United States Patent Office

2,777,874

Patented Jan. 15, 1957

2,777,874

METAL COMPLEXES AND METHODS OF MAKING SAME

Peter A. Asseff, Cleveland, Thomas W. Mastin, Willoughby, and Alan Rhodes, Euclid, Ohio, assignors to The Lubrizol Corporation, Wickliffe, Ohio, a corporation of Ohio

No Drawing. Application November 3, 1952, Serial No. 318,528

26 Claims. (Cl. 260—504)

This application is a continuation-in-part of our co-pending application Serial No. 216,101, filed March 16, 1951, and is a continuation-in-part also of our related co-pending applications Serial No. 216,102, now Patent No. 2,617,049; 216,103, now Patent No. 2,616,924; 224,458, now Patent No. 2,695,910; 263,961, now Patent No. 2,616,925; 263,962, now Patent No. 2,616,911; 263,963, now Patent No. 2,616,904; 276,461, now abandoned; and 276,462, now Patent No. 2,616,905.

In our aforesaid parent application Serial No. 216,101, there is disclosed the process of producing certain novel organic salt complexes and the novel products resulting from such processes.

The present invention is concerned with the use of certain features of the process to which our said parent applications relate for the production of complexes which have particular properties which suit them for particular uses.

From the processes contemplated by our said parent applications, it is possible to produce organic metal complexes in which the metal content thereof is derived at least in part from the metal present in the normal salt of the starting acid, and metal contributed to the complex by an inorganic basically reacting material; and, optionally, according to the processes of our said parent applications, metal in the complex may be derived from the so-called promoter material.

The present invention is concerned with a process wherein the metal is derived from only two sources: specifically, (1) from the normal salt of the starting acid; and (2) from the so-called promoter material. The present process is characterized further in that the reaction mass which thus includes the starting acid, or, more particularly, its normal salt, and the metal containing promoter material is subjected to an acid treatment step utilizing for that purpose an acidic material which has an ionization constant greater than the ionization constant of the organic acid reacting compound from which the anion of the promoter material is derived.

Where reference is made throughout this specification and in the attendant claims to the starting acid, or the "acidic material," we shall presently give examples. We intend to include in the product of a single complex material, or product, one or more of different such acids or the normal salts, since as will be presently explained, there are unusual advantages to be derived from the use of an admixture of different starting acids.

When we refer to the fact that the entire metal content of the complexes of this invention are derived from the normal salt of the starting acids and from the promoter material, it is to be understood that in confecting the reaction mass, we may use either the starting acid, as such, together with an amount of basically reacting material substantially equal to that required stoichiometrically to neutralize the amount of acids used, or we may utilize the normal metal salt with no free base present in the reaction mass. Throughout the following description there will be given numerous examples of starting acids and numerous examples of metals. As indicated above, it is within the contemplation of our invention to utilize mixtures of different acids as well as mixtures of different metals. The various combinations of reaction mass components which may thus be utilized include, for example, the following:

1. A single acid entirely neutralized with a single metal employed in conjunction with a promoter containing the same metal;
2. A single acid in which different portions thereof are neutralized by different metals employed in conjunction with a promoter material which may contain one or more metals, as by having a plurality of different metals associated with the same kind of anions, or a plurality of different kinds of anions associated with the same type cation.

From the foregoing, it will be apparent that there are many possible ways in which a plurality of starting acid anions and a plurality of metals may be included in the resultant complex. At this point, it should be observed also that, whereas all of the metal in the complex other than that derived from the normal salt of the starting acid is contributed to the complex by the promoter material used, it is nevertheless within the contemplation of our invention to use along with such metal containing promoter materials, promoters which are metal free. It is also within the contemplation of our invention to use, in lieu of the metal containing promoter, an admixture of metal-free promoter plus an amount of free inorganic metal base up to but not greater than that amount required stoichiometrically to form the salt of the metal-free promoter. This refinement finds particular utility when the inorganic metal base is highly alkaline in nature, for example, the alkali and alkaline earth oxides and hydroxides, particularly barium oxide and barium hydroxide. The use of some metal-free promoter material is highly desirable for certain purposes since the complex produced thereby tends to be more truly homogeneous, and the behavior of the reaction mass during the processing is such that the processing is easier when some metal-free promoter is used.

In the following section of the specification, we shall first list the acidic materials which may thus be used in providing the anion of the normal metal salt, it being understood, as indicated above, that various combinations of such acidic starting metals may be used or their salts.

THE OIL SOLUBLE ACIDIC ORGANIC COMPOUNDS AND/OR THE SALTS THEREOF

The oil-soluble acidic organic compounds and/or the salts thereof employed for the purposes of the present invention include a variety of classes of compounds, such as the aliphatic or aromatic organic acids e. g., the sulfur acids, the carboxylic acids, acids of phosphorus, etc., or the salts of such acids, including the corresponding thio acids of any of the foregoing as well as mixtures of the same. The aromatic compounds include the mono- or polynuclear types of the benzenoid and heterocyclic classes; whereas the aliphatic compounds are for example the acyclic and cyloaliphatic compounds. It is intended that all such compounds be oil soluble for this invention, and in the preferred instance "oil solubility" is meant that the salt of the acidic organic compound will possess a solubility of at least about 10% in Pennsylvania conventionally refined mineral oil having a viscosity of about 150 SUS at 100° F., or what is commonly known as Pennsylvania 150 neutral oil.

More specific illustrations of the types of oil-soluble acidic organic compounds or the salts thereof which can be employed are, for example,

- (1) Organic acids in which:
  - (*a*) Sulfur is the acid-forming element, for example:
    - Organic acids containing the $-SO_3H$ radical, e. g.:
      - Sulfonic acids
      - Sulfamic acids
    - Thiosulfonic acids
    - Organic acids containing the $-SO_2H$ radical, e. g.:
      - Sulfinic acids
      - Thionamic acids
    - Sulfenic acids
    - Partial esters of polybasic inorganic sulfur acids, e. g.:
      - Mono-esters of sulfuric acid
      - Mono-esters of sulfurous acid
      - Mono-esters of thiosulfuric acid
  - (*b*) Selenium is the acid-forming element, for example:
    - Selenonic acids
    - Seleninic acids
    - Partial esters of polybasic inorganic selenium acids, e. g.:
      - Mono-esters of selenic acid
      - Mono-esters of selenious acid
  - (*c*) Tellurim is the acid forming element, for example:
    - Telluronic acids
    - Tellurinic acids
    - Partial esters of polybasic inorganic tellurium acids, e. g.:
      - Mono-esters of telluric acid
      - Mono-esters of tellurous acid
  - (*d*) Carbon is the acid-forming element, for example:
    - Organic acids containing the $-CO_2H$ radical, e. g.:
      - Carboxylic acids
      - N-substituted carbamic acid
    - Organic acids containing the $-CX_2H$ radical, where X is either O or S and at least one X is sulfur, e. g.:
      - Thiocarboxylic acids
      - N-substituted thiocarbamic acid
    - Seleno-carboxylic acids
    - Telluro-carboxylic acids
  - (*e*) Nitrogen is the acid-forming element, for example:
    - Nitrolic acids: $R-C(:NOH)NO_2$
    - Nitrosolic acids: $R-C(:NOH)NO$
    - Nitronic acids: $R_2C:NOOH$
    - Nitroic acids: $RNO(OH)_2$
    - Carbazylic acids: $R-C(:NH)NH_2$
  - (*f*) Phosphorus is the acid-forming element, for example:
    - Phosphinic acids; $R_xP(OH)_{3-x}$ where x is 1 or 2
    - Phosphonic acids; $R_xPO(OH)_{3-x}$ where x is 1 or 2
    - Thiophosphinic acids; $R_xP(ZH)_{3-x}$ where x is 1 or 2, and where Z is either O or S and at least one Z is sulfur
    - Thiophosphonic acids; $R_xPZ(ZH)_{3-x}$ where x is 1 or 2, and where Z is either O or S and at least one Z is sulfur
    - Partial esters of polybasic inorganic phosphorus acids, for example:
      - Mono-esters of phosphorous acid
      - Mono-esters of thiophosphorous acids
      - Mono- and di-esters of phosphoric acid
      - Mono- and di-esters of thiophosphoric acids
      - Partial esters of pyrophosphoric acid
      - Partial esters of pyrophosphorous acid
      - Partial esters of polyphosphoric acids
      - Partial esters of polyphosphorous acids
      - Partial esters of pyrothiophosphoric acids
      - Partial esters of pyrothiophosphorous acids
      - Partial esters of thiopolyphosphoric acids
      - Partial esters of thiopolyphosphorous acids
  - (*g*) Arsenic is the acid-forming element, for example:
    - Arsinic acids
    - Arsonic acids
    - Partial esters of polybasic, inorganic, arsenic-derived acids, e. g.:
      - Mono-esters of arsenious acid
      - Mono- and di-esters of arsenic acid
  - (*h*) Antimony is the acid-forming element, for example:
    - Stibonic acids
    - Partial esters of polybasic inorganic antimony acids, e. g.:
      - Mono-esters of antimonous acid
      - Mono- and di-esters of antimonic acid
  - (*i*) Silicon is the acid-forming element, for example:
    - Siliconic acids: $RSiOOH$
    - Partial esters of silicic acid
  - (*j*) Tin is the acid-forming element, for example: stannonic acids; $RSnOOH$
  - (*k*) Lead is the acid-forming element, for example: plumbonic acids; $R_2Pb(OH)_2$ and $RPbOOH$
- (2) Salts of the organic acids listed under (1).

The salts included under (2) are metal salts and organic salts. The metal salts include the mono or polyvalent metals, such as the light or heavy metals, or the alkali and alkaline earth metals such as sodium, lithium, potassium, calcium, barium, strontium, magnesium, and other specific examples, are zinc, cadmium, mercury, lead, tin, iron, cobalt, copper, manganese, aluminum, chromium, nickel, etc. The organic salts include those formed with ammonia and substituted ammonias, such as mono-, di-, and tri-ethanolamines; ethyl-, propyl-, butyl-, and amylamines, etc., piperidine, pyridine, etc.

The following list of compounds serve to more specifically illustrate the types of acidic organic compounds which are contemplated for this invention. However, it should be understood that for every acidic organic compound enumerated, a corresponding specific metal or organic salt of the types discussed above and illustrated below are intended.

- Mahogany sulfonic acids
- Petrolatum sulfonic acids
- Substituted aromatic sulfonic acids, e. g.:
  - Mono- and poly-wax substituted naphthalene sulfonic acids
  - Mono- and poly-wax substituted phenol sulfonic acids
  - Mono- and poly-wax substituted diphenyl ether sulfonic acids
  - Mono- and poly-wax substituted naphthalene disulfide sulfonic acids
  - Mono- and poly-wax substituted diphenyl amine sulfonic acids
  - Mono- and poly-wax substituted thiophene sulfonic acids
  - Mono- and poly-wax substituted alpha-chloronaphthalene sulfonic acids
  - N,N-di-wax aniline sulfonic acids
  - Fuel oil substituted naphthalene sulfonic acids
  - Fuel oil substituted diphenyl ether sulfonic acids
  - Kerosene substituted diphenyl ether sulfonic acids
  - Petrolatum substituted naphthalene sulfonic acids
  - Petrolatum substituted phenol sulfonic acids
  - Petrolatum substituted anthracene sulfonic acids
  - Petrolatum substituted naphthalene disulfide sulfonic acids
  - Ceryl-diphenylene sulfonic acids
  - Cetyl chloro-benzene sulfonic acids
  - Cetyl-phenol sulfonic acids
  - Cetyl-phenol disulfide sulfonic acids
  - Cetyl-phenol monosulfide sulfonic acids
  - Di-cetyl thianthrene sulfonic acids
  - Cetoxy capryl benzene sulfonic acids
  - Di-lauryl chlorophenol sulfonic acids
  - Di-lauryl beta-naphthol sulfonic acids
  - Tri-lauryl phenothioxine sulfonic acids
  - Di-lauryl mono-chloro diphenyl ether sulfonic acids
  - Bis-(di-isobutyl-carbinyl) naphthalene sulfonic acids
  - Di-capryl nitro-naphthalene sulfonic acids
  - Tri-capryl benzene sulfonic acids
  - Tri-capryl diphenyl sulfide sulfonic acids
  - Di-capryl methyl naphthalene sulfonic acids
  - Di-capryl ortho-phenylphenol sulfonic acids
  - Tetra-capryl meta-terphenyl sulfonic acids
  - Di-capryl thiophene sulfonic acids
  - Diisobutyl (2,4,5-trichlorobenzyloxy) benzene sulfonic acids
  - p-Capryl-o-cyclohexyl phenol sulfonic acids
  - Bis-(diisobutyl) naphthalene sulfonic acids
  - Tris-(diisobutyl) anthracene sulfonic acids
  - Bis-(diisobutyl) diphenylene sulfide sulfonic acids
- Aliphatic sulfonic acids (acyclic), e. g.:
  - Paraffin wax sulfonic acids
  - Unsaturated paraffin wax sulfonic acids
  - Hydroxyl-substituted paraffin wax sulfonic acids
  - Nitroso-substituted paraffin wax sulfonic acids
  - Chloro-substituted paraffin wax sulfonic acids
  - Unsaturated sulfonic acids derived from polyalkylenes containing at least 15 carbon atoms, e. g.:
    - Tetraisobutylene sulfonic acids
    - Tetra-amylene sulfonic acids
- Cycloaliphatic sulfonic acids, e. g.:
  - Petroleum naphthene sulfonic acids
  - Cetyl-cyclopentyl sulfonic acids
  - Lauryl-cyclohexyl sulfonic acids
  - Bis-(diisobutyl) cyclohexyl sulfonic acids
  - Mono- and poly-wax substituted cyclohexyl sulfonic acids

Additional examples of sulphonic acids and/or salts thereof which can be employed as starting materials are disclosed in the following U. S. patents: 2,174,110; 2,174,506; 2,174,508; 2,193,824; 2,197,800; 2,202,791; 2,212,786; 2,213,360; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,276,097; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,259; 2,337,552; 2,346,568; 2,366,027; 2,374,193; and 2,383,319.

However, preferably, it is intended to use as starting materials, the products derived in accordance with the processes of the above enumerated patents on the following initial materials:

- Lubricating oil fractions
- Petrolatum
- Paraffin wax
- Paraffin oil
- Petroleum naphthenes
- White oil
- Gas oil
- Abietane
- The higher alkylated cyclohexanes, e. g.:
  - Cetyl-cyclohexane
  - Bis-(diisobutyl) cyclohexanes
- The higher alkylated cyclopentanes, e. g.: paraffin wax substituted cyclopentane
- The higher alkylated decahydro-naphthalenes, e. g.: di-lauryl decahydronaphthalenes
- The higher alkylated benzenes, e. g.:
  - Paraffin wax substituted benzene
  - Mono- and poly-(triisobutyl) benzenes
  - Mono- and poly-(tetraisobutyl) benzenes
- The higher alkylated naphthalenes, e. g.:
  - Petrolatum substituted naphthalene
  - Paraffin wax substituted naphthalene
- Terpene polymers, e. g.:
  - Polymerized turpentine
  - Polymerized menthenes
- Alkylene and alkadiene polymers, e. g.:
  - Polyethylenes
  - Polypropylenes
  - Polybutenes
  - Polyisoprenes, e. g. natural rubber
  - Polybutadienes
  - Polycaprylenes

- Co-polymers, e. g.:
  - Styrene-butadiene co-polymers
  - Styrene-methyl acrylate co-polymers
  - p-Methyl-alpha-methyl-styrene-vinyl chloride co-polymers
- The higher aliphatic hydrocarbons, e. g.:
  - Octadecane
  - Eicosane
  - Tetracosane
  - Pentacosane
  - Heptacosane
  - Triacontane

For the purposes of this specification and appended claims, it should be understood that petroleum sulphonic acids or salts thereof are intended to cover those compounds derived from petroleum.

It has been found that metal complexes of considerable utility may be produced when using as the starting material a mixture of at least two different sulfonic acid compounds.

Highly useful in this respect are mixtures containing (*a*) at least one petroleum derived sulfonic acid compound, and (*b*) at least one alkyl-aromatic sulfonic acid compound. Particularly preferred are mixtures of mahogany sulfonic acids or salts with alkyl-benzene sulfonic acids or salts. The ratio of equivalents of *a*/*b* is preferably between 0.1 and 10.

The following examples illustrate a number of specific combinations of different sulfonic acid compounds which may be used as starting materials for the production of our metal complexes. In each instance, the corresponding salts of the sulfonic acids are also contemplated.

Mixture No.	Components	chemical equivalents
1	Mahogany sulfonic acid	1.0
	Di-isododecyl benzene sulfonic acid	1.0
2	White oil sulfonic acid	1.0
	Mahogany sulfonic acid	1.0
	Di-isododecyl benzene sulfonic acid	2.0
3	White oil sulfonic acid	1.0
	Di-isododecyl benzene sulfonic acid	2.0
4	Mahogany sulfonic acid	10.0
	Wax-substituted phenol sulfonic acid	1.0
5	Mahogany sulfonic acid	5.0
	Wax-substituted naphthalene sulfonic acid	1.0
6	Mahogany sulfonic acid	1.0
	Wax-substituted benzene sulfonic acid	9.0
7	Petrolatum sulfonic acid	1.0
	White oil sulfonic acid	2.0
8	Mahogany sulfonic acid	1.0
	Petrolatum sulfonic acid	1.0
9	Mahogany sulfonic acid	1.0
	White oil sulfonic acid	1.0
10	Polybutene sulfonic acid	1.0
	Mahogany sulfonic acid	5.0
11	Wax sulfonic acid	1.0
	Mahogany sulfonic acid	2.0
12	Eicosyl diphenyl ether sulfonic acid	1.0
	Mahogany sulfonic acid	7.0
13	Tri-capryl diphenyl ether sulfonic acid	1.0
	Mahogany sulfonic acid	2.5
14	Bis-(diisobutyl)-phenol sulfonic acid	1.0
	White oil sulfonic acid	3.0
15	Cetyl-chlorobenzene sulfonic acid	1.0
	Mahogany sulfonic acid	8.0
16	Di-cetyl naphthalene sulfonic acid	10.0
	Mahogany sulfonic acid	1.0
17	Mahogany sulfonic acid	2.0
	White oil sulfonic acid	1.0
	Di-lauryl diphenyl ether sulfonic acid	1.0
	Di-isononyl benzene sulfonic acid	1.0
18	White oil disulfonic acid	1.0
	Di-isooctadecyl benzene sulfonic acid	2.0
19	Petroleum naphthene sulfonic acids	1.0
	Mahogany sulfonic acid	1.0
	Polybutene-substituted benzene sulfonic acid	1.0
20	Di-keryl benzene sulfonic acid	2.0
	Mahogany sulfonic acid	1.0
21	Fuel oil substituted benzene sulfonic acid	1.5
	Mahogany sulfonic acid	1.0
22	Stearyl naphthalene sulfonic acid	3.0
	White oil sulfonic acid	1.0
23	Wax-substituted phenothioxine sulfonic acid	1.0
	Mahogany sulfonic acid	3.5

Organic acids in which:

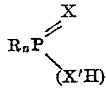
- (*a*) Sulfur is the acid-forming element, for example:
  - Organic acids containing the —SO_3H radical, e. g.:
    - Sulfonic acids (prior lists give specific examples)
    - Sulfamic acids, e. g.:
      - Di-lauryl sulfamic acid
      - Di-(3,9-diethyl-tridecyl-6) sulfamic acid
      - Di-(cetyl-phenyl) sulfamic acids
      - Di-(n-octyl-cyclohexyl) sulfamic acids
    - Thiosulfonic acids, e. g.:
      - Eicosane thiosulfonic acids
      - Paraffin wax thiosulfonic acids
      - Paraffin wax substituted benzene sulfonic acids
      - Cetyl-cyclohexane thiosulfonic acids
  - Organic acids containing the —SO_2H radical, e. g.:
    - Sulfinic acids, e. g.:
      - n-Octadecano sulfinic acids
      - Paraffin wax sulfinic acids
      - Petroleum sulfinic acids
      - Paraffin wax substituted naphthalene sulfinic acids
      - Petroleum naphthene sulfinic acids
      - Di-capryl-cyclohexane sulfinic acids
  - Thionamic acids, e. g.:
    - Myricyl thionamic acid
    - Di-cetyl thionamic acid
    - Di-(lauryl-phenyl) thionamic acids
    - Paraffin wax substituted cyclohexyl thionamic acids
  - Partial esters of polybasic inorganic sulfur acids, e. g.
    - Mono-esters of sulfuric acid, e. g.
      - Mono-docosyl sulfate
      - Mono-(diisobutyl-phenyl) sulfates
      - Mono-(cetyl-cyclohexyl) sulfates
    - Mono-esters of sulfurous acid, e. g.:
      - Mono-octadecyl sulfites
      - Mono-(eicosyl-phenyl) sulfites
      - Mono-(hydroabietyl) sulfites
    - Mono-esters of thiosulfuric acid, e. g.:
      - Mono-pentacosyl thiosulfate
      - Mono-(di-capryl naphtheyl) thiosulfates
      - Mono-(myristyl-cyclopentyl) thiosulfates
- (*b*) Selenium is the acid-forming element, for example:
  - Selenonic acids, e. g.:
    - Paraffin wax selenonic acids
    - Di-lauryl-benzene selenonic acids
    - Cetyl-cyclohexane selenonic acids
  - Seleninic acids, e. g.:
    - Heneicosane seleninic acids
    - Tri-capryl-naphthalene seleninic acids
    - Paraffin wax substituted cyclohexane seleninic acids
  - Partial esters of polybasic inorganic selenium acids, e. g.:
    - Mono-esters of selenic acid, e. g.:
      - Mono-tricosyl selenate
      - Mono-(nonadecyl-phenyl) selenates
      - Mono-(di-n-octyl-cyclohexyl) selenates
    - Mono-esters of selenious acid, e. g.:
      - Mono-myricyl selenite
      - Mono-(eicosyl-naphthyl) selenites
      - Mono-(cetyl-cyclopentyl) selenites
- (*c*) Tellurium is the acid-forming element, for example:
  - Telluronic acids, e. g.:
    - Paraffin wax telluronic acids
    - Di-capryl-anthracene telluronic acids
    - Pentacosyl-cyclohexane telluronic acids
  - Tellurinic acids, e. g.:
    - Heptacosane tellurinic acids
    - Di-nonyl-benzene tellurinic acids
    - Di-lauryl-cyclohexyl tellurinic acids
  - Partial esters of polybasic inorganic tellurium acids, e. g.:
    - Mono-esters of telluric acid, e. g.:
      - Mono-heneicosyl tellurate
      - Mono-(docosyl-phenyl) tellurates
      - Mono-(tetracosyl-cyclohexyl) tellurates
    - Mono-esters of tellurous acid, e. g.:
      - Mono-octadecyl tellurites
      - Mono-(di-octyl-phenyl) tellurites
      - Mono-(cetyl-cyclohexyl) tellurites
- (*d*) Carbon is the acid-forming element, for example:
  - Organic acids containing the —CO_2H radical, e. g.:
    - Carboxylic acids, e. g.:
      - Stearic acid
      - Behenic acid
      - Carnaubic acid
      - Cerotic acid
      - Mellissic acid
      - High molecular weight acids from the oxidation of paraffin wax and other petroleum fractions
      - Oleic acid
      - Erucic acid
      - Cetoleic acid
      - Cetyl-benzoic acids
      - Eicosyl-naphthoic acids
      - Paraffin wax substituted hydroxy-benzoic acids
      - Di-lauryl-anthracene carboxylic acids
      - Petroleum naphthenic acids
      - Abietic acid
      - Hydroabietic acid
      - Tetracosyl-cyclohexane carboxylic acids
  - N-substituted carbamic acid, e. g.:
    - Di-octyl-carbamic acids
    - Mono-cetyl carbamic acids
    - Di-(hexyl-phenyl) carbamic acids
    - Mono-(lauryl-phenyl) carbamic acids
    - Di-(amyl-cyclohexyl) carbamic acids
    - Mono-(lauryl-cyclohexyl) carbamic acids
  - Organic acids containing the —OX_2H radical, where X is oxygen, sulfur, selenium, or tellurium, and at least one X is other than oxygen, e. g.:
    - Thiocarboxylic acids, e. g.:
      - Mono- and di-thio stearic acids
      - Mono- and di-thio oleic acids
      - Mono- and di-thio mellissic acids
      - Mono- and di-thio paraffin wax substituted benzoic acid
      - Mono- and di-thio eicosyl-naphthoic acids
      - Mono- and di-thio octadecyl-cyclohexane carboxylic acids
      - Mono- and di-thio petroleum naphthenic acids
  - N-substituted thiocarbamic acids, e. g.:
    - Cetyl mono- and di-thio carbamic acids
    - Di-capryl mono- and di-thio carbamic acids
    - Lauryl-phenyl mono- and di-thio carbamic acids
    - Di-(octyl-phenyl) mono- and di-thio carbamic acids
    - Nonadecyl-cyclohexyl mono- and di-thio carbamic acids
    - Di-(heptyl-cyclohexyl) mono- and di-thio carbamic acids

- Selenocarboxylic acids, e. g.:
  - Mono- and di-seleno stearic acids
  - Mono- and di-seleno oleic acids
  - Mono- and di-seleno tetracosyl-benzoic acids
  - Mono- and di-seleno petroleum naphthenic acids
- Tellurocarboxylic acids, e. g.:
  - Mono- and di-telluro oleic acids
  - Mono- and di-telluro cetyl-naphthoic acids
  - Mono- and di-telluro hydroabietic acid
- Partial esters of polybasic inorganic carbon acids, e. g.:
  - Mono-esters of carbonic acid, e. g.:
    - Mono-eicosyl carbonate
    - Mono-(cetyl-phenyl) carbonates
    - Mono-(lauryl-cyclohexyl) carbonates
  - Mono-esters of thiocarbonic acids, e. g.:
    - Mono-docosyl esters of mono, di-, and tri-thio carbonic acids
    - Mono-(myristyl-phenyl) esters of mono-, di-, and tri-thio carbonic acids
  - Mono-esters of selenocarbonic acids, e. g.:
    - Mono-pentacosyl esters of mono-, di-, and tri-seleno carbonic acids
    - Mono-ceryl-phenyl esters of mono-, di-, and tri-seleno carbonic acids
    - Mono-(lauryl-cyclohexyl) esters of mono-, di-, and tri-seleno carbonic acids
  - Mono-esters of tellurocarbonic acids, e. g.:
    - Mono-octadecyl esters of mono-, di-, and tri-telluro carbonic acids
    - Mono-(paraffin wax substituted phenyl) esters of mono-, di-, and tri-telluro carbonic acids
    - Mono-(cetyl-cyclopentyl) esters of mono-, di-, and tri-telluro carbonic acids.

It is also intended to employ as starting materials those high molecular weight acids which are prepared from the well-known "Oxo" and Fischer-Tropsch processes.

(*e*) Nitrogen is the acid-forming element, for example:
- Nitrolic acids, e. g.:
  - Docosyl nitrolic acid
  - Octadecyl-naphthyl nitrolic acids
  - Paraffin wax substituted cyclohexyl nitrolic acids
- Nitrosolic acids, e. g.:
  - Hexacosyl nitrosolic acid
  - Nonadecyl-phenyl nitrosolic acids
  - Di-octyl-cyclohexyl nitrosolic acids
- Nitronic acids, e. g.:
  - Heneicosane nitronic acids
  - Phenyl-cetane nitronic acids
  - Cyclohexyl-octadecane nitronic acids
- Nitroic acids, e. g.:
  - Octacosyl nitroic acid
  - Cetyl-phenyl nitroic acids
  - Lauryl-cyclohexyl nitroic acids
- Carbazylic acids, e. g.:
  - Eicosane carbazylic acid
  - Cetyl-benzene carbazylic acids
  - Lauryl-cyclohexane carbazylic acids

Also useful as starting materials for the production of metal complexes are the pentavalent organic acids of phosphorus which contain at least one carbon-to-phosphorus bond; i. e., those acids of the general formula:



$$R_nP(=X)(X'H)_{3-n}$$

wherein X and X' are oxygen or sulfur, R is an organic radical bonded to phosphorus through a carbon atom, *n* is 1 or 2, and R_n contains a total of at least 12 carbon atoms.

When *n* is 2, there are of course two organic radicals present. Such radicals may be the same or different; for example, R_2 may represent two octyl radicals or a decyl radical and a hexyl radical.

Other useful carbon-to-phosphorus bonded pentavalent organic acids of phosphorus, but whose exact structures have not yet been ascertained, are those acids prepared from aliphatic, cycloaliphatic and/or aromatic compounds which are devoid of hydroxyl, sulfhydryl, and keto groups by treating such compounds with at least one sulfurizing and phosphorizing reagent such as $PSCl_3$, P_2S_5, P_4S_7, P_4S_3, P_4S_5, P_2S_5 plus sulfur, PCl_3 plus sulfur, elemental phosphorus plus sulfur, and the like, and optionally further treating with a hydrolyzing agent such as water, steam, and/or metallic base. The preparation of such materials is disclosed in U. S. Patents Nos. 2,316,085; 2,316,086; 2,316,087; 2,316,088; 2,316,089; 2,316,091; 2,316,078; 2,316,079; 2,316,080; 2,316,081; 2,316,082; 2,316,083; 2,316,084; and 2,367,468.

Typical organic starting materials for the production of these acids are given hereinbelow:

- Lubricating oil fractions, especially those of high aromaticity
- Petrolatum
- Paraffin wax
- Paraffin oil
- Petroleum naphthenes
- White oil
- Gas oil
- Abietane
- Cycloaliphatic hydrocarbons and their alkylated derivatives, e. g.:
  - Cyclohexane
  - Methyl-cyclohexane
  - Di-methyl-cyclohexanes
  - Ethyl-cyclohexane
  - Butyl-cyclohexanes
  - Hexyl-cyclohexanes
  - Decahydronaphthalene
  - Cetyl-cylcohexane
  - Bis-(diisobutyl) cyclohexanes
  - The alkylated cyclopentanes, e. g.:
    - Ethyl-cyclopentane
    - Paraffin wax substituted cyclopentane
  - The alkylated decahydro-napthalenes, e. g.:
    - Di-ethyl decahydronaphthalene
    - Di-lauryl decahydronaphthalenes
- Aliphatic hydrocarbons, e. g.:
  - Hexanes
  - Heptanes
  - Octanes, e. g.:
    - n-Octane
    - Diisobutane
  - Decanes
  - Dodecanes
  - Mixtures of the lower aliphatic hydrocarbons such as those found in e. g.:
    - Gasoline
    - Kerosene
    - Naphtha
  - Octadecane
  - Eicosane
  - Tetracosane
  - Pentacosane
  - Heptacosane
  - Triacontane
- Aromatic hydrocarbons and their alkylated derivatives, e. g.:
  - Benzene
  - Toluene
  - Xylenes
  - Ethyl-benzene
  - Amyl-benzenes
  - Octyl-benzenes
  - Naphthalene
  - Methyl-naphthalenes
  - Ethyl-naphthalenes
  - Butyl-naphthalenes
  - Anthracene
  - Methyl-anthracenes
  - Diphenyl
  - Terphenyl
  - The Higher alkylated benzenes, e. g.:
    - Paraffin wax substituted benzene
    - Mono- and poly-(triisobutyl) benzenes
    - Mono- and poly-(tetraisobutyl) benzenes
  - The higher alkylated naphthalenes, e. g.:
    - Petroleum substituted naphthalene
    - Paraffin wax substituted naphthalene
- Terpene polymers, e. g.:
  - Polymerized turpentine
  - Polymerized menthenes
- Alkylene and alkadiene polymers, e. g.:
  - Polyethylenes
  - Polypropylenes
  - Polybutenes
  - Polyisoprenes, e. g. natural rubber
  - Polybutadienes
  - Polycaprylenes
- Co-polymers, e. g.:
  - Styrene-butadiene co-polymers
  - Styrene-methyl acrylate co-polymers
  - p-Methyl-alpha-methyl-styrene-vinyl chloride co-polymers

Acids of phosphorus having at least one carbon-to-phosphorus bond, when used in admixture with at least one oil-soluble sulfonic acid compound, have been found to provide highly useful starting materials for producing our metal complexes. Particularly valuable metal complexes for some uses, as for example in lubricants, are obtained when using as a starting material a combination of petroleum sulfonate and the carbon-to-phosphorus bonded acid obtained by treating polybutylenes in the molecular weight range of 300 to 5000 with a mixture of P_2S_5 and sulfur.

(*f*) Phosphorus is the acid-forming element, for example:
- Phosphinic acids; $R_xP(OH)_{3-x}$ where *x* is 1 or 2, e. g.:
  - Pentacosyl phosphinic acid
  - Di-lauryl phosphinic acid
  - Cetyl-phenyl phosphinic acids
  - Di-(octyl-phenyl) phosphinic acids
  - Octadecyl-cyclohexyl phosphinic acids
  - Di-(nonyl-cyclohexyl) phosphinic acids
- Phosphonic acids; $R_xP(OH)_{3-x}$ where *x* is 1 or 2, e. g.:
  - Octadecyl phosphonic acid
  - Di-lauryl phosphonic acid
  - Ceryl-naphthyl phosphonic acid
  - Di-(capryl-naphthyl) phosphonic acid
  - Cetyl-cyclohexyl phosphonic acid
  - Di-(decyl-cyclohexyl) phosphonic acid

- Thiophosphinic acids; $R_xP(ZH)_{3-x}$, where x is 1 or 2 and Z is either O or S with at least one Z being sulfur, e. g.:
  - Mono- and di-thio cetyl phosphinic acids
  - Di-lauryl thiophosphinic acid
  - Mono- and di-thio eicosyl-phenyl phosphinic acids
  - Di-capryl-phenyl thiophosphinic acid
  - Mono- and di-thio octadecyl-cyclohexyl phosphinic acids
  - Di-(nonyl-cyclohexyl) thiophosphinic acids
- Thiophosphonic acids; $R_xPZ(ZH)_{3-x}$, where x is 1 or 2 and Z is either O or S with at least one Z being sulfur, e. g.:
  - Mono-, di-, and tri-thio octadecyl phosphonic acids
  - Di-decyl thiolphosphonic acids
  - Di-decyl thionophosphonic acids
  - Mono-, di-, and tri-thio docosyl-phenyl phosphonic acids
  - Di-(amyl-phenyl) dithiophosphonic acid
  - Mono-, di-, and tri-thio cetyl-cyclohexyl phosphonic acids
  - Di-(nonyl-cyclohexyl) dithiophosphonic acid
- Partial esters of polybasic inorganic phosphorus acids, e. g.:
  - Mono-esters of phosphorous acid, e. g.:
    - Mono-eicosyl phosphite
    - Mono-(lauryl-phenyl) phosphites
    - Mono-(cetyl-cyclohexyl) phosphites
  - Mono-esters of thiophosphorous acids, e. g.:
    - Mono-S-docosyl thiophosphite
    - Mono-O-docosyl dithiophosphite
    - Mono-(O-cetyl-phenyl) dithiophosphites
    - Mono-(octyl-cyclohexyl) trithiophosphites
  - Mono- and di-esters of phosphoric acid, e. g.:
    - Mono- and di-lauryl phosphates
    - Mono- and di-(dodecyl-phenyl) phosphates
    - Mono- and di-(nonyl-cyclohexyl) phosphates
  - Mono- and di-esters of thiophosphoric acids, e. g.:
    - O,O-di-n-hexyl thiolthionophosphate
    - O,O-di-n-hexyl thionophosphate
    - O,O-di-(4-methyl-sec-amyl) thiolthionophosphate
    - O,S-di-n-heptyl dithiolthionophosphate
    - O,O-di-(2-ethyl-hexyl) thiolthionophosphate
    - O,O-di-capryl thiolthionophosphate
    - O,O-di-(2,4,4-trimethyl-amyl) thiolthionophosphate
    - O,S-di-n-nonyl dithiolphosphate
    - O,O-di(3,5,5-trimethyl-hexyl) thiolthionophosphate
    - O,O-di-n-decyl thiolthionophosphate
    - S,S-di-n-undecyl dithiolphosphate
    - O,O-di-lauryl thiolthionophosphate
    - S-cetyl dithiolphosphate
    - O,O-di-cetyl thiolthionophosphate
  - Thiolthionophosphates of the general formula $(C_nH_{2n+1}O)_2PSSH$, where n is a number of from 20 to 50, e. g.:
    - O-O-di-(paraffin wax) thilthionophosphates
    - O,O-di-myricyl thiolthionophosphate
    - O,O-di-carnaubyl thiolthionophosphate
  - O,O-di-(tert-amyl-phenyl) thiolthionophosphates
  - O,O-bis-(diisobutyl-phenyl) thiolthionophosphate
  - O,O-di-(decyl-phenyl) thionophosphates
  - O-cetyl-phenyl-O-napthyl thiolthionophosphates
  - O,O-di-(methyl-cyclohexyl) thiolthionophosphates
  - O,O-di-(amyl-cyclohexyl) thiolthionophosphates
  - Pentacosyl-cyclohexyl tetrathiophosphates
  - O,S-di-(heptyl-cyclohexyl) dithiolthionophosphates
- Partial esters of pyrophosphoric acid
  - Mono-, di-, and tri-eicosyl pyrophosphates
  - Mono-, di-, and tri-(ceryl-phenyl) pyrophosphate
  - Mono-, di-, and tri-(cetyl-cyclohexyl) pyrophosphates
- Partial esters of pyrophosphorus acid
  - Mono-, di-, and tri-octadecyl pyrophosphites
  - Mono-, di-, and tri-(myricyl-phenyl) pyrophosphites
  - Mono-, di-, and tri-(cetyl-cyclopentyl) pyrophosphites
- Partial esters of polyphosphoric acids, e. g.:
  - Mono-, di-, tri-, and tetra-ceryl triphosphates
  - Mono-, di-, tri-, tetra-, and penta-(di-laurylphenyl) tetraphosphates
  - Mono-, di-, tri-, tetra-, and penta-, and hexa-(docosyl-cyclohexyl) pentaphosphates
- Partial esters of polyphosphorous acids, e. g.:
  - Mono-, di-, tri-, and tetra-ceryl triphosphites
  - Mono-, di-, tri-, tetra-, and penta-(stearylphenyl) tetraphosphites
  - Mono-, di-, tri-, tetra-, penta-, and hexa-(paraffin wax substituted cyclohexyl) pentaphosphites
- Partial esters of pyrothiophosphoric acids, e. g.:
  - Mono-, di-, and tri-eicosyl pyrodithionophosphates
  - Mono-, di-, and tri-(cetyl-naphthyl) pyroheptathiophosphates
  - Mono-, di-, and tri-(hydroabietyl) pyrothionophosphates
- Partial esters of pyrothiophosphorus acids, e. g.:
  - Mono-, di-, and tri-ceryl S-pyro thiophosphites
  - Mono-, di-, and tri-(docosyl-phenyl) O-pyrotetrathiolphosphites
  - Mono-, di-, and tri-(lauryl-cyclohexyl) pyropentathiophosphites
- Partial esters of thiopolyphosphoric acids, e. g.:
  - Mono-, di-, tri-, and tetra-ceryl decathiotriphosphates
  - Mono-, di-, tri-, tetra-, and penta-(di-caprylphenyl) tetrathionotetraphosphates
  - Mono-, di-, tri-, tetra-, penta-, and hexahydroabietyl pentathionopentaphosphates
- Partial esters of thiopolyphosphorous acids, e. g.:
  - Mono-, di-, tri-, and tetra-myricyl heptathiotriphosphites
  - Mono-, di-, tri-, tetra-, and penta-(laurylphenyl) trithiotetraphosphites
  - Mono-, di-, tri-, tetra-, penta-, and hexa- (petroleum naphthenyl) tetrathiopentaphosphites

(*g*) Arsenic is the acid-forming element, for example:

- Arsinic acids, e. g.:
  - Mono-cetyl arsinic acid
  - Di-(lauryl-phenyl) arsinic acids
  - Mono-hydroabietyl arsinic acid
- Arsonic acids, e. g.:
  - Mono-ceryl arsonic acid
  - Di-(octyl-naphthyl) arsonic acids
  - Mono-(myricyl-cyclohexyl) arsonic acids
- Partial esters of polybasic, inorganic, arsenic-derived acids, e. g.:
  - Mono-esters of arsenious acids, e. g.:
    - Mono-ceryl arsenite
    - Mono-(stearyl-naphthyl) arsenites
    - Mono-(petroleum naphthenyl) arsenites
  - Mono- and di-esters of arsenic acid, e.g.:
    - Mono- and di-eicosyl arsenates
    - Mono- and di-(lauryl-naphthyl) arsenates
    - Mono- and di-(cetyl-cyclopentyl) arsenates

(*h*) Antimony is the acid forming element, for example:

- Stibonic acids, e.g.:
  - Di-lauryl stibonic acid
  - Di-(ceryl-phenyl) stibonic acids
  - Di-(octyl-cyclohexyl) stibonic acids
- Partial esters of polybasic inorganic antimony acids, e.g.:
  - Mono-esters of antimonous acid, e.g.:
    - Mono-ceryl antimonite
    - Mono-(eicosyl-phenyl) antimonites
    - Mono-(lauryl-cyclohexyl) antimonites
  - Mono- and di-esters of antimonic acid, e.g.:
    - Mono- and di-cetyl antimonic acids
    - Mono- and di-(tetradecyl-naphthyl) antimonic acids

(*i*) Silicon is the acid-forming element, for example:

- Siliconic acids; R–SiOOH, e.g.:
  - Ceryl siliconic acid
  - Myristyl-phenyl siliconic acids
  - Hydroabietyl siliconic acid
- Partial esters of silicic acids, e.g.:
  - Mono-myricyl metasilicate
  - Di-(lauryl-naphthyl) orthosilicate
  - Mono-(petroleum-naphthenyl) orthosilicate

(*j*) Tin is the acid-forming element, for example:

- Stannonic acids; R–SnOOH, e. g.:
  - Eicosyl stannonic acid
  - Cetyl-phenyl stannonic acids
  - Di-capryl-cyclohexyl atannonic acids

(*k*) Lead is the acid-forming element, for example:

- Plumbonic acids; R-PbOOH, e. g.:
  - Ceryl plumbonic acid
  - Di-lauryl-phenyl plumbonic acid
  - Hydroabietyl plumbonic acid

While the above compounds and classes thereof are useful for the purposes of this invention, it should be understood that they are not all equivalent, but that under certain conditions some are more desirable or effective than others.

THE PROMOTER

The materials useful in the present process as so-called promoters have a function which is somewhat different from the function of the materials referred to as promoters in our co-pending parent applications. In certain of the processes contemplated in said parent applications, the promoter material has a function of assisting, to a certain extent at least, in bringing at least some of the so-called basing material into the complex. In the present case the promoter does not have that function in that no free basing material is present in the reaction mass. In the present case, therefore, the so-called promoter material serves first as the source for the metal present in the complex which is in excess of that present as the metal of the normal salt of the starting acid. The anion of the promoter liberated from the promoter material by the subsequent acid treatment may, of course, have an effect upon the nature of the ultimate complex formed between the normal salt of the starting acid and a compound formed from the metal derived from the promoter, and it is possible that this last-named effect may be similar to the effect of the promoter in those processes of our parent applications wherein the promoter material is employed in conjunction with added inorganic basing material.

The promoter materials which have been found most useful in the present processes are compounds of the phenols and enols. The phenolic and enolic organic compounds are such that the anions thereof may be readily liberated from the metal compounds thereof by a simple acid treating process, as utilizing, for example, CO_2 and SO_2, as well as H_2S and CS_2. While promoter materials formed from acid-reacting compounds having ionizations constants higher than phenols and enols might be useful under certain circumstances, they would require the use of such a strongly acidic material in the subsequent acid treating step that great care would need to be exercised during such step to prevent unfavorable effects on the metal complex which is desired as the end product. Therefore, in the present case, we are concerned only with the use as promoter materials of phenolic and enolic compounds, since by the use of these together with the type of acid treating materials mentioned above, it is possible to very easily and economically produce complexes which have great utility. The phenolic compounds which may be used as promoter materials include the following:

- Organic compounds:
    - (1) Phenolic compounds, for example:
        - Phenol
        - Naphthols, e. g.:
            - Alpha-naphthol
            - Beta-naphthol
        - Anthranol
        - Poly-hydroxy-benzenes, e. g.:
            - Hydroquinone
            - Catechol
            - Pyrogallol
            - Phloroglucinol
        - Poly-hydroxy-naphthalenes, e. g.:
            - Naphthohydroquinone
            - Naphthoresorcinol
        - Phenyl-phenols, e. g.:
            - o-Phenyl-phenol
            - p-Phenyl-phenol
        - Alkylated phenols, e. g.:
            - Cresols
            - Xylenols
            - Thymol
            - Carvacrol
            - Ethyl-phenols, e. g.:
                - p-Ethyl-phenol
                - Di-ethyl-phenols
                - Tri-ethyl-phenols
            - Propyl phenols, e. g.:
                - n-Propyl-phenols
                - Iso-propyl-phenols
                - Di-iso-propyl-phenols
            - Butyl-phenols, e. g.:
                - p-t-Butyl-phenols
                - n-Butyl-phenols
                - Di-t-butyl-phenols
            - Amyl-phenols, e. g.:
                - n-Amyl-phenols
                - p-t-Amyl phenols
                - Di-amyl phenols
                - Cyclopentyl-phenols, e. g.:
                    - p-Cyclopentyl-phenols
                    - Di-cyclopentyl-phenols
            - Hexyl-phenols, e. g.:
                - n-Hexyl-phenols
                - Sec-hexyl-phenols
                - Di-n-hexyl-phenols
                - Cyclohexyl-phenols, e. g.:
                    - p-Cyclohexyl-phenols
                    - o-Cyclohexyl-phenols
                    - Di-cyclohexyl-phenols
            - Heptyl-phenols, e. g.:
                - n-Heptyl-phenols
                - Sec-heptyl-phenols
                - Di-heptyl-phenols
            - Octyl-phenols, e. g.:
                - Diisobutyl-phenols
                - Capryl-phenols
                - n-Octyl-phenols
                - Bis-(diisobutyl)-phenols
                - Di-capryl-phenols
            - Nonyl-phenols, e. g.: 3,5,5-trimethyl-n-hexyl-phenols
            - Decyl-phenols, e. g.: n-decyl-phenols
            - Dodecyl-phenols, e. g.:
                - Lauryl-phenols
                - Triisobutyl-phenols
            - Hexadecyl-phenols, e. g.: cetyl-phenols
            - Propyl-naphthols, e. g.: iso-propyl-alpha-naphthols
            - Butyl-naphthols, e. g.:
                - t-Butyl-beta-naphthols
                - Di-t-butyl-alpha-naphthols
            - Hexyl-naphthols, e. g.:
                - n-Hexyl-alpha-naphthols
                - Cyclohexyl-beta-naphthols
            - Octyl-naphthols, e. g.:
                - Diisobutyl-alpha-naphthols
                - Capryl-beta-naphthols
                - Di-capryl-beta-naphthols
            - Alkylated anthranols, e. g.: t-butyl-anthranols
            - Alkylated poly-hydroxy-benzenes, e. g.:
                - t-Butyl-hydroquinones
                - Octyl-catechols, e. g.:
                    - Capryl-catechols
                    - Bis-(diisobutyl)-catechols
                - Dodecyl-pyrogallols, e. g.: triisobutyl-pyrogallol
                - Butyl-phloroglucinols, e. g.: t-butyl-phloroglucinol
                - Alkoxy-phenols, e. g.:
                    - Guaiacol
                    - Eugenol
                    - Lauroxy-phenols
                    - Cetoxy-phenols
        - Phenols and alkylated phenols which contain at least one inorganic substituent, for example:
            - Chloro-phenols, e. g.:
                - o-Chlorophenol
                - Di-chloro-phenols
                - Butyl-chlorophenols, e. g.: t-butyl chloro-phenol
                - Chloro-naphthols
            - Nitro-phenols, e. g.:
                - p-Nitro-phenol
                - Tri-nitro-phenols, e. g.: picric acid
            - Chloro-nitro-phenols, e. g.:
                - p-Nitro-o-chloro-phenol
                - Di-chloro-nitro-naphthols
            - Amino-phenols, e. g.:
                - p-Amino-phenol
                - Butyl-amino-phenols, e. g.:
                    - N, N-di-t-butyl-amino-phenol
                    - o-t-Butyl-p-amino-phenol
        - Hydroxy-aromatic carboxylic acids and their derivatives, for example:
            - Hydroxy-benzoic acids, e. g.:
                - Salicylic acid
                - Chloro-salicylic acid
                - Nitro-salicylic acid
                - Alkylated salicylic acids, e. g.:
                    - Di-iso-propyl-salicylic acids
                    - Capryl-salicylic acids
                - Gallic acid
                - Syringic acid
                - Resorcylic acid
                - Gentisic acid
            - Hydroxy-naphthoic acids, e. g.: 4-hydroxy-1-naphthoic acid
            - Hydroxy-benzoic acid sulfates, e. g.:
                - Salicylic acid sulfides
                - Iso-propyl-salicylic acid sulfides
                - t-Butyl salicylic acid sulfides
                - m-Hydroxy-benzoic acid sulfides
                - p-Hydroxy-benzoic acid sulfides
                - Resorcylic acid sulfides
                - Gallic acid sulfides
            - Hydroxy-naphthoic acid sulfides, e. g.: alpha-hydroxy-beta-naphthoic acid sulfides
            - Hydroxy-benzoic acid disulfides, e. g.:
                - Salicylic acid disulfides
                - t-Amyl salicylic acid disulfides
                - Cyclohexyl-p-hydroxy-benzoic acid disulfides
                - Resorcylic acid disulfides
                - Gentisic acid disulfides
            - Hydroxy-naphthoic acid disulfides
            - Anthranol carboxylic acid disulfides
            - Dihydroxy-anthracene carboxylic acid disulfides, e. g.:
                - Rufol carboxylic acid disulfides
                - Chryazol carboxylic acid disulfides
            - Hydroxy-benzoic acid sulfoxides, e. g.:
                - Salicylic acid sulfoxides
                - Ethyl-salicylic acid sulfoxides, e. g.:
                    - Mono-ethyl salicylic acid sulfoxides
                    - Di-ethyl salicylic acid sulfoxides
                - p-Hydroxy-benzoic acid sulfoxides
                - Resorcylic acid sulfoxides
                - Syringic acid sulfoxides
            - Hydroxy-naphthoic acid sulfoxides
            - Di-hydroxy-phenanthrone carboxylic acid sulfoxides, e. g.: morphol carboxylic acid sulfoxides
            - Hydroxy-benzoic acid sulfones, e. g.:
                - Salicylic acid sulfones
                - Iso-butyl salicylic acid sulfones
                - Resorcylic acid sulfones
                - Gallic acid sulfones
                - Gentisic acid sulfones
            - Hydroxy-naphthoic acid sulfones
            - Anthranol carboxylic acid sulfones
        - Hydroxy-aromatic sulfonic acids, e. g.:
            - Cresol sulfonic acids, e. g.:
                - p-Cresol sulfonic acids
                - o-Cresol sulfonic acids
            - Butyl-phenol sulfonic acids, e. g.: p-t-butyl-phenol sulfonic acids
            - Octyl-phenol sulfonic acids, e. g.:
                - Capryl-phenol sulfonic acids
                - Diisobutyl-phenol sulfonic acids
            - Naphthol sulfonic acids, e. g.: beta-naphthol alpha-sulfonic acid
            - p-(Hydroxyphenyl) benzene sulfonic acid
        - Hydroxy-aromatic sulfonic acids having an additional sulfur-bearing substituent group, for example:
            - Phenol sulfonic acid sulfides
            - Naphthol sulfonic acid sulfides
            - Catechol sulfonic acid sulfides
            - Naphthohydroquinone sulfonic acid sulfides
            - Butyl-phenol sulfonic acid sulfides, e. g.: p-t-butyl-phenol sulfonic acid sulfide
            - Ethyl-naphthol sulfonic acid sulfides, e. g.:
                - Ethyl-alpha-naphthol sulfonic acid sulfides
                - Di-ethyl-alpha-naphthol sulfonic acid sulfides
            - Propyl-catechol sulfonic acid sulfides, e. g.: iso-propyl-catechol sulfonic acid sulfides
            - Amyl-naphthoresorcinol sulfonic acid sulfides
            - Phenol sulfonic acid disulfides
            - Naphthol sulfonic acid disulfides
            - Resorcinol sulfonic acid disulfides
            - Naphthoresorcinol sulfonic acid disulfides
            - Propyl-phenol sulfonic acid disulfides, e. g.:
                - Iso-propyl-phenol sulfonic acid disulfides
                - Di-iso-propyl-phenol sulfonic acid disulfides
            - Butyl-naphthol sulfonic acid disulfides, e. g.: t-butyl-alpha-naphthol sulfonic acid disulfides
            - Ethyl-di-hydroxy-anthracene sulfonic acid disulfides, e. g.: ethyl-rufol sulfonic acid disulfide
            - Phenol sulfonic acid sulfoxides
            - Naphthol sulfonic acid sulfoxides
            - Hydroquinone sulfonic acid sulfoxides
            - Naphthoresorcinol sulfonic acid sulfoxides
            - Butyl-phenol sulfonic acid sulfoxides, e. g.: p-t-butyl-phenol sulfonic acid sulfoxides
            - Propyl-naphthol sulfonic acid sulfoxides, e. g.: iso-propyl-beta-naphthol sulfonic acid sulfoxides
            - Ethyl-di-hydroxy-anthracene sulfonic acid sulfoxides, e. g.:
                - Ethyl-rufol-sulfonic acid sulfoxides
                - Di-ethyl-rufol sulfonic acid sulfoxides
            - Phenol sulfonic acid sulfones
            - Anthrol sulfonic acid sulfones
            - Catechol sulfonic acid sulfones
            - Naphthohydroquinone sulfonic acid sulfones
            - Propyl-phenol sulfonic acid sulfones, e. g.: p-iso-propyl-phenol sulfonic acid sulfones
            - Butyl-naphthol sulfonic acid sulfones, e. g.: t-butyl-beta-naphthol sulfonic acid sulfones
            - Ethyl-dihydroxy-phenanthrene sulfonic acid sulfones, e. g.:
                - Ethyl-morphol sulfonic acid sulfones
                - Tri-ethyl morphol sulfonic acid sulfones
            - Amyl-resorcinol sulfonic acid sulfones

- Hydroxy-aromatic sulfinic acids, e. g.:
  - Phenol sulfinic acids
  - Butyl-phenol sulfinic acids, e. g.: p-t-butyl-phenol sulfinic acids
  - Naphthol sulfinic acids, e. g.: beta-naphthol alpha-sulfinic acid
- Phenols and alkylated-phenols having a sulfur-bearing substituent group other than $-SO_3H$ or $-SO_2H$, for example:
  - Phenol sulfides, e. g.: di-(p-hydroxy-phenyl) sulfide
  - Naphthol sulfides, e. g.:
    - Alpha-naphthol sulfides
    - Beta-naphthol sulfides
  - Anthrol sulfides
  - Poly-hydroxy-aryl sulfides, e. g.:
    - Hydroquinone sulfide
    - Catechol sulfides
    - Resorcinol sulfides
    - Pyrogallol sulfides
    - Phloroglucinol sulfide
    - Naphthoresorcinol sulfides
    - Di-hydroxy-anthracene sulfides, e. g.:
      - Rufol sulfides
      - Chrysazol sulfides
  - Propyl-phenol sulfides, e. g.: p-iso-propyl-phenol sulfides
  - Butyl-phenol sulfides, e. g.:
    - p-t-Butyl-phenol sulfides
    - o-sec-butyl-phenol sulfides
  - Ethyl-naphthol sulfides, e. g.:
    - Ethyl alpha-naphthol sulfides
    - Di-ethyl-beta-naphthol sulfides
  - Amyl-resorcinol sulfides
  - Methyl-cyclohexyl-catechol sulfides
  - Phenol disulfides, e. g.: di-(p-hydroxy-phenyl) disulfide
  - Naphthol disulfides
  - Anthrol disulfides
  - Poly-hydroxy-aryl disulfides, e. g.:
    - Hydroquinone disulfide
    - Resorcinol disulfides
    - Naphthoresorcinol disulfides
    - Di-hydroxy-anthracene disulfides, e. g.:
      - Rufol disulfides
      - Chrysazol disulfides
  - Cresol disulfides, e. g.:
    - p-Cresol disulfides
    - o-Cresol disulfides
  - Butyl-phenol disulfides, e. g.: p-t-butyl-phenol disulfides
  - Amyl-naphthol disulfides, e. g.: t-amyl-alpha-naphthol disulfides
  - Hexyl-catechol disulfides
  - Propyl-naphthohydroquinone disulfides
  - Amyl-dihydroxy-phenanthrene disulfides
  - Phenol sulfoxides, e. g.: di-(o-hydroxy-phenyl) sulfoxide
  - Naphthol sulfoxides
  - Anthrol sulfoxides
  - Resorcinol sulfoxides
  - Naphthoresorcinol sulfoxides
  - Ethyl-phenol sulfoxides, e. g.:
    - p-Ethyl-phenol sulfoxides
    - Di-ethyl-phenol sulfoxides
  - Butyl-phenol sulfoxides, e. g.: p-t-butyl-phenol sulfoxides
  - Octyl-catechol sulfoxides, e. g.:
    - Capryl-catechol sulfoxides
    - Diisobutyl-catechol sulfoxides
  - Amyl-naphthol sulfoxides
  - Methyl-cyclohexyl-naphthohydroquinone sulfoxides
  - Phenol sulfones, e. g.: di-(p-hydroxy-phenyl) sulfone
  - Naphthol sulfones
  - Phloroglucinol sulfones
  - Naphthohydroquinone sulfones
  - Rufol sulfones
  - Butyl-phenol sulfones, e. g.: p-t-butyl-phenol sulfones
  - Propyl-naphthol sulfones, e. g.: iso-propyl-beta-naphthol sulfones
  - Hexyl-catechol sulfones
  - Ethyl-naphthohydroquinone sulfones
- Sulfur analogs of phenolic compounds, for example:
  - Thiophenol
  - p-Ethyl-thiophenol
  - Iso-propyl-thiophenol
  - p-t-Butyl-thiophenol
  - p-t-Amyl-thiophenol
  - Sec-hexyl-thiophenols
  - Cyclo-hexyl-thiophenols
  - n-Heptyl-thiophenols
  - Diisobutyl-thiophenols
  - 3,5,5-trimethyl-n-hexyl-thiophenol
  - n-Decyl-phenols
  - Hexadecyl-thiophenols
  - o-Chloro-thiophenol
  - p-Nitro-thiophenol
  - p-Amino-thiophenol
  - Thiosalicylic acid
  - 4-Mercapto-1-naphthoic acid

From the examples of phenolic compounds given above, it will be observed that throughout the specification and its claims when use is made of the term "a phenol," we intend to include all those organic compounds which contain in their molecule a benzene ring containing at least one hydroxyl or sulphydroxyl group irrespective of what other substituents may be contained in the molecule. Thus, this term is inclusive not only of the oxy-phenols but the thio-phenols as well as the substituted derivatives thereof. Likewise, throughout the specification and in the claims where use is made of the term "a phenolic compound" we intend to include not only compounds which can be referred to as "a phenol" as above defined, but also all derivatives thereof including the metal salts. It should be noted also that from the examples given above, the term "a phenol" is inclusive of those compounds in which the 6-membered ring to which the characterizing hydroxyl group is attached may have one or more other ring structures connected thereto or fused therewith.

THE ENOLIC COMPOUNDS

The term enolic organic compounds as used in the specification and appended claims refers to tautomeric organic compounds of the established type, for example, as illustrated in "Advanced Organic Chemistry," by G. W. Wheland, John Wiley & Sons, New York, 1949, chap. 14, pp. 580 to 646.

Generally, the enolic organic compounds include a variety of classes of compounds such as aliphatic nitro compounds (i. e. aci-nitro compounds), oximes, imines, imides, amides, keto-esters, polyesters, and polyketones. It will be noted that the term enolic carbonyl includes keto-esters, polyesters, and polyketones.

The aliphatic nitro compounds (aci-nitro compounds) useful as promoters include, for example, 1-(para-nitrophenyl)-2-nitrobutane; gamma-nitro methyl hexoate, 1-chloro 1-nitropropane, 1-nitropropane, etc.

The oximes useful as promoters include, for example, benzalacetone oxime, quinone mono-oxime, isophorone oxime, etc.

The amides useful as promoters include, for example, N-ethyl benzamide, ortho-chlorobenzamide, benzamide, acetanilide, thiodiglycolic acid diamide, acatamide, etc.

The enolic carbonyl compounds useful as promoters include, for example: keto-esters, such as, phenyl acetoacetate, ethyl acetoacetate, benzyl acetoacetate, chloronaphthol acetoacetate, etc.; polyesters, such as, dibenzyl malonate, diethyl malonate, triethylcarballyate, etc.; and polyketones, such as, benzoyl acetone, acetyl acetone, etc.

THE ACIDIC MATERIAL

As previously indicated, one form of the process of the present invention includes the step of treating the immediate product with an acidic material for the purpose of liberating therefrom at least a portion of the material previously referred to as the promoter. A particularly effective acidic material which has been utilized for this purpose is carbon dioxide. We are aware of the fact that Mertes in his above-identified Patent No. 2,501,731 suggested transforming a sodium hydroxide-calcium sulphonate complex into the sodium carbonate-calcium sulphonate complex or the corresponding bicarbonate complex by blowing the hydroxide complex with carbon dioxide at elevated temperatures.

In our process, the step of treating with an acidic material such as carbon dioxide or even with air has the effect of liberating from the immediate product formed a part at least of the anionic radical of the compound used as the promoter material. Thus the presence in the immediate product of the promoter material, in combined form, clearly distinguishes the immediate product from any organic salt complex type material heretofore produced. Moreover, the nature of the product formed by regenerating from the immediate product at least a portion of the anionic radical of the promoter material leaves that product with a composition which is quite different from prior art organic complexes. It is recognized that in accordance with the present invention, the salt form of promoter can be employed in forming the salt complex. However, notwithstanding this fact, upon treating the salt complex with the acidic material to be more particularly defined below, this salt compound is released or liberated from association in the salt complex as the ionizable compound and not the salt.

The acidic material employed for this purpose can be either a liquid, gas, or solid just so long as the material when present in the mass containing the salt complex will possess an ionization constant greater than the promoter which is released or liberated from association in the salt complex. Thus, for the purpose of this specification and the appended claims, it is to be understood that the acidic material includes a liquid, gas, or solid prior to being incorporated in the mass which contains the salt complex.

In the present invention, the acidic material usually employed is an acid or a gas. The acids can include the strong or weak types, such as, for example, hydrochloric, sulphuric, nitric, carbonic, acetic acids, etc., whereas the gas is for the most part an anhydride or an acid or an "acid anhydride gas."

The large number and variety of acidic materials can be best illustrated by the following specific examples, viz. HCl, SO_2, SO_3, CO_2, air, NO_2, H_2S, N_2O_3, PCl_3, $SOCl_2$, ClO_2, H_2Se, BF_3, CS_2, COS, etc.

From the above examples of compounds and classes of compounds which can be used as acidic materials, it should be understood that all of them are not equivalent for this invention because under certain conditions some are more desirable or effective than others.

Generally, the complex formed is prepared by heating the components, at a superatmospheric temperature while insuring thorough mixing and then further heating said mixture to substantially remove all free water or alcohol, including water and alcohol of hydration which may be present. The following methods illustrate the manner by which the complex can be formed, namely:

(*a*) The compound AH or the salt thereof, is added to the oil-soluble salt of an acidic organic compound, followed by addition of an aqueous solution or suspension the salt or base thereto. The mixture is held at a superatmospheric temperature for a reasonable length of time while insuring thorough mixing, and then the total mixture is further heated to substantially remove all free water or alcohol including water or alcohol of hydration which may be present.

(*b*) The salt or base in a dry state is added to a mixture of oil-soluble acidic organic compound or salt thereof, the compound AH or the salt thereof and either water, alcohol, or mixtures of alcohols or water and alcohol; heated to a superatmospheric temperature while insuring thorough mixing and then further heated to remove substantially all free water or alcohol including water or alcohol of hydration which may be present;

(*c*) The acidic organic compound is mixed with the compound AH or the salt thereof, when an aqueous solution or suspension or an alcoholic solution or suspension of the salt or base is added thereto. The mixture is heated and agitated at a superatmospheric temperature for a time sufficient to insure thorough mixing and followed by subjecting the total mixture to dehydration conditions in order to remove substantially all free water or alcohol including water or alcohol of hydration which may be present.

(*d*) A mixture of the oil-soluble acidic organic compound or the salt thereof, the compound AH or the salt thereof, and the salt or base is heated and agitated at a superatmospheric temperature for a time sufficient to insure thorough mixing, and followed by heating the total mixture in order to remove substantially all free water or water of hydration which may be present.

(*e*) The sediment when formed from any of the aforementioned methods can be employed either alone or with an additional amount of compound AH or the salt thereof in any of the three methods given above.

(*f*) In any of the methods discussed herein for preparing a salt complex, a substantial increase in cationic salt-forming radical content is effected by treating the mass with an acidic material just after substantial amounts of water or alcohol or both, are driven off and just before the mass is filtered.

In all of the methods described above for preparing the salt complex, the step of removing substantially all free water or alcohol including water or alcohol of hydration which may be present is accomplished at a temperature not substantially in excess of 350° C., preferably about 110° to 200° C. The technique employed to remove the alcohol or water includes, for example, a conventional flash operation, heating under subatmospheric, atmospheric, or superatmospheric pressures. It can, therefore, be seen that the temperature as well as the time for effecting the substantial removal of the alcohol of water will generally vary considerably depending on the technique employed therefor. Generally, the time required to effect substantial removal of water or alcohol when employing drying other than flash techniques is about 15 minutes or less, and can be as high as 10–15 hours. Usually, however, atmospheric pressures will be employed for such an operation, and consequently it will usually require about 1 to 5 hours to remove substantially all water or alcohol which may be present. At a later stage of the process, the acidic material when used in gaseous form may be used to remove the last portion of water.

For the purposes of this specification and the appended claims, the relative amounts of (1) the oil-soluble acidic organic compounds or salts thereof, and (2) the promoter is expressed as the "ratio of equivalents" of the former (1) to the latter (2). In accordance therewith, the ratio of equivalents is from about 1 to 10 to about 10 to 1, preferably from about 3 to 2 to about 7 to 2. The amount of salt or base employed in the process will be sufficient to have present in the total mass at least more than about one equivalent of cationic salt-forming radicals including those present in the oil-soluble acidic organic compound or the salt thereof and the promoter per equivalent of oil-soluble acidic organic compound or salt thereof plus the promoter.

The treatment of the salt complex with an acidic material is employed when it is desirable to lower the basic number of the salt complex and/or partially or substantially recover the promoter. This treatment is effected at a temperature of about 25° to 250° C., preferably about 120° to 170° C., and by employing about 0.5 to 20% of acidic material based on the weight of salt complex. The time of treatment with the acidic material can vary considerably depending on the desired result. As would be expected, short periods of treatment might cause only partial liberation or release of the promoter or relatively small decreases in the basic number of the salt complex; however, in general, periods of treatment will range from about 0.25 to 30 hours. In most cases, and particularly where it is desired to recover the promoter, the amount of acidic material used should be at least equivalent to the amount of cationic salt forming radicals present as the salt of the ionizable form of promoter. When it is desired to produce a product having substantially neutral reaction, the amount of acidic material used should be at least equivalent to the total cationic salt forming radicals in excess of that present as the normal salt of the oil soluble organic acid.

In those instances where salts or bases containing metal are employed as the basing agent the metal content of the complex will be defined as the ratio of the total metal in the salt complex to the amount of metal which is in the form of a normal salt of the oil-soluble acidic organic compound. In accordance therewith the present invention includes salt complexes containing metal ratios greater than 1, and up to about 10 or more. As for those complexes which are treated with an acidic material, it is to be noted that the metal ratio is substantially the same as in the complex prior to treating. Consequently, for acidic material treated complexes, the same metal ratios will apply as given above. Likewise, when the salt complex is treated with an acidic material and the promoter is removed from the resultant product by distillation or otherwise, it is found that the metal ratio will be substantially the same as in the salt complex before treating with the acidic material.

Since the present invention includes complexes which do not contain metal in combination therewith, it is convenient, therefore, as a means of designating the amount of overbasing to employ the ratio of total cationic salt-forming radicals in the salt complex to the amount of cationic salt-forming radicals which are in the form of a normal salt of the oil-soluble acidic organic compound. Hereinafter, this ratio will be referred to as the "cationic salt-forming radical ratio." In accordance therewith, the cationic salt-forming radical ratio of the salt complex will be in the same range as given hereinabove for the metal ratio.

It has been found that the salt complex can be prepared by using small quantities of water, alcohol, or mixtures of both, such as about 1 mole of same per mole of salt or base which is employed as the basing agent. However, more usually about 5 to 50 moles of water, alcohol or mixtures of both per mole of salt or base used, and preferably about 15 to 30 moles per mole.

To substantially increase the metal content of the salt complex, the total mass is treated with an acidic material just prior to filtering same to separate the desired salt complex. This treatment is effected at a temperature of about 25° to 250° C., preferably about 120° to 170° C., using about 0.5 to 20% of acidic material, based on the total mass, and for a period of about 0.25 to 30 hours. Treatment with an acid anhydride gas may be accelerated by superatmospheric pressure.

In order to better understand the present invention, the following specific examples thereof are given; however it should be understood that no undue limitations or restrictions should be imposed by reason thereof.

The following examples give the preparation of a plurality of products which range in cationic salt forming radical content from about that of the normal salt up to many times that amount.

We have found that sulphate ash and/or metal content values, and the metal ratio values calculated therefrom, are one of the most reliable means for characterizing certain of the salt complexes. As the description of the invention proceeds, it will become apparent that the neutralization number of a salt complex is in certain instances an unreliable index of the amount of excess cationic salt forming radicals in such complex, since it is greatly affected by the type of basing agent employed and can be varied within wide limits without significantly changing the cationic salt forming radical content of the product by treatment of the mass with air, CO_2, or the like.

The above is not to be construed as a statement that the neutralization number is not an important property of a salt complex. For some uses, for example in lubricants, it is advantageous in certain instances to employ a salt complex of a substantially neutral character, whereas in other instances a salt complex of high alkalinity has been found to produce the desired results.

Example 1

3408 grams of polymerized isobutylene having an average molecular weight of about 750 were heated to 210° C. and an intimate mixture of 672 grams of P_2S_5 and 84 grams of sulfur flowers was added thereto over a period of 1.75 hours. After all of the P_2S_5—S mixture had been added, the whole was heated for 1.5 hours at 210° C., diluted with 2600 grams of low viscosity mineral oil, and blown with steam for 5 hours at 210°–215° C. The filtered material, a high molecular weight organo-phosphorus acid of undetermined structure, had an acid no. of 68 and contained 0.9% sulfur and 2.14% phosphorus.

820 grams (1.0 equivalent) of this organo-phosphorus acid, 56 grams (1.5 equivalents) of $Ca(OH)_2$, and 200 ml. of water were refluxed for 2 hours and then elevated to 150° C. to remove substantially all of the water (2 hours at 150° C. required). The filtered process mass comprises an oil solution of the calcium salt of the organo-phosphorus acid.

In a separate vessel, 488 ml. of water, 458 grams (4.88 equivalents) of phenol, and 90 grams (2.44 equivalents) of $Ca(OH)_2$ were refluxed for 2 hours to prepare calcium phenate in situ and in the presence of an excess of phenol. To this vessel were added 333 grams (0.5 equivalent) of the above-described calcium salt of organo-phosphorus acid and 525 grams (0.5 equivalent) of a 45% oil solution of calcium petroleum sulfonate (6.5% sulfate ash content). The process mass was refluxed for 2 hours at 100°–110° C. and then heated to 150° C. where it was blown with CO_2 for one hour. The substantially neutral process mass was then heated to 200° C. under reduced pressure. Phenol, freed from calcium phenate by the carbonation step, was recovered to the extent of 91% in the distillate. The residue was diluted with 300 grams of low viscosity mineral oil and filtered. The filtrate, the desired end-product, was a brown, oil-soluble liquid having the following analyses:

Percent sulfur	1.16
Percent phosphorus	0.50
Percent calcium	4.18
Percent sulfate ash (calculated)	14.2
Basic no.	16.2
Metal ratio	2.57

Example 2

738 grams of the organo-phosphorus acid described in Example 1, 902 grams of low viscosity mineral oil, and 800 ml. of water were stirred at 70° C. Then 111 grams (3.0 equivalents) of $Ca(OH)_2$ were added and the mass was refluxed for 0.5 hour. Thereafter, 185 grams (5.0 equivalents) of $Ca(OH)_2$, 1050 grams (1.0 equivalent) of a 45% oil solution of calcium petroleum sulfonate, and 1315 grams (14.0 equivalents) of phenol were added and the process mass was refluxed for 3 hours to prepare calcium phenate in situ and in the presence of an excess of phenol. Substantially all of the water was removed by heating to 150° C., at which temperature CO_2 was blown through the mass for 2 hours to render it substantially neutral on titre. A vacuum was then applied and the temperature of the mass was raised to 200° C. to remove substantially all of the original phenol used. The phenol was liberated from the calcium phenate in the process mass by the carbonation step.

After substantially all of the phenol had been removed, the residue was filtered. The filtered end product was a brown, oil-soluble liquid having the following analyses:

Percent sulfur	1.32
Percent phosphorus	0.47
Percent calcium	4.47
Percent sulfate ash (calculated)	15.2
Basic no.	11.5
Metal ratio	3.22

Example 3

The experiment described in Example 2, was repeated using 590 grams (1.0 equivalent) of a 65% oil solution of di-isododecyl benzene sulfonic acid in lieu of the 1.0 equivalent of calcium petroleum sulfonate specified therein. The filtered end product in this instance was a brown, oil-soluble liquid having the following analyses:

Percent sulfur	1.08
Percent phosphorus	0.49
Percent calcium	4.1
Percent sulfate ash (calculated)	14.0
Basic no.	11.5
Metal ratio	2.96

Example 4

1046 grams (1.0 equivalent) of a 45% oil solution of calcium petroleum sulfonate of 6.5% sulfate ash content were mixed with 228 grams (2.44 equivalents) of phenol and heated to 100° C. while adding 124 grams (2.44 equivalents) of calcium methoxide to form calcium phenate in situ. After the process mass had been stirred for 2 hours at 100°–120° C., 22 grams of H_2O were added and the whole was stirred for one hour at 105° C. The temperature was then elevated to 120° C. and CO_2 was blown through the mass as the temperature was again elevated to 150° C. Thereafter, the mass was maintained for 1 hour at 150° C., stripped of phenol liberated by the carbonation step at 210° C. and 20 mm. Hg absolute pressure, and filtered. (Approximately 90% of the phenol was recovered.)

The filtered end-product was a brown, oil-soluble liquid having the following analyses:

Percent sulfur	2.52
Percent sulfate ash	17.9
Basic no	9.3
Metal ratio	3.03

Example 5

500 grams (0.49 equivalent) