

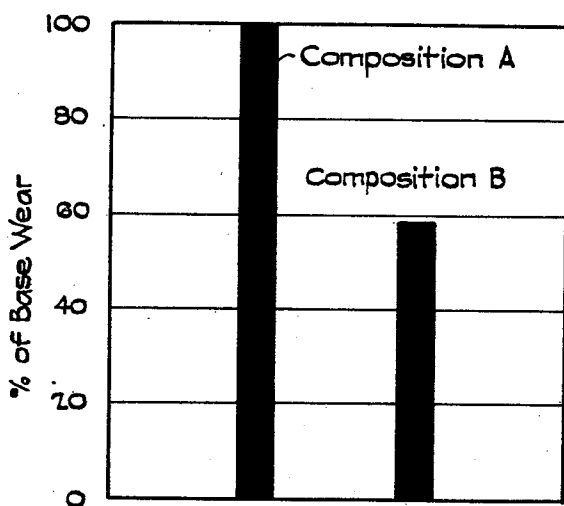
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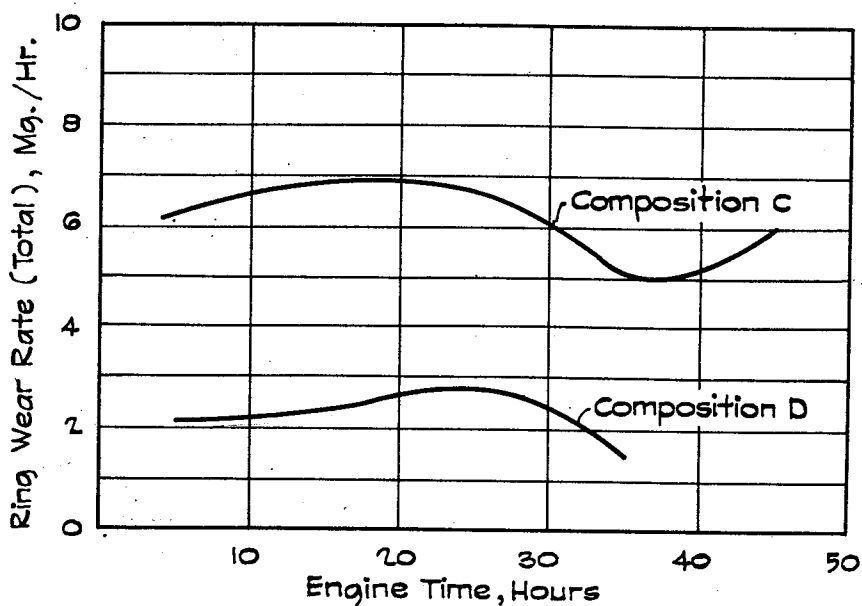
COLLOIDAL COMPOSITIONS AND DERIVATIVES THEREOF

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COLD AUTOMOTIVE CFR WEAR TEST

Figure I



SUPERCHARGED DIESEL CFR WEAR TEST.
1% S FUEL

Figure II

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COLLOIDAL COMPOSITIONS AND
DERIVATIVES THEREOF

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This invention relates to a new and novel method of stabilizing materials containing or forming acidic products which act adversely upon the base materials as a whole, and to improved compositions thus formed. More particularly, this invention pertains to the formation of novel metallic base materials and organic salts thereof possessing outstanding properties when incorporated, admixed or reacted with various base compositions which it is desired to stabilize and improve.

It is well known that various base materials and compositions thereof for use in numerous industrial applications present a serious problem due to the inherent presence, or formation, during storage or use, of acidic materials which are very detrimental to the overall efficiency of the composition itself and in many instances are the cause of serious damage to the material with which these acidic materials come in contact.

For example, it is well known that various lubricants, whether doped or undoped, tend to oxidize and to form corrosive bodies and sludge, when used for their intended purpose. Some of the deterioration products of lubricants, formed during their use, are hard carbonaceous materials which adhere to metal surfaces and cause scratching and scuffing of movable metal parts and sticking of valves and piston rings in engines. In addition, lubricants are generally incapable of maintaining a continuous lubricating film between movable parts in many present-day machines, resulting in gradual or rapid wearing away of metal parts. The damage thus caused requires replacement of such parts or even the complete overhauling of engines and machines, resulting in loss of production and time.

In the case of mineral lubricating oils which have been highly refined for specific uses, or of synthetic lubricants developed for specific or special uses, it has been observed that such oils or lubricants are generally highly susceptible to oxidation and deterioration, becoming progressively more corrosive in engines and machines even under ordinary operating conditions.

To improve the lubricating properties of oils and synthetic lubricants, it has become the practice to blend with various lubricants one or more addition agents, which additives have the effect or property of inhibiting deterioration of lubri-

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cants and imparting to them certain beneficial properties. Thus, additives have been specifically designed which have the property of inhibiting corrosion of alloyed bearings such as copper-lead, cadmium-silver and the like, developed for automotive, diesel and aircraft engines. Acidic oxidation or decomposition components formed in lubricants during use readily attack these bearings but are inhibited or prevented from doing this by the formation of a corrosion-protective film formed on the bearing surface with the aid of certain additives. Additives have also been developed which possess the property of modifying the carbonaceous materials formed by deterioration of lubricants. Such additives modify this carbonaceous material so that it can be removed easily, and the tendency of engine parts to become stuck is inhibited so that ringsticking, piston scuffing, scratching and wearing-away of other engine parts and material reduction of engine efficiency are prevented or materially inhibited.

Other additives have been developed for the purpose of acting as detergents in lubricants in order to assist in the removal of soot or sludge, varnish and lacquer formed from deterioration of the oil when subjected to high operating temperatures. Detergents prevent the build-up of these deleterious materials on the metal parts and assist in removing those formed. Anti-wear additives have the property of reducing friction between movable metal parts, thus reducing frictional contact of metals. Also, additives have been developed to withstand extreme pressures, disperse impurities, solubilize certain additives and the like.

Most, if not all, additives function essentially in substantially only one specific manner. Thus, a good antioxidant might not be able to inhibit lacquer and varnish formation on piston rods or act as a detergent or as a corrosion inhibitor. In many cases, it is found that an additive which possesses very good properties in one respect is actually detrimental as an additive in another respect. Therefore, other additives are frequently required to obtain a satisfactory lubricant. The combination of compatible additives in lubricants wherein each additive exerts its influence without interfering adversely with the function of other additives is a difficult matter to attain.

Besides lubricating oils and fuels, acidic decomposition products form in greases and adversely affect the oxidation and storage stability of the grease as well as having a marked effect on its mechanical stability, bleeding characteristics, and the like.

It is well known that moisture, corrosive fluids and gases, e. g., H_2S , SO_2 , etc., readily attack not only metallic surfaces but non-metallic surfaces and cause corrosion, rusting, pitting and other damage to such surfaces. Also, aqueous solutions, when in contact with a metallic surface, readily attack it and cause corrosion and rusting. Under certain conditions, the problem of corrosion becomes exceedingly serious because once started, it becomes progressively accelerated. Thus, oils containing small amounts of water become very corrosive to contacting metals. This is due to the fact that oils, and particularly liquid petroleum hydrocarbons, are relatively good solubilizers of oxygen, and any moisture present therein becomes surrounded by an almost inexhaustible store of oxygen. Moisture under such conditions is inhibited from evaporating and since the rate of transfer of oxygen from hydrocarbons, such as mineral oil or gasoline, to water is limited, ideal conditions for rusting and corrosion are set up. The presence of electrolytes and formation of corrosive decomposition products in oils and the like also greatly increase the rate of corrosivity.

