperature of 150°-200° C. The succinic anhydride thus obtained has an acid number of 130. A mixture of 874 grams (1 mole) of the succinic anhydride and 1.04 grams (1 mole) of neopentyl glycol is mixed at 240-250° C./30 mm. for 12 hours. The residue is a mixture of the esters resulting from the esterification of one and both hydroxy radicals of the glycol. It has a saponification number of 101 and an alcoholic hydroxyl content of 0.2%.

(C) The dimethyl ester of a substantially saturated hydrocarbon-substituted succinic anhydride of Example 4(B) is prepared by heating a mixture of 2,185 grams of the anhydride, 480 grams of methanol, and 1,000 cc. of toluene at 50°-65° C. while hydrogen chloride is bubbled through the reaction mixture for three hours. The mixture is then heated at 60°-65° C. for two hours, dissolved in benzene, washed with water, dried and filtered. The filtrate is heated at 150° C./60 mm. to rid it of volatile components. The residue is the desired dimethyl ester.

(D) A partial ester of sorbitol is obtained by heating a xylene solution containing the substantially hydrocarbon substituted succinic anhydride of Example 4(B) and sorbitol (0.5 mole per mole of the anhydride) at 150°-155° C. for six hours while water is removed by azeotropic distillation. The residue is filtered and the filtrate is heated at 170° C./11 mm. to distill off volatile components. The residue is an ester having a saponification number of 97 and an alcoholic hydroxyl content of 1.5%.

The following examples demonstrate the process of the invention. The resulting products are the desired metal-containing compositions discussed hereinbefore.

EXAMPLE I

(A) To a reaction vessel are added 249 parts mineral oil, 35.6 parts heptylphenol, and 400 parts of a 40% oil solution of the acylated nitrogen compound produced according to Example 1(A). This mixture is heated to about 148° C. over a 1.5-hour period. Then 139 parts of barium hydroxide monohydrate are added over a 1.1 hour period. Subsequently, carbon dioxide is bubbled through the mixture at a rate of 10 parts per hour for eight hours while maintaining the temperature of the mass at 150°-160° C. Thereafter, the mass is filtered, the filtrate is characterized by a barium content of 11.7%, a nitrogen content of 0.52%, and an oil content of 50%.

(B) The general procedure of Example I(A) is repeated using 2618 parts of the oil solution of the product of 1(A), 231 parts of heptylphenol, 1515 parts of barium hydroxide monohydrate, and 3031 parts of diluent oil. This mixture is blown with carbon dioxide via a submerged line for 2.5 hours at a rate of 5 parts per hour. The reaction mass is blown with nitrogen for two hours while maintaining the temperature of the mass at 165° C. and thereafter filtered. 6000 parts of the filtrate is recovered. The filtrate is a blown viscous liquid characterized by a barium sulfate ash content of 24%, a nitrogen content of 0.39%, and an oil content of 54.7%.

(C) To a three-liter flask equipped with a reflux condenser and containing 655 grams of the filtrate of Example 1(A), 80 grams of propylene tetramer-substituted phenol, 211 grams of mineral oil, and 18 grams of isooctanol, there is added 184 grams of barium oxide over a 15-minute period while the temperature of the mixture is maintained at 90°-105° C. Then 22 grams of water is added and the temperature of the mixture is elevated to 120° C. This mixture is blown with carbon dioxide at 1 cubic foot per hour for two hours while maintaining a

temperature of 145°–170° C. Subsequently, the carbonated mass is blown with nitrogen at 2 cubic feet per hour for one hour during which the temperature is 145°–155° C. and then filtered. The filtrate is a brown liquid containing 40% oil and is characterized by a nitrogen and barium sulfate ash content of 0.56% and 23.14%, respectively.

(D) The general procedure of I(C) is followed utilizing 2618 grams of the filtrate of Example I(A), 232 grams of heptylphenol, 1129 grams of barium oxide, 2725 grams of diluent oil, 144 grams of water, and 100 grams of iso-octanol. The reaction mixture is blown with carbon dioxide at 4 cubic feet per hour for 0.5-hour and then blown with nitrogen (to assist in the removal of water) at 2 cubic feet per hour for one hour. A filtrate weighing 6408 grams is obtained. The filtrate contains 51.7% diluent oil and is characterized by a barium sulfate ash content of 23.1% and a nitrogen content of 0.38%.

(E) A half-zinc salt half-acylated nitrogen stabilizing agent is prepared as follows: A reaction mixture containing 402 parts mineral oil, 13 parts water, and 560 parts of a polyisobutenyl (N.Y.—1000)-substituted sebacic anhydride is heated at 75°, 82° C. for 0.5-hour to convert the anhydride to acid. Thereafter, 20.5 parts of zinc oxide is added over a 0.5-hour period while maintaining the temperature at about 80° C. This mixture is then heated at 93°–98° C. for four hours under reflux conditions and then at about 120° C. for 0.5-hour. To the resulting mixture is added 20.6 parts of the commercial amine mixture of Example 1(A) while maintaining the temperature at about 120°–125° C. Thereafter the mixture is heated for six hours at 150°–155° C., the last five hours being accompanied by nitrogen blowing to facilitate water removal. After filtration, 980 parts of filtrate are obtained characterized by a zinc content of 1.63% and a nitrogen content of 0.72%.

Following the general procedure of Example I(D), 4000 grams of the above filtrate, 231 grams of heptylphenol, 2287 grams of mineral oil (diluent), 911 grams of barium hydroxide monohydrate are carbonated at a rate of three cubic feet per hour, blown with nitrogen for 2.5 hours, and filtered. The filtrate weighs 6885 grams and is characterized by an oil content of 52%, a zinc content of 0.92%, a nitrogen content of 0.37% and a barium content of 8.23%.

(F) The general procedure of Example I(B) is repeated by carbonating a mixture of 549 grams of the product of Example 1(D), 116 grams of heptylphenol, 455 grams of barium hydroxide monohydrate, and 1100 grams of oil for two hours at 1.5 cubic feet per hour. The carbonated mixture is blown with nitrogen for one hour and filtered. The filtrate is a brown liquid characterized as follows: weight—1974 grams; oil content—59%; nitrogen content—0.58%; BaSO₄ ash content—24.35%.

(G) A mixture comprising 1820 grams of a filtrate prepared as in Example 1(B) having an oil content of 40%, 58 grams of heptylphenol, and 300 grams of mineral oil is heated to 70° C. and 249 grams of barium oxide are added. The mixture is then carbonated at a rate of 5 cubic feet of CO₂ per hour until the carbonated mixture is slightly acidic. During carbonation the reaction mass is heated to 150° C. The carbonated mixture is filtered. The filtrate contains 41.5% oil and is characterized by a barium sulfate ash content of 13.58% and a nitrogen content of 1.1%.

EXAMPLE II

(A) A mixture of 4032 grams of filtrate prepared as in Example 1(A) and 1801 grams of oil in a 12-liter flask fitted with a reflux condenser is heated to 65° C. Then 401 grams of heptylphenol, 180 grams of methanol, 218 grams of isobutanol, 118 grams of amyl alcohol, and 40 grams of a 50% aqueous solution of calcium chloride are added to the mixture which is then heated to 80° C. Calcium hydroxide (474 grams) is added and the mixture is carbonated for 1.2 hours at 6 cubic feet per hour while

maintaining a temperature of 78°–80° C. Water and alcohols are stripped at 150° C. and the resulting mixture filtered. The filtrate weighs 5109 grams and contains 49.5% oil. It has a barium sulfate ash content of 9.35% and a nitrogen content of 0.65%.

(B) A mixture of 588 grams of the filtrate prepared according to Example 1(C), adjusted to an oil content of 40%, 971 grams of diluent oil, 85 grams of 1-nitropropane, 56 grams of isobutanol, 29 grams of amyl alcohol, and 10 grams of a 50% aqueous calcium chloride solution are refluxed at 100° C. for 2 hours. This mixture is carbonated (2 cubic feet per hour) at 100°–105° C. for 1.5 hours. The carbonated mixture is then dried at 150° C. with nitrogen blowing and filtered. The filtrate is characterized as follows: oil—71.8%; N—0.84%; calcium sulfate ash content—9.1%.

EXAMPLE III

A mixture comprising 2520 grams of a filtrate prepared according to Example 1(A), adjusted to 40% oil content, and 558 grams of mineral oil is heated to 150° C. To this mixture is added over a 3.5-hr. period of solution of 252 grams of lithium hydroxide monohydrate in 1260 grams of water while maintaining a temperature of 150°–160° C.

Two-thirds of the above mixture is diluted with an additional 546 grams of oil and heated to a temperature of 50° C. To the dilute mixture there is added 200 grams of methanol, 33 grams of isobutanol, and 17 grams of amyl alcohol. While maintaining a temperature of 65–70° C., the mixture is carbonated for 1.75 hrs. at a rate of 3 cubic feet per hour. This carbonated mass is stripped by heating to 160° C. while blowing with nitrogen and filtered. The filtrate is the desired product and is characterized by lithium sulfate ash content of 8%, an oil content of 57.7%, and a nitrogen content of 1.65%.

EXAMPLE IV

A reaction mixture comprising 3942 grams of a filtrate prepared according to Example 1(A), 347 grams of heptylphenol, 1284 grams of mineral oil, and 877 grams of strontium hydroxide is carbonated at a rate of 3.5 cubic feet per hour for 5 hours and filtered. The filtrate is characterized by a weight of 4808 grams, a nitrogen content of 0.72%, and a lithium sulfate ash content of 6.62%.

EXAMPLE V

(A) A reaction mixture containing 1008 grams of a filtrate prepared according to Example 1(A), adjusted to a 40% oil content, 812 grams mineral oil, 115 grams of 1-nitropropane, 75 grams of isobutanol, 40 grams of amyl alcohol, 10 grams of a 50% aqueous solution of calcium chloride, and 119 grams of calcium hydroxide is heated under reflux conditions for 5 hours at 100° C. and then carbonated at the rate of 2 cubic feet per hour for 2 hours during which time the reaction mixture temperature rises to 130° C. The mixture is stripped at 150° C. during which time carbonation is continued and subsequently filtered. The filtrate is characterized as follows: weight—1741 grams; oil content—61.6%; nitrogen content—0.78%; calcium sulfate ash content—9.9%.

(B) The procedure of Example V(A) is repeated but 1012 grams of oil are used and 115 grams of 2-nitropropane are substituted for the 1-nitropropane of (A). The filtrate has a calcium sulfate ash content of 10%.

EXAMPLE VI

Following the general procedure of Example V(A), a mixture of 1008 grams of the product of Example 1(A), 551 grams of diluent mineral oil, 10 grams of a 50% aqueous solution of calcium chloride, 240 grams of ethylene glycol, and 89 grams of calcium hydroxide is carbonated at a rate of 2.5 cubic feet of carbon dioxide per hour for 1 hour. The carbonated mixture is stripped by heating to 170° C. at 40 mm. (Hg) and subsequently filtered. The filtrate is characterized by a calcium sulfate ash content of 2.64%.

EXAMPLE VII

A lithium-containing dispersion is prepared by first forming a mixture of 3120 grams of an ester prepared according to Example 4(A), adjusted to an oil content of 40%, and 1368 grams of mineral oil. The mixture is heated to 150° C. and a solution of 285 grams of lithium hydroxide monohydrate in 1350 grams of water is added. The water is removed from the mixture by heating to 160° C. for 0.5 hours while blowing with nitrogen. To this dried mixture which is cooled to 70° C., there is added 326 grams of methanol, 42 grams of isobutanol, and 23 grams of amyl alcohol. Thereafter the mass is carbonated at a rate of 3 cubic feet of carbon dioxide per hour for 2.5 hours while maintaining a temperature of 55°-60° C., stripped by heating to 160° C. while blowing with nitrogen, and filtered. The filtrate is characterized as follows: weight—3987 grams; oil content—56.3%; lithium sulfate ash content—8.1%.

The foregoing examples are merely illustrative. Obviously, many modifications can be made in accord with the general description of the invention presented hereinabove. For example, other acidic materials, stabilizing agents, promoters, and/or basically reacting metal compounds can be substituted for those of the particular illustrative examples with good results. Such modifications are clearly within the skill of the art in view of the present specification and require no further discussion herein. All that is required to achieve these substitutions is to replace all or a portion of the reactants in the examples with an equivalent amount of the reactant to be substituted.

However, certain general conclusions have been drawn as a result of conducting the above and similar reactions. These conclusions should serve as useful guide lines to those desiring to practice the invention. First, when a nitroalkane is used as a promoter, water should be removed as soon as formed as the reaction mixture is being contacted with the acidic material (e.g., during carbonation) for best results. On the other hand, when phenolic promoters or alcoholic promoters or combinations thereof are employed, best results are obtained when at least some water is permitted to remain in the reaction mass during the time the mixture is being contracted with the acidic material. Furthermore, a mixture of monohydric lowr alkanols (e.g., methanol, propanol, butanol, etc.) and 1-nitropropane is generally more effective in dispersing calcium metal than either the alkanols or 1-nitropropane alone. Moreover, with basically reacting calcium compounds, 1-nitropropane is more effective than 2-nitropropane. Generally, calcium chloride is an effective co-promoter when preparing calcium dispersions.

Normally, the barium compounds are readily formed using alcoholic promoters, phenolic promoters or combinations thereof. However, combinations of alcoholic and phenolic promoters or phenolic promoters alone are particularly effective in preparing barium dispersion.

Obviously, the stabilizing agents of the present invention can be used alone or in combination with each other in preparing the metal-containing dispersions. However, these stabilizing agents can be used in conjunction with other known stabilizing agents or peptizing agents as they are denominated in the prior art. These peptizing agents are quite diverse and include the oil-soluble organic acids and the Group I and Group II metal salts thereof such as the petrosulfonic acids, barium petrosulfonate, oleic acid, calcium oleate, the phosphorus acid mixture produced by steam blowing the reaction product of polyisobutylene and P_2S_5 , and the like. Other peptizing agents are aliphatic amines such as N-octadecyl propylene diamine and the condensation product of such amines with lower aldehydes such as formaldehyde. These and other peptizing agents are well-known in the art and require no further discussion herein.

The metal-containing dispersions of the present invention can be incorporated directly into various lubricating and fuel compositions. The amount to be used depends upon whether the additive is added to a lubricant, a fuel, and the environment under which the lubricant or fuel is to be employed. For example, these metal-containing dispersions can be successfully employed as detergent-dispersant additives for crankcase lubricating oils when employed in an amount sufficient to impart a sulfate ash content to the lubricating oil of 0.01% to 20%, preferably 0.01% to 10% by weight. If the lubricating oil is to be used as a crankcase lubricant for gasoline engines, it normally will contain up to about 1% ash. On the other hand for diesel engines, sufficient additive should be used to provide the lubricant with an ash content of up to about 2%-5% ash while marine diesels may require enough additive to provide an ash content of 10% or more.

When the metal-containing dispersions are added to fuel as anti-screenclogging agents, they will normally be employed in amounts such that the ash content of the fuel will be from about 0.001% to about 0.05%. If, however, the additive is used in a diesel fuel to suppress the formation of black exhaust smoke upon combustion of the fuel in a diesel engine, enough additive should be employed to impart a sulfate ash content to the diesel fuel of about 0.01% to about 1% preferably 0.01% to 0.5%. The alkaline earth metal dispersions are preferred when it is desired to impart smoke suppression qualities to diesel fuels. Barium dispersions are particularly effective.

The metal-containing dispersions of the present invention can be used alone or in combination with other fuel and lubricating additives known in the prior art. These additives include for example, other detergents of the ash-containing type, ashless dispersants, viscosity index improving agents pour point depressing agents, anti-foam agents, extreme pressure agents, rust inhibiting agents, and oxidation and corrosion inhibitors.

The ash-containing detergents are the well known neutral and basic alkali or alkaline earth metal salts of sulfonic acids, carboxylic acids, or organic phosphorus containing acids. These latter are characterized by at least one direct carbon-to-phosphorus linkage. Such acids can be prepared by the steam-treating an olefin polymer (e.g., polyisobutene having a molecular weight of 1000) with a phosphorizing agent such as phosphorus trichloride, phosphorus heptasulfide, phosphorus pentasulfide, phosphorus trichloride and sulfur, white phosphorus and a sulfur halide, or phosphorothioic chloride. The most commonly used salts of such acids are the sodium, potassium, lithium, calcium, magnesium, strontium, and barium salts. The calcium and barium salts are used more extensively than the others. The "basic salts" are those metal salts known in the art wherein the metal is present in a stoichiometrically larger amount than that necessary to neutralize the acid. The calcium and the barium overbased petrosulfonic acids are typical examples of such basic salts.

The ashless dispersants are also a well known class of materials used as additives for lubricating oils and fuels. They are particularly effective as dispersants at lower temperatures. The stabilizing agents of the present invention are representative of these dispersants.

Extreme pressure agents, corrosion inhibiting agents, and oxidation-inhibiting agents are exemplified by chlorinated aliphatic hydrocarbons such as chlorinated wax; organic sulfides and polysulfides such as benzyldisulfide, bis-(chlorobenzyl)disulfide, dibutyltetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid, sulfurized alkylphenol, sulfurized dipentene, and sulfurized terpene, sulfurized Diels-Alder adducts such as sulfurized adduct of butadiene and butylacrylate; phosphosulfurized hydrocarbons such as the reaction product of a phosphorus sulfide with terpentine or methyl oleate; phosphorus esters

such as the dihydrocarbon and trihydrocarbon phosphites, e.g., dibutylphosphite, diheptylphosphate, dicyclohexylphosphite, pentylphenylphosphite, dipentylphenylphosphite, tridecylphosphite, distearylphosphite, and polypropylene (molecular weight 500)-substituted phenylphosphite; metal thiocarbonates exemplified by zinc dioctyl-dithiocarbonate and barium heptylphenyldithiocarbonate; Group II metal salts of phosphorodithioic acids such as zinc dicyclohexylphosphorodithioate, zinc dioctylphosphorodithioate, barium di(heptylphenyl) phosphorodithioate, cadmium dinonylphosphorodithioate, and the zinc salt of a phosphorodithioic acid produced by the reaction of phosphorus pentasulfide with an equimolar mixture of isopropyl alcohol and n-hexyl alcohol.

These additional additives are well known to those skilled in the art and the foregoing listing is merely to illustrate the types of additional additives which can be present in the lubricating and fuel compositions in which the metal-containing dispersions of the present invention are employed. A brief survey of additives for lubricating compositions is contained in *Lubricant Additives*, C. V. Smalheer and R. Kennedy Smith, published by The Lazius-Hiles Company, Cleveland, Ohio, 1967.

When additional additives are present, they will normally be employed in amounts such that they comprise from about 0.001% to about 20% by weight of the total composition. For example additional ashless dispersants can be employed in amounts of from about 0.1% to about 10% while additional metal-containing detergents will be present in amounts of from about 0.1% to about 20% by weight. Since the present metal-containing dispersions contain both a dispersant and metal compound, it will be obvious to those skilled in the art that the present compositions can be substituted in known lubricating compositions in such a manner that the metal-containing dispersions replaces all or a portion of the metal and the stabilizing agents replaces all or a portion of the ashless dispersants in the known compositions. Pour point depressants, extreme pressure additives, viscosity index improving agents, and anti-forming agents, and the like are normally employed in amounts up to about 0.001% to about 10% by weight of the total composition depending on the nature and purpose of the particular additive.

The following compositions exemplify typical useful embodiments of the metal-containing dispersions of the present invention.

Composition A

SAE 10W-30 mineral lubricating oil containing 3% of the product of Example I(C), 0.06% of phosphorus as zinc di-n-octylphosphorodithioate, and 0.2% sulfate ash as basic barium mahogany sulfonate.

Composition B

SAE 30 mineral lubricating oil containing 6% of the filtrate of Example I(A).

Composition C

SAE 80 mineral lubricating oil containing 1% of the reaction product of polyisobutenyl-substituted succinic anhydride and tetraethylene pentamine reacted in an equivalent ratio of 1:1, 1% of the product of Example I(A), 0.1% phosphorus as zinc di-n-hexylphosphorodithioate, 10% of a chlorinated paraffin wax having a chlorine content of 40%, 2% of dibyltetrasulfide, 2% of sulfurized dipentene, 0.2% of oleyl amide, 0.003% of an anti-foam agent, 0.03% of a pour point depressant and 3% of a viscosity index improver.

Composition D

SAE 10 mineral lubricating oil containing 2% of the product of Example II(B), 0.075% of phosphorus as the adduct of zinc di-cyclohexylphosphordithioate treated with 0.3 mole of ethylene oxide, 2% of sulfurized sperm oil having a sulfur content of 10%, 3.5% of a poly-(alkyl-

methacrylate) viscosity index improver, 0.02% of a poly-(alkylmethacrylate) pour point depressant, 0.003% of a poly-(alkylsiloxane) anti-foam agent.

Composition E

SAE 20 mineral lubricating oil containing 1% of the product of Example III.

Composition F

SAE 20 mineral lubricating oil containing 2% of the product of Example VII, and 0.07% of phosphorus as zinc di-n-octylphosphorodithioate.

Composition G

Diesel fuel containing 0.15% barium sulfate ash from the product of Example I(A).

Composition H

Kerosene containing 0.01% sulfate ash of the product of Example I(A).

While the foregoing generally refers to the use of the metal-containing dispersions in mineral lubricating oils or petroleum distillate fuels, it should be understood that the present invention is not limited to use in mineral oil-based lubricating compositions. Other lubricating oils, natural as well as synthetic can be used as the base of the lubricating oil and grease compositions contemplated by the present invention. Such natural and synthetic bases include hydrocarbon oils produced from alkylene oxides such as polyethylene oxide and polypropylene oxide polymers or the esters and ethers thereof. The synthetic esters oils such as those produced from polycarboxylic acids and alcohols including glycols and polyglycols are also contemplated as being within the scope of the invention. Examples of these oils are dibutyl adipate, di-(2-ethylhexyl) sebacate, dilauryl azelate, etc.

What is claimed is:

1. The process comprising contacting at a temperature of from about 75° C. to about 300° C. an inorganic acid material selected from the class consisting of CO₂, SO₂, H₂S with at least one basically reacting Group I or Group II metal compound in the presence of (a) at least one promoter selected from the class consisting of phenols, alcohols, and lower nitroalkanes, (b) at least one stabilizing agent selected from the class consisting of the esters of mono- and polycarboxylic acids prepared by reacting under esterification conditions at least one mono- or polycarboxylic acid acylating agent characterized by the presence within its structure of a high molecular weight, substantially saturated, oil-solubilizing group having at least about 50 aliphatic carbon atoms with at least one member selected from the group consisting of mono- and polyhydroxy alcohols and phenols and alkylene oxides wherein the ratio of equivalents of stabilizing agent to equivalents of basically reacting Group I or Group II metal compound is about 1:0.1 to about 1:30, the amount of inorganic acidic material employed is such that the ratio of equivalents of inorganic acidic material employed to said basically reacting metal compound is at least 1:1; and the amount of promoter is such that the ratio of equivalents of promoter to equivalents of basically reacting Group I or Group II metal compound is about 0.05:1 to about 1:1.

2. The process according to claim 1 wherein the process is conducted in the presence of at least one substantially inert, essentially nonpolar organic liquid diluent.

3. The process of claim 1 comprising contacting the inorganic acidic gas with at least one basically reacting Group II metal compound selected from the class consisting of oxides, hydroxides, and lower alkoxides in the presence of (a) at least one promoter selected from the class consisting of mono- and dialkylated phenols in which each alkyl substituent contains from about 6 to about 200 carbon atoms and mono- and polyhydric alcohols having one to 12 carbon atoms and (b) at least one

stabilizing agent selected from the class consisting of the esters of mono- and polycarboxylic acids prepared by reacting under esterification conditions at least one mono- or polycarboxylic acid or anhydride with at least one polyhydric aliphatic alcohol containing 2 to 10 hydroxy groups and up to about 40 aliphatic carbon atoms, wherein the equivalent ratio of stabilizing agent to Group II metal compound is about 1:0.5 to about 1:12, the ratio of equivalents of inorganic acidic material employed to said Group II metal compound is about 1:1 to about 1:10, and the ratio of equivalents of promoter to equivalents of basically reacting Group II metal compound is about 0.1:1 to 0.5:1.

4. The process according to claim 3 wherein the inorganic acidic material is CO_2 , the basically reacting Group II metal compound is at least one member selected from alkaline earth metal oxides and hydroxides, the promoter is at least one member selected from the group consisting of mono- and di-alkylated phenols where the alkyl groups contains from 6 to 20 carbon atoms and lower monohydric alcohols having up to about seven carbon atoms.

5. The process according to claim 4 wherein there is present at least one substantially inert, essentially non-polar organic liquid diluent.

6. The process according to claim 5 wherein the stabilizing agent is at least one ester prepared by reacting under esterification conditions at least one polyolefin-substituted succinic acid or anhydride and at least one alkane polyol containing three to six hydroxy groups.

7. The process according to claim 6 wherein the stabilizing agent is at least one ester of a polyhydric alkanol selected from the class consisting of glycerol, pentaerythritol, and sorbitol.

8. The metal-containing dispersions produced according to claim 1.

9. The metal-containing dispersions produced according to claim 3.

10. The metal-containing dispersions produced according to claim 4.

11. The metal-containing dispersions produced according to claim 5.

12. The metal-containing dispersions produced according to claim 6.

13. The metal-containing dispersions produced according to claim 7.

14. A lubricant containing a major amount of lubricating oil and an amount of a metal-containing dispersion according to claim 1 sufficient to impart a sulfate ash content of about 0.01% to 20% by weight.

15. A lubricant comprising a major amount of a lubricating oil and an amount of a metal-containing dispersion according to claim 10 sufficient to impart a sulfate ash content of about 0.01% to 10% by weight.

16. A lubricant comprising a major amount of a lubricating oil and an amount of a metal-containing dispersion according to claim 13 sufficient to impart a sulfate ash content of 0.01% to 10% by weight.

17. A fuel comprising a major amount of a normally liquid petroleum distillate fuel and an amount of a metal-containing dispersion according to claim 8 sufficient to impart a sulfate ash content of 0.001% to about 1%.

18. A fuel comprising a major amount of a normally liquid petroleum distillate fuel and an amount of a metal-containing dispersion according to claim 10 sufficient to impart a sulfate ash content of about 0.001% to about 1%.

19. A fuel comprising a major amount of a normally liquid petroleum distillate fuel and an amount of a metal-containing dispersion according to claim 10 sufficient to provide a sulfate ash content of about 0.001% to about 1%.

References Cited

UNITED STATES PATENTS

2,695,910	11/1954	Asseff et al.	252—39 X
3,163,603	12/1964	Le Suer	252—18 X
3,194,823	7/1965	Le Suer et al.	252—18 X
3,451,931	6/1969	Kahn et al.	252—32.7

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44—51, 57, 70; 252—18, 25, 41, 56

UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,515,669

June 2, 1970

William M. Le Suer

It is certified that error appears in the above identified patent and that said Letters Patent are hereby corrected as shown below:

Column 17, line 6, "corbon" should read -- carbon --. Column 18, line 5, "containing" should read -- comprising --; line 26, "mount" should read -- amount --; line 27, claim reference numeral "10" should read -- 13 --.

Signed and sealed this 23rd day of March 1971.

(SEAL)
Attest:

EDWARD M. FLETCHER, JR.
Attesting Officer

WILLIAM E. SCHUYLER, JR.
Commissioner of Patents