Countless materials and compositions have been tried for protecting surfaces by forming on said surfaces a non-reactive corrosion-protective film. Metal surfaces have been coated or treated with greases, fatty compositions, waxes, organic compounds, e. g., organic acids, amines, inorganic compounds and the like, in order to protect them against corrosion. In most cases where no chemical reaction occurs between the surface treated and the corrosion or rust inhibitor, very little benefit has been derived. This is due to the fact that non-reactive inhibitors are incapable of penetrating the surface being protected and are incapable of displacing the contaminant therefrom. In cases where such inhibitors are able to form protective coatings on surfaces, usually they are easily displaced by moisture or rupture readily. They are relatively ineffective against corrosive acidic materials and gases such as are formed during operation of combustion and turbine engines and are easily destroyed when applied to surfaces which are subjected to high temperatures.

The problem of combatting the detrimental effects of acidic formation is also encountered in detergent compositions, pickling baths, asphaltic compositions suitable for road, roofing and other protective applications or compositions suitable for protecting ships' bottoms, boilers, heat-transfer compositions, insecticidal and fungicidal compositions and the like.

It is an object of this invention to provide a method for combatting and rendering ineffective acidic materials present or formed in compositions broadly. Another object of this invention is to prepare in a novel manner agents capable of meeting successfully this problem. Still another object of this invention is to prepare novel organic salts from certain materials of this invention which can be used per se or in combination with various bases or compositions. It is also an object of this invention to provide improved compositions applicable in various industrial applications. Still another object of this

invention is to improve various industrial and non-industrial compositions by addition thereto of an additive or additives of this invention. Other objects of this invention will appear as the description proceeds.

Broadly stated, the present invention resides in the use of colloidal metallic inorganic bases or organic salts thereof, that is, reaction products thereof with organic compounds, and preparation of such colloidal metal bases and of the organic salts thereof for making improved compositions of the character as mentioned above. By the term "colloidal," as used herein and throughout the rest of the application and in the claims as applied to basic metallic inorganic material, is meant a material of critical dimension such that at least one dimension of the colloiddally dispersed material must be within the limits of 0.001 to 0.5 micron and may be prepared by any suitable means.

The colloidal basic metallic inorganic materials having particle size of at least one dimension within the critical range and not exceeding 1.0 micron (μ) in the largest dimension, and preferably within the limits of from 0.001 μ to 1.0 μ may include the alkali and alkaline earth metal oxides, hydroxides, sulfides, and the like, as well as the basic oxides, hydroxides, sulfides, etc., of Al, In, Zn, Sn, Bi, Cr, Fe, Co, Ni, Pb, etc. Specifically preferred both as an additive and as agents for the preparation of organic salts thereof are colloidal calcium oxide and hydroxide, colloidal calcium sulfide, colloidal magnesium oxide or hydroxide, colloidal barium oxide or hydroxide, colloidal strontium hydroxide, colloidal sodium oxide, colloidal sodium hydroxide, colloidal potassium hydroxide, colloidal aluminum hydroxide, colloidal iron oxide, colloidal vanadium pentoxide, colloidal iron sulfide, colloidal lead oxide, colloidal bismuth oxide, colloidal zinc oxide and hydroxide. In all cases, the largest dimension of the particle of the above colloidal metallic materials should not exceed 1.0 μ in its inorganic state or when used to form organic salts thereof when used to improve base materials or compositions for combatting acidic agents or stabilizing and/or improving such materials or compositions. Mixtures of the colloidal inorganic base materials and organic salts therefore also can be used to improve various bases and compositions.

The organic radical or anionic part used to form organic salts with the colloidal basic materials mentioned above may include those derived from the following acidic materials, including their anhydrides and other corresponding acyl derivatives, and from other organic substances containing a metal-replaceable hydrogen atom:

I.

A. Saturated alkyl monocarboxylic acids:

Capric	Lignoceric
Undecylic	Cerolic
Lauric	Montanic
Myristic	Melissic
Palmitic	Ethyl butyric
Arachidic	Ethyl hexoic acids, etc.
Stearic	

B. Unsaturated alkyl monocarboxylic acids:

Acrylic	Linolenic
Crotonic	Brassicic
Pentenolic	Elaidic
Tiglic	Corn oil acids
Tetracylic	Lard oil acids
Hypogallic	Soy oil acids
Oleic	Tung oil acids
Linoleic	Stearoleic
Erucic	Cocoonut fatty acids
	Cottonseed oil acids, etc.

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C. Hydroxyl alkyl carboxylic acids:

Dimethyl hydroxy
caprylic
Dimethyl hydroxy
capric
Ricinoleic, ricine-
laidic
12-hydroxystearic
9,10-dihydroxy ste-
aric
4-hydroxy palmitic

D. Keto acids:

Pyronacenic
Propanoyl formic
Butyryl formic
Aceto butyric
Licanic
12 keto stearic
13 keto behenic acids,
etc.

E. Aldehyde alkyl carboxylic acids.

Aldovaleric
Formylacrylic
Mucolonic acids, etc.

F. Polycarboxylic alkyl acids:

Alkyl and alkenyl
malonic
Alkyl and alkenyl
succinic
Alkyl and alkenyl
glutaric
Alkyl and alkenyl
adipic
Pimelic
Suberic
Azelaic
Brassylic
Alkyl maleic
Fumaric
Itaconic
Citraconic
Mesaconic
Glutaconic
Tartronic
Malic
Aspartic
Mesoxalic
Tricarballic acids and
homologues, e. g.—
Aconitic
Tartaric
Citric acids, etc.

The alkyl group of the acid preferably should contain at least six carbon atoms.

G. Miscellaneous alkyl acids:

Acidic products produced by oxida-
tion of hydrocarbons
Mercapto oleic
Mercapto stearic
Thiostearic
Amino caprylic
Mercapto succinic
Cetyl amino succinic
Phosphonato fatty acids, e. g., phos-
phonato butyric to stearic acids
Cyano fatty acids, e. g., cyano butyric
to stearic acids

These phosphonato and cyano acids may also include the polycarboxylic acids, e. g., phospho-
nato alkyl succinic acid, etc.

Either or both of the oxygen atoms in the carboxylic acid radical of A to G may be replaced by sulfur, selenium, and/or tellurium atoms resulting in the following acid radicals: CXOH, COXH, CXXH, wherein X is sulfur, selenium or tellurium. Also, these acids may contain substituent groups attached in appropriate position of the acid molecule so as to aid in solubilizing and enhancing their lubricating properties.

The following are examples of substituent polar groups that may be present also in the anion:

Hydroxyl	Alkyl or aryl stibono
Amino	Alkyl or aryl borate
Alkoxy or aryloxy	Alkyl or aryl silicate
Oxo	Azo
Carbamyl	Cyano
Mercapto	Isocyano
Alkyl or arylthio	Thiocyanate
Sulfinyl	Nitroso
Sulfonyl	Nitro
Imino	Phospho
Alkamino or arylamino	Alkyl or aryl phosphate
Arsino	Alkyl or aryl phosphite
Alkyl or aryl arsenate	Alkyl or aryl phosphinate
Alkyl or aryl arsenite	Alkyl or aryl phosphonate
Alkyl or aryl antimonate	

II. Aromatic acids, represented by the general formula:

wherein Ar is an aromatic nucleus; X' may be a non-polar or polar radical attached to the aryl

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nucleus; X may be a hydrocarbon radical containing, if desired, a polar group; Z is a carboxylic acid group such as CYYH, wherein both Y's are selected independently from oxygen, sulfur, selenium and tellurium, said acid group being attached directly to the aryl nucleus or linked to it through X; m may be zero or an integer of from 1 to 3; n may be zero or one and y may be an integer of 1 or 2.

Representative acids are:

Benzoic
Phthalic
Toluic

15 Xylic

Phenyl fatty acids, e. g., phenyl acetic to phenyl stearic acids

Cinnamic acid

Salicylic acid

20 Mandelic acid

Phenyl glyoxylic

Benzoyl propionic acid

Phenyl laevulinic acid

Phenyl alkyl succinic acid

25 Benzyl alkyl succinic acid

Phenyl alkyl glutaric acid

o-Vinyl benzoic acid

Phenyl angelic acid

Naphthoic acid

30 Naphthyl stearic acid

Anthranilic acid

Mercapto (phenyl, tolyl, xylyl, xenyl, naphthyl anthracyl) fatty acids, e. g.—

Phenyl mercapto acetic to phenyl mercapto stearic acid

35

Ethyl mercapto phenyl acetic acid

Aryl mercapto benzene-4-carboxylic acid

III. Cyclic acids:

Naphthenic acids derived from petroleum hydrocarbons

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Hexahydrobenzoic acid

Tetrahydrotoluic acid

Alkyl cyclohexadiene carboxylic acid

Abietic acid

Alkyl hexahydrophthalic acid

45

Camphene-3-carboxylic acid

Camphoric acid

Cholic acid

Cyclohexylacetic acid

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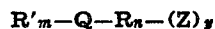
Cyclohexylbutyric acid

Cyclohexylcaproic acid

Cyclohexylpropionic acid

Cyclohexylvaleric acid

Fencholic acid, etc.

55**IV. Heterocyclic acids represented by the general formula:**

wherein Q is a mono- or polyheterocyclic nucleus containing at least one pentatomic or hexatomic ring; R' and R may be alkyl, aryl alkaryl, aryl-alkyl, alkoxy, aryloxy radicals; Z is a carboxyl radical; m may be zero or an integer of 1 and 2 and n may be zero or 1 and y may be an integer of 1, 2 or 3. Suitable heterocyclic acids include:

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Picolinic acid

Isonicotinic acid

Nicotonic acid

Quinolinic acid

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Vinchomeronic acid

Lutidinic acid

Berberonic acid

Alpha- and beta-carbocinchomeronic acid

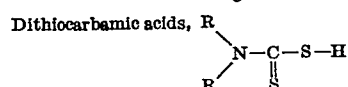
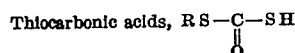
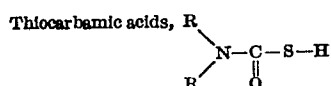
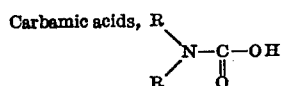
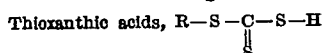
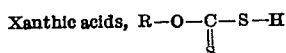
Quinic acid

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Pyrrole carboxylic acids

Quinoline carboxylic acids
Thiazole carboxylic acids
Thiophene carboxylic acids
B-indoleacetic acid
Ethyl furoic acid

V. Miscellaneous acids such as:



wherein R represents alkyl, aryl, arylalkyl, alkyl-aryl cyclo radicals and the like. Some specific compounds are:

Dibutyl mono and dithiocarbamic acid
Diethyl mono and dithiocarbamic acid
Dimethyl mono and dithiocarbamic acid
Diamyl mono and dithiocarbamic acid
Diocetyl mono and dithiocarbamic acid
Dipropyl mono and dithiocarbamic acid
N-ethyl-N-phenyl mono and dithiocarbamic acid
Octyl-butyl mono and dithiocarbamic acid
Dicyclohexyl mono and dithiocarbamic acid
Methyl-octyl mono and dithiocarbamic acid
Dibenzyl amyl dithiocarbamic acid
Abietic acid, shellac acids, etc.

VI. Organic compounds containing an inorganic acid radical:

- A. Benzene sulfonic acid
Toluene sulfonic acid
Triisopropyl naphthalene sulfonic acid
Diphenyl sulfonic acid
Polyalkyl aromatic sulfonic acid, e. g.—
Polyamyl naphthalene sulfonic acid
Diwax benzene sulfonic acid
Xylene sulfonic acid
Benzene disulfonic acid
Alkane sulfonic acids, e. g.—
Pentane- Nonane-
Octane- Dodecanesulfonic acid
Petroleum sulfonic acids derived from various petroleum fractions, such as:
Gas oil
Kerosene
Light oil
Turbine oil
Mineral lubrication oil
Heavy oil
Petroleum waxes, e. g.—
Petrolatum
Paraffin wax and mixtures of various hydrocarbon fractions
Wax sulfo salicylic acid
Diwax naphthalene sulfonic acids, etc.

B. Substituted phosphorus acids containing an organic substituent, e. g., the aliphatic, cyclo aliphatic and aromatic acid esters of phosphoric

acid, thiophosphoric acids, phosphorous acids and thiophosphorus acids, obtained by reacting $POCl_3$, P_2O_5 , PCl_5 , P_2S_5 , P_4S_7Br with any of the acids of groups I through VI and the alcohols of groups XI and XII. These inorganic phosphorus compounds may also be reacted with any of the materials listed under groups VII through X, as well as the alcohols and phenols of groups XI and XII and their esters with the acids of groups I through VI.

VII. Aliphatic hydrocarbons—acylic compounds:
A. Unsaturated paraffinic hydrocarbons, such as:

- Olefinic and polyolefinic materials, e. g.—
Hexylene
Heptylene
Butadiene
Pentadiene
and may include broadly-termed polyalkylene, e. g., polypropene, polypentenes as well as branched-chain unsaturated hydrocarbons, such as: isoolefins and isopolyolefins

Cyclic compounds:

- B. Saturated—
Cyclobutane
Cyclohexane
Cyclooctane and the like
C. Unsaturated—
Cyclopentadiene
Cyclohexene
Cyclooctene and the like

VIII. Aromatic hydrocarbons:

- A. Benzene
Naphthalene
Anthracene
Phenanthrene
Diphenyl
Diphenyl alkane
Stilbene and the like
B. Cyclic terpenes—
Cymene
Limonene
Pinene
Bornylene
Methene
Terpin, etc.

IX. Aldehydes:

- A. Aliphatic (saturated and unsaturated)—
Acetaldehyde
Propionaldehyde
Butyraldehyde
Caproaldehyde and the like
Acrolein
Citral, etc.
B. Aromatic—
Benzaldehyde
Cinnamaldehyde
Salicylaldehyde
Naphthaldehyde
Vanillin, etc.

X. Ketones:

- A. Aliphatic (saturated and unsaturated)—
Acetone
Butanone
Hexanone
Oleone
Palmitone
Methyl ethyl ketone
Methyl propyl ketone
Butenone

- Pentanone
Phorone
Pentanedione
Mesityl oxide
Diethyl ketone
3-methyl-heptanone
Diisobutyl ketone
Diacetone alcohol and the like
- B. Aromatic ketones—
Acetophenone
Propiophenone
Dibenzyl ketone
Benzyl phenyl ketone
Benzophenone and the like
- C. Cyclic ketones—
Cyclobutanone
Cyclopentanone
Quinones
Cycloheptanone
Pure isophorone
Cyclohexanone
Carvomenthone
Menthone
Pulegone
Carbone
Muscone

and isophorone bottoms, the manufacture of which will be fully described hereinafter.

Alcohols and phenols can be reacted with the colloidal basic metal compounds to form alcoholates and phenolates and derivatives thereof and used as improving agents.

XI. Alcohols and thioalcohols (RXH) wherein X is O, Se, Te and S and R represents alkyl, cycloalkyl, aralkyl radical or derivatives thereof:

- A. Aliphatic—
Methyl
Ethyl
Propyl
Butyl
Amyl
Hexyl
Octyl
Decyl
Dodecyl
Octadecyl
Carnaubyl
Crotonyl
Propargyl
Oleyl alcohols
Amyl
Butyl
Hexyl mercaptans, etc.
- B. Cyclic alcohols—
Cyclohexanol
Alkyl cyclohexanol, e. g.:
Methyl cyclohexanol
Amyl cyclohexanol
Cyclobutanol
Naphthenic alcohol, etc.
- C. Aromatic alcohol—
Benzyl
Phenyl ethyl
Dibenzyl
Tolyl
Phenyl octyl
Octadecyl benzyl alcohols, etc.
- D. Polyhydric aliphatic alcohols—
Glycols
Pinocols
Erythritol
Sorbitols and the like

E. Natural-occurring alcohols and synthetic alcohols—

- Alcohols as found in wool fat, sperm oil
- 5 Alcohols produced by oxidation of hydrocarbons, e. g.,
paraffin wax
sweat wax
petrolatum and the like
- 10 XII. Phenolic compounds (R—Ar—X—H)
wherein Ar is an aryl nucleus, X is O, S, Se, Te and R is a substituent non-polar and/or polar group:
- Phenol
- 15 Alkyl phenol
Dibutyl phenol and its thiophenols
Amyl phenol and its thiophenols
Tertiary butyl-, p-tertiary amyl-, octyl-, p-isooctyl-, isobutyl-, nonyl-, and cetyl phenols and thiophenols
- 20 Alkylamino phenol
Alkylamino naphthol
Catechol
Resorcinol
- 25 Pyrogallol

All of these compounds may contain substituent groups such as:

- Alkyl
- 30 Hydroxy
Amine
Nitro
Nitroso
Halogen
- 35 Carboxyl
Mercaptan, etc.

Illustrative products are: hydroquinone, quinone, orcinol, phloro-glucinol, cresols, thymol, saligenin, cinnamyl alcohol, methyl phenyl carbinol, eugenol, cardanols, etc. Also, the thiophenolic derivatives of these phenolic compounds may be used as well as various reaction products thereof such as obtained by reacting phenolic compounds with: SCl_2 , S_2Cl_2 , H_2S , ammonium hydrosulfide $\text{—H}_2\text{S}$, S, SO_2 and the like to form sulfide derivatives which may be represented broadly by the formula:



wherein Ar is an aryl nucleus, R is an alkyl, arylalkyl radical and the like, X is O, S, Se or Te, u is an integer of from 1 to 4 and Y may be a polar radical such as listed above either or both m and n may be zero or an integer of 1 or 2.

Phenolic condensation products may also be formed by reacting products under group X with aldehydes of the aliphatic, aromatic or cyclic type, specifically represented by formaldehyde, acetaldehyde, crotonaldehyde, butyraldehyde, benzaldehyde, furfuraldehyde and the like. The condensation reaction may be carried out at an elevated temperature using an acid or basic catalyst. Typical condensation reaction products may be formed as indicated:

- Octyl phenol-formaldehyde
- 70 Octyl phenol-acetaldehyde
Isooctyl phenol-acetaldehyde
Isooctyl phenol-crotonaldehyde
Octyl phenol-benzaldehyde
Octyl phenol-furfuraldehyde
- 75 Octyl thiophenol-furfuraldehyde

Octyl thiophenol-formaldehyde
Amyl phenol-formaldehyde
Amyl phenol-furfuraldehyde

XIII. Natural fats, oils and waxes and their derivatives and miscellaneous compounds:

A. Vegetable and animal oils, fats and waxes, such as—

Castor oil
Cocoanut oil
Corn oil
Cottonseed oil
Horse fat
Lard oil
Mutton tallow
Beef tallow
Neat's-foot oil
Palm oil
Peanut oil
Rapeseed oil
Soya bean oil
Sperm oil
Whale oil
Wool fat
Japan wax
Olefin waxes
Paraffin waxes
Wax tallings
Petrolatum
Vegetable and animal phosphatidic materials
Montan wax
Carnauba wax
Beeswax
Spermaceti
Castor oil distillate
Ozokerite, tall oil and the like

XIV. The products of the invention may contain additional substituent groups including:

Hydroxy, cyano, isocyano, cyanate,
Isocyanate, nitroso, nitro, and phospho

Preparation of colloidal inorganic bases

The preparation of the colloidal basic inorganic metal compounds can be varied depending upon the starting material and the end product desired. In the preparation of colloidal calcium hydroxide, for example, calcium chloride and sodium hydroxide in an organic solvent such as alcohol, e. g., methanol or ethanol or the like, are reacted, and the salt is removed by washing the colloidal mass formed decantation-wise with methanol.

The colloidal material in this stage is believed to comprise a mixture of colloidal calcium hydroxide and calcium alcoholate. This mixture can be hydrolyzed to convert the entire mixture to colloidal calcium hydroxide, and either the mixture or the colloidal calcium hydroxide or the organic salts thereof can be used to improve various compositions. In carrying out the hydrolysis step, the mixture can be hydrolyzed in the solvent or the mixture can be first dispersed in the base to be stabilized, which can be a hydrocarbon fuel or mineral oil, and hydrolysis carried out therein. In either case, the water and/or solvent can be removed from the mixture by distillation, vaporization and the like. Instead of starting with calcium chloride, other alkaline earth metal chlorides such as magnesium chloride, barium chloride and the like can be used to form the basic colloidal alkaline earth metal hydroxides or mixtures of said col-

loidal hydroxides and alcoholates. Other water-soluble salts may be utilized, such as nitrates, acetates, etc.

EXAMPLE A

A particularly desirable colloidal material of this invention was prepared in the following manner: About 2 mols of calcium chloride and 4 mols of sodium hydroxide were separately dissolved in an alcohol, such as methyl alcohol. The solutions were clarified to remove impurities and the calcium chloride solution then added rather rapidly to the sodium hydroxide solution and the entire mixture agitated and additional alcohol added until it was equal to about 9 to 10 liquid volumes. The mixture was damp-dried to form a cake and filtered to remove impurities. The damp cake containing colloidal calcium hydroxide was treated with isopropyl alcohol until the cake had a consolute temperature of between 60° and 65° C. with lubricating oil. If desired, the damp cake, after being dissolved in isopropyl alcohol, can be first hydrolyzed and the hydrolyzed product added to a mineral oil or any other desirable base. The colloidal product had a maximum particle dimension of less than 0.5 micron.

EXAMPLE B

About one-half of a mol of calcium chloride and about 1 mol of sodium hydroxide were separately dispersed or dissolved in isopropyl alcohol. The solutions were clarified to remove impurities, and the calcium chloride solution was added rather rapidly to the sodium hydroxide solution, and the entire mixture agitated and additional alcohol added, if desired. The mixture was damp-dried, and any entrained sodium chloride in the mixture was removed by conventional means, such as filtration, sedimentation, centrifuging, etc., and the damp cake colloidal calcium material was added to mineral oil. There was no tendency of the colloidal calcium material to separate out of the mineral oil even on storage for long periods of time.

A particularly preferred embodiment of the present invention is the use of the colloidal inorganic bases as neutralizing agents for organic acidic materials, and this is particularly applicable in the direct conversion of oil-soluble sulfonic acids formed during the sulfonation of hydrocarbon oils, into salts, which product can be used per se as a lubricant or the sulfonates thus formed can be extracted from the oil phase and used as detergents, rust-inhibitors, oil and fuel additives, in heat-transfer media, as emulsion breakers, insecticidal agents and the like. The sulfonates formed by the method briefly outlined above and which will hereinbelow be set forth in detail have entirely different properties from sulfonates made by the conventional methods well known in the art. For example, the basicity of calcium petroleum sulfonate can be expressed by the control ratio as follows:

$$\text{Control ratio} = \frac{\text{alkalinity (mg. KOH/g.)}}{\text{per cent of calcium sulfate ash}}$$

In the preparation of calcium petroleum sulfonate by conventional means, as will be described below, the control ratio generally varies between 2.0 and 2.7 with 2.4 as an average. Calcium petroleum sulfonates prepared by the method of this invention can have a control ratio substantially above 2.7 and even approaching a limiting value of 8.2.

The conventional method of producing petro-

leum sulfonates is by treating suitable petroleum stock with sulfuric acid. For example, a turbine oil having a Saybolt Universal viscosity at 100° F. of from about 400 to 540 seconds is treated with fuming sulfuric acid, preferably in small increments. After a calculated amount of sulfuric acid has been added to the oil, the sludge which is formed is removed and the acid-treated oil containing the oil-soluble sulfonic acids is neutralized with a solution of sodium hydroxide. The aqueous alkali solution is removed from the mixture, and the sodium sulfonate extracted with alcohol. The alcohol in the layer containing the sulfonates can be removed by distillation or by any other suitable means.

The conversion of sodium sulfonate to calcium sulfonate presents many difficulties. Acidifying the sodium sulfonate to free sulfonic acids and then neutralizing the free acid with lime is involved, and the product thus obtained contains a large amount of impurities. Also, the conversion of sodium sulfonates to calcium sulfonate by double decomposition is unsatisfactory due to the fact that stable emulsions of soap, water and oil form, which emulsions are difficult to resolve.

Preparation of organic sulfonates of inorganic colloidal bases

By the method of the present invention, highly basic sulfonates, having extremely high control ratio and which are free of contaminants can be prepared quickly and efficiently. For example, a turbine oil having a Saybolt Universal viscosity at 100° F. of about 400 to 540 seconds is treated with fuming sulfuric acid, and the sludge formed is removed. The acid-treated oil containing dissolved oil-soluble sulfonic acids is neutralized at a temperature ranging from room temperature to about 100° C. and preferably from 50° to 60° C. directly with colloidal calcium hydroxide or a mixture of colloidal calcium hydroxide and calcium alcoholate. The product after removal of the alcohol by conventional means thus formed can be used as a lubricant per se or the calcium sulfonate can be concentrated or extracted from the oil by any suitable means and thereafter used for any desired purpose.

The difference in properties of the two calcium petroleum sulfonates prepared by the methods set forth above are given below:

	Impurities			
	Control ratio	Na ₂ SO ₄	NaOH	Water
Ca sulfonate of this invention.	6.5	0	0	0
Commercial Ca sulfonate....	2.0-2.4	3-6.5%	.3-3.5	8.8

The versatility of the colloidal inorganic bases of this invention or mixtures containing them or products formed from them in compositions suitable for various uses is illustrated hereinbelow.

Lubricating compositions

EXAMPLE I

A mineral oil containing about 0.2% Ca salt of an oil-soluble condensation product of octyl phenol and formaldehyde was divided into two portions, and to one of them about 0.5% colloidal calcium hydroxide was added, and the detergency and anti-wear properties of the two samples were determined by the detergency test

as described in Ind. Eng. Chem. (Anal.) and the four-ball wear test, as described in the magazine Engineer, vol. 136, July 14, 1933. The results were as follows:

	Detergency	Wear, Percent
(1) Mineral oil.....	Poor.....	100
(2) Mineral oil+.2% Ca salt of oil-soluble condensation product of octyl phenol-formaldehyde.	Fair.....	50-60
(3) Mineral oil+.2% Ca salt of oil-soluble condensation product of octyl phenol-formaldehyde+.5% colloidal calcium hydroxide.	Excellent....	10

EXAMPLE II

Following the procedure as in Example I, a mineral oil containing 0.5% commercial calcium petroleum sulfonate and the same composition to which about 0.58% S. A. colloidal calcium hydroxide was added, and the compositions were subjected to the detergency and wear tests. The results were as follows:

	Detergency	Wear, Percent
(1) Mineral oil.....	Poor.....	100.
(2) Mineral oil+.5% calcium petroleum sulfonate.	Fair.....	above 70.
(3) Mineral oil+.5% calcium petroleum sulfonate+.58% S. A. colloidal calcium hydroxide.	Excellent....	10.

¹ S. A.=sulfate ash.

EXAMPLE III

The following compositions were tested in the manner described above, and the results were as follows:

	Detergency	Wear, Percent
(1) Mineral oil.....	Poor.....	100
(2) Mineral oil+.2% S. A. Ca salt of octyl phenol-formaldehyde condensation+.2% wt. Zn dibutyl dithiocarbamate+.0.2% wt. phenyl-alphanaphthyl amine.	Fair.....	40
(3) Composition 2)+.58% S. A. colloidal calcium hydroxide.	Excellent....	0

EXAMPLE IV

The following compositions were tested in the manner described above, and the results were as follows:

	Detergency	Wear, Percent
(1) Mineral oil.....	Poor.....	100.
(2) Mineral oil+.2% S. A. commercial Ca petroleum sulfonate.	Fair.....	above 70.
(3) Composition 2)+.58% of a mixture of colloidal calcium hydroxide and calcium methylate.	Excellent....	below 10.

EXAMPLE V

The following compositions were tested in the manner described above, and the results were as follows:

	Detergency	Wear, Percent
(1) Mineral oil.....	Poor.....	100
(2) Mineral oil+.1% dibutyl trichloromethane phosphonate.	Poor.....	15
(3) Composition 2)+.58% S. A. colloidal calcium hydroxide.	Excellent....	0

EXAMPLE VI

In order to show the effectiveness of lubricants compounded with colloidal materials of this invention as anti-wear agents, the following engine tests were made using the compositions identified below, and the results are graphically represented in Figures I and II.

Test	Composition
Figure I—Cold automotive wear as measured by the CFR gasoline test, 15 hours.	A. Mineral oil+0.15% S. A. Ca salt of octyl+phenol-formaldehyde condensation. B. Mineral oil plus colloidal calcium hydroxide in an amount equal to composition A. C. Mineral oil+0.2% S. A. Ca petroleum sulfonate. 0.2% S. A. Ca salt of octyl phenol-formaldehyde condensation product. 0.4% wt. zinc dibutyl dithiocarbamate. 0.2% wt. phenyl-alpha-naphthyl amine.
Figure II—Supercharged CFR diesel engine test.	D. Mineral oil+additives of composition C, but in which the calcium salts were made with colloidal calcium hydroxide and additionally the composition contains about 0.5% free colloidal calcium hydroxide.

Other lubricating compositions of this invention which are equivalent working examples of compositions as enumerated above are as follows:

- (1) Mineral oil containing from 0.1 to 1% of barium petroleum sulfonate and up to 5% colloidal barium hydroxide.
- (2) Mineral oil containing from 0.1 to 1% of calcium dichlorophenylstearate and up to 5% of colloidal calcium hydroxide.
- (3) Mineral oil containing from 0.1 to 5% of a mixture of colloidal calcium hydroxide and calcium methyleate.
- (4) Di(2-ethylhexyl) sebacate containing from 0.01 to .5% dibutyl trichloromethane phosphonate and colloidal calcium hydroxide.
- (5) Polymeric silicon compound containing from 0.1 to 5% of colloidal calcium hydroxide.
- (6) Mineral oil containing from 0.1 to 1% zinc petroleum sulfonate and colloidal zinc hydroxide.
- (7) Mineral oil containing from 0.1 to 1% zinc naphthenate and up to 5% colloidal zinc oxide and zinc alcoholate.
- (8) Mineral oil containing from 0.1 to 1% Pb naphthenate and up to 5% of colloidal lead hydroxide.
- (9) Mineral oil containing minor amount of potassium salt of P_2S_5 -olefin reaction product and colloidal calcium hydroxide.
- (10) Mineral oil containing a minor amount of calcium stearate and colloidal ferric sulfide.

Fuel compositions

Various hydrocarbon fuels and particularly high sulfur fuels can be markedly improved by addition thereto of the colloidal materials of this invention. Also, tetra-alkyl lead containing fuels as well as hydrocarbon fuels stabilized with aromatic amines and other improving agents can be still further improved by addition thereto of the colloidal material of this invention or organic salt formed from these colloidal materials.

EXAMPLE Ia

A diesel engine was operated with a high sulfur hydrocarbon fuel (above 1% sulfur) for 72 hours, and the condition of the engine parts was observed. The engine was reconditioned and was

again operated for 72 hours with a high sulfur hydrocarbon fuel (above 1% sulfur) but to which about 1% colloidal calcium hydroxide was added. The results were as follows:

	Condition of Engine
High sulfur fuel.....	Very poor, badly fouled, and considerable wear noted.
High sulfur fuel containing colloidal calcium hydroxide.....	Engine clean and no wear noted.

EXAMPLE IIa

- A one-cylinder, four-stroke cycle, liquid-cooled diesel engine having a 3¼-inch cylinder bore and a 4½-inch stroke was operated at 1400 revolutions per minute under a load of 4½ brake horsepower; the jacket and oil temperatures were 100° C. and 70° C., respectively; SAE grade 30 oil was used as the lubricant. The operations were effected with a diesel fuel having a cetane number of 50 and containing 0.25% sulfur, and with the same fuel also containing 0.04% calcium naphthenate and 0.1% colloidal calcium hydroxide. The results were as follows:

	Wear (mg./hr.)
No additive.....	1.55
Fuel containing 0.04% calcium naphthenate and 0.1% colloidal calcium hydroxide.....	1.20+

EXAMPLE IIIa

- A motor fuel for internal combustion engines containing 3 to 4 cc. TEL per gallon of the fuel and about one theoretical equivalent of a scavenger mixture in the ratio of 2:1 of ethylene bromide and ethylene chloride was divided into two portions to one of which was added about 0.1% colloidal calcium hydroxide, and the two compositions were then subjected to the ASTM Proposed Test for Gum Formation, modified June 1942. The fuel improved by addition of colloidal calcium hydroxide was substantially free of any gum-forming tendencies while the fuel free from the colloidal calcium hydroxide tended to form heavy gum deposits.

Grease compositions

- Stable greases having outstanding structure, texture and stability can be prepared by use of the colloidal inorganic bases of this invention as the saponifying or neutralizing agents. A simple procedure for preparing greases using neutralizing agents of this invention consists in adding a calculated amount of fatty acid or glyceride thereof or their mixtures to a base oil which can be a natural mineral oil or a synthetic base such as esters of polycarboxylic acid [di-(2-ethylhexyl)sebacate] and the entire mixture heated to an elevated temperature of above 350° F. and preferably above 400° F. The mixture is heated with constant stirring until a homogeneous mixture is obtained, and then the colloidal inorganic base is added in an amount sufficient to completely neutralize the fatty material. An excess of the colloidal inorganic base can be used. The colloidal inorganic base can be incorporated in an aqueous or alcoholic solution and the entire mass heated until a grease has formed. The grease is then cooled, homogenized if necessary and packaged.

EXAMPLE I*B*

A mixture of hydrogenated fish oil acids and hydrogenated castor oil in the mol ratio of about 7 to 1 was admixed with about twice the amount of mineral oil, and the mixture heated at about 80° C. until the fatty materials were melted. Heating was continued, and while continuously stirring, an aqueous solution of colloidal calcium hydroxide in an amount which is in slight excess (.1 and .5% excess) to that which is necessary to neutralize the fatty materials is added to the mixture. The temperature is increased to 180° to 250° C. and sufficient mineral oil is slowly added so that the soap concentration in the final product should vary between 6 and 8% by weight. The grease is allowed to cool slowly to room temperature and packaged.

EXAMPLE II*B*

Following the above procedure, a novel grease was prepared by using as the neutralizing agent (in slight excess) a mixture of colloidal calcium hydroxide and calcium alcoholate.

These greases had high drop points, improved water resistance and were extremely stable under static and dynamic conditions.

EXAMPLE III*B*

Following the above procedure of Example I*a*, a synthetic base grease was prepared by using di-(2-ethylhexyl) sebacate as the base.

The soap content can be varied over wide limits such as from 6 to 30% and, in addition, oxidation stabilizers, e. g., phenyl-alpha-naphthylamine, corrosion inhibitors, anti-wear agents (zinc dibutyl dithiocarbamate) as well as various fillers, such as graphite, mica, clays, asbestos and the like, can be incorporated into the grease composition.

Other grease compositions which can be produced using colloidal inorganic bases as the neutralizing agents to form soaps include: barium stearate, magnesium stearate, calcium oleate, calcium oleate-12-hydroxy stearate, zinc stearate, barium stearate-acetate, lead oleate and the like.

Rust-preventive compositions

Rust-preventive compositions for metal surface can be improved by addition thereto of colloidal inorganic bases of this invention and/or organic salts produced from such colloidal materials. The base can be volatile hydrocarbons, waxes, asphaltic materials and mixtures thereof.

EXAMPLE I*c*

A rust-inhibiting composition can be made by heating and mixing about 1 part of an oxidized paraffin wax and about 4 parts of a light volatile hydrocarbon until a homogeneous mass has been obtained. To this mass is added a minor amount of from 2 to 10% of calcium petroleum sulfonate prepared in the manner described on pages 19 and 20 and about 1 to 5% isobutyl alcohol.

EXAMPLE II*c*

A rust-inhibiting composition was prepared in the manner as disclosed above, but instead of calcium petroleum sulfonate, a mixture of colloidal calcium salt of naphthenic acid and colloidal lead salt of naphthenic acid was used.

In order to determine the protective properties of compositions I*c* and II*c*, metal panels were coated with these compositions and subjected to the salt spray test. In this test, polished steel

panels which have been coated with compositions I*c* and II*c* were exposed continuously at a constant temperature (95° or 100° F.) to a salt mist or fog which is produced by the atomization of a 20% sodium chloride solution. The average time until rusting occurs on the face of the panel is taken as the life of the coating.

Composition	Time	Observation
Example I <i>c</i>	10 days.....	No rust.
Example II <i>c</i>	do.....	Do.
Mineral oil.....	2 hours.....	Rust.
Paraffin wax.....	5 hours.....	Do.

Miscellaneous compositions and uses for additives of this invention

A. Colloidal inorganic materials of this invention or derivatives thereof can be used in various other industrial applications from those enumerated above. Thus, in the open-hearth steel process, the fuel used must be selected judiciously. High sulfur fuels although desirable because of low cost cannot be used in certain cases because of the tendency of the sulfur to combine with the limestone over the steel puddles. By addition of colloidal calcium hydroxide and/or organic salts thereof to such fuels, this can be overcome without affecting the steel produced in any way. Additionally, by use of fuels containing colloidal additives of this invention, the thickness of the limestone layer can be reduced, the steel thereby can be heated faster, the decreased heat load lengthening the life of the furnace lining, resulting in considerable saving in fuel.

B. Colloidal materials of this invention can also be used as flattening or anti-gloss agents in varnish and lacquers without affecting transparency of the product. Thus, the addition of from 0.1 to 5% of colloidal calcium hydroxide to varnish and/or lacquers results in a product having good anti-gloss properties.

C. Colloidal materials of this invention can be used as stabilizers of various polymeric materials. For example, polyvinyl chloride polymers and copolymers can be stabilized against the deteriorating effects of heat and light by addition thereto of from about 0.01% to about 5% of colloidal calcium hydroxide or a mixture of colloidal calcium hydroxide and calcium methylate.

Colloidal inorganic metallic bases and derivatives thereof can be used to produce improved limed oils for use as gloss oils, as well as in cleaners and polishes or as binding agents or as adhesive improving agents and the like.

The vehicles to which additives of this invention can be added, generally in amounts of from 0.01 to 10% and preferably from 0.1 to 5%, should preferably be substantially neutral, although they may be weakly acidic or basic, preferably having acidic or basic dissociation constants not above 10⁻⁸. Both polar and non-polar vehicles may be employed. Among the former are water; water-soluble and water-insoluble alcohols such as methyl, ethyl, propyl, isopropyl, butyl, hexyl, cyclohexyl, methylcyclohexyl, lauryl, cetyl, stearyl, oleyl, allyl, benzyl, etc., alcohols; monomeric polyhydric alcohols such as ethylene glycol, propylene glycol, butylene glycol, cetene glycol, glycerol, methyl glycerol, etc.; phenols, and various alkyl phenols and thiophenols; ketones such as acetone, methyl ethyl ketone, diethyl ketone, methyl propyl ketone, methyl butyl ketone, di-

propyl ketone, cyclohexanone, and higher ketones; keto alcohols; ethers such as diethyl ether, diisopropyl ether, beta-beta-dichlorodiethyl ether, diphenyl oxide, chlorinated diphenyl oxide, diethylene glycol, triethylene glycol; neutral esters of carboxylic and other acids such as ethyl, propyl, butyl, amyl, octyl, stearyl, oleyl, phenyl, cresyl and higher acetates, propionates, butyrates, lactates, laurates, myristates, palmitates, stearates, oleates, ricinoleates, phthalates, salicylates, carbonates; natural waxes such as carnauba wax, candelilla wax, japan wax, jojoba oil, sperm oil; fats such as tallow, lard oil, olive oil, cottonseed oil, Perilla oil, linseed oil, tung oil, soya bean oil, flaxseed oil, castor oil, etc.; as well as fractions and derivatives thereof.

Vehicles of little or no polarity comprise hydrocarbons such as liquid butane, pentanes; hexanes, heptanes, octanes, octenes, benzene, toluene, xylene, cumene, indene, hydrindene, alkyl naphthalenes, gasoline, kerosene, hydrocarbon fuel oil, gas oil, turbine oil, motor oil, mineral spirits, aromatic solvents, petroleum lubricating oils which may or may not be refined as by solvent extraction, and treatment, etc., and which may be soap thickened to form greases, petrolatum, paraffin waxes, albino asphalts, etc.

Also, synthetic oils may be used as the vehicles, such as polymerized olefins, polymers and copolymers of alkylene glycols and alkylene oxides; organic esters, e. g., 2-ethylhexyl sebacate, allyl laurate, and polymers thereof; dioctyl phthalate, trioctyl phosphate, polymeric tetrahydrofuran, polyalkyl siloxanes and silicates fluorohydrocarbons and the like. Mixtures of synthetic and natural lubricants and oils may be used. In addition, resinous materials such as petroleum resins, natural resins as rosin, resins formed by polymerization of drying fatty oils, phenol-formaldehyde resins, glyptal-type resins formed by esterification of polyhydric alcohols with polycarboxylic acids can be used.

Still another class of vehicles to which condensation products of this invention are suitably added are water-in-oil and oil-in-water emulsions suitable for various uses such as lubricating, cooling, rust inhibiting, and the like, as well as hydraulic fluids, heat-transfer fluids, fireproofing compositions, agricultural compositions such as insecticides, fungicides, etc.

To compositions of this invention containing the colloidal materials or organic salts of this invention can be added, e. g., non-metallic detergents such as the phosphatides lecithin and cephalin, certain fatty oils as rapeseed oils, voltolized fatty or mineral oils and the like.

Anti-oxidants comprise several types, for example, alkyl phenols such as 2,4,6-trimethyl phenol, 2,4-dimethyl-6-tertiary-butyl phenol, 2,6-ditertiary-butyl-4-methyl-phenol, and the like; amino phenols as benzyl amino phenols; amines such as dibutyl-phenylene diamine, diphenyl amine, phenyl beta-naphthylamine, phenyl-alpha-naphthylamine and dibutylamine.

Corrosion inhibitors or anti-rusting compounds may also be present, such as dicarboxylic acids of 16 and more carbon atoms, e. g., octadeceny succinic acid; alkali metal and alkaline earth metal salts of sulfonic acids and fatty acids, organic compounds containing an acidic radical in close proximity to a mercapto, nitrile, nitro or nitroso group (e. g., alpha cyano stearic acid).

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g., urethanes,

allophanates, carbazides, carbazones, etc.; polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high molecular weight oil-soluble compounds.

Depending upon the additional additive used and conditions under which it is used, the amount of additive used may vary from 0.01 to 2% or higher. However, substantial improvement is obtained by using amounts ranging from 0.1 to 0.5% in combination with reaction products of this invention.

The invention claimed is:

1. An organic oleaginous fluid stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a detergent amount of an oil dispersible detergent of the class consisting of phosphatides, fatty oils, voltolized fatty oils, voltolized mineral oils, polyvalent metal salts of carboxylic acids, polyvalent metal salts of sulfonic acids, polyvalent metal salts of phosphorus acids and polyvalent metal salts of alkyl phenol-formaldehyde condensation products and a minor amount of a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 1.0μ , said colloidal material being prepared in an organic solvent by reaction of an inorganic salt of a polyvalent metal and an alkali metal alcoholate whereby a basic inorganic compound of said polyvalent metal is prepared in colloidal form.

2. An organic oleaginous fluid stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a detergent amount of an oil dispersible detergent of the class consisting of phosphatides, fatty oils, voltolized fatty oils, voltolized mineral oils, polyvalent metal salts of carboxylic acids, polyvalent metal salts of sulfonic acids, polyvalent metal salts of phosphorus acids and polyvalent metal salts of alkyl phenol-formaldehyde condensation products and a minor amount of a salt of an organic acid and of a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared in an organic solvent by reaction of an inorganic salt of a polyvalent metal and an alkali metal alcoholate whereby a basic inorganic compound of said polyvalent metal is prepared in colloidal form.

3. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a detergent amount of an oil dispersible detergent of the class consisting of phosphatides, fatty oils, voltolized fatty oils, voltolized mineral oils, polyvalent metal salts of carboxylic acids, polyvalent metal salts of sulfonic acids, polyvalent metal salts of phosphorus acids, and polyvalent metal salts of alkyl phenol-formaldehyde condensation products, and a minor amount of a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared in an organic solvent by reaction of an inorganic salt of a polyvalent metal and an alkali metal basic compound soluble in said solvent whereby a basic inorganic compound of said polyvalent metal is prepared in colloidal form.

4. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of an organic salt of a colloidal metallic inorganic base, the colloidal

particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared in an organic solvent by reaction of an inorganic salt of a polyvalent metal and an alkali metal basic compound soluble in said solvent, whereby a basic inorganic compound of said polyvalent metal is prepared in colloidal form.

5 5. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a detergent amount of an oil dispersible detergent of the class consisting of phosphatides, fatty oils, voltolized fatty oils, voltolized mineral oils, polyvalent metal salts of carboxylic acids, polyvalent metal salts of sulfonic acids, polyvalent metal salts of phosphorous acids and polyvalent metal salts of alkyl phenol-formaldehyde condensation products, and a minor amount of a colloidal inorganic alkaline earth metal basic compound, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared in an organic solvent by reaction of an inorganic salt of a polyvalent metal and an alkali metal basic compound soluble in said solvent, whereby a basic inorganic compound of said polyvalent metal is prepared in colloidal form.

6. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a detergent amount of an oil dispersible detergent of the class consisting of phosphatides, fatty oils, voltolized fatty oils, voltolized mineral oils, polyvalent metal salts of carboxylic acids, polyvalent metal salts of sulfonic acids, polyvalent metal salts of phosphorous acids and polyvalent metal salts of alkyl phenol-formaldehyde condensation products, and a minor amount of colloidal calcium hydroxide, the colloidal particles of which have at least one dimension of 0.001μ to 0.5μ , said colloidal calcium hydroxide being prepared by dispersing a mixture of calcium chloride and sodium hydroxide in alcohol, reacting said mixture, and thereafter removing the colloidal calcium hydroxide formed by decantation.

7. An improved method of producing petroleum sulfonates by direct neutralization of an acid-oil containing oil-soluble sulfonic acids with a colloidal anhydrous inorganic metallic base compound of dimensional range of from 0.001μ to 0.5μ .

8. An improved method of producing petroleum sulfonates by direct neutralization of an acid-oil containing oil-soluble sulfonic acids with a colloidal anhydrous alkaline earth metal compound of dimensional range of from 0.001μ to 0.5μ .

9. An improved method of producing petroleum sulfonates by direct neutralization of an acid-oil containing oil-soluble sulfonic acids with colloidal anhydrous calcium hydroxide of dimensional range of from 0.001μ to 0.5μ .

10. An organic lubricating oil stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 1.0μ , said colloidal material being prepared by dispersal of a base metal alcoholate in an organic solvent and thereafter hydrolyzing said alcoholate.

11. An organic lubricating oil stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of a salt of an aromatic hydroxy compound, the cationic portion being a colloidal me-

tallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared by dispersal of a base metal alcoholate in an organic solvent and thereafter hydrolyzing said alcoholate.

12. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared by dispersal of a base metal alcoholate in an organic solvent and thereafter hydrolyzing said alcoholate.

13. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of an organic salt, the cationic portion being a colloidal metallic inorganic base, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared by dispersal of a base metal alcoholate in an organic solvent and thereafter hydrolyzing said alcoholate.

14. A hydrocarbon composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of a colloidal inorganic alkaline earth metal compound, the colloidal particles being of dimensional range of from 0.001μ to 0.5μ , said colloidal material being prepared by dispersal of a base metal alcoholate in an organic solvent and thereafter hydrolyzing said alcoholate.

15. A petroleum composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of colloidal calcium hydroxide, the colloidal particles of which have at least one dimension of from 0.001μ to 0.5μ , said colloidal calcium hydroxide being prepared by dispersing a mixture of calcium chloride and sodium hydroxide in alcohol, reacting said mixture, and thereafter removing the colloidal calcium hydroxide formed by decantation.

16. A mineral oil composition of matter stabilized against deterioration due to acidic impurities and degradation products by addition thereto of a minor amount of colloidal calcium hydroxide, the colloidal particles of which have at least one dimension of from 0.001μ to 0.5μ , said colloidal calcium hydroxide being prepared by dispersing a mixture of calcium chloride and sodium hydroxide in alcohol, reacting said mixture, and thereafter removing the colloidal calcium hydroxide formed by decantation.

17. A mineral oil composition stabilized against deterioration by addition thereto of a petroleum sulfonate produced by the method of claim 7.

18. A mineral oil composition stabilized against deterioration by addition thereto of a petroleum sulfonate produced by the method of claim 8.

19. A mineral oil composition stabilized against deterioration by addition thereto of a petroleum sulfonate produced by the method of claim 9.

20. A mineral oil composition containing between about 0.01% and about 10% by weight each of an oil-soluble hydrocarbon sulfonate and a colloidal calcium hydroxide as defined in claim 6.

21. A mineral oil composition containing between about 0.01% and about 10% by weight each of a calcium salt of an oil-soluble condensation product of octyl phenolformaldehyde and a colloidal calcium hydroxide as defined in claim 6.

22. A mineral oil composition containing be-

tween about 0.01% and about 10% by weight each of a calcium petroleum sulfonate and a colloidal calcium hydroxide as defined in claim 6.

23. A mineral oil composition containing between about 0.01% and about 10% by weight each of a calcium salt of oil-soluble condensation product of octyl phenolformaldehyde, zinc dibutyl dithiocarbamate, phenyl-alpha-naphthyl amine, and a colloidal calcium hydroxide as defined in claim 6.

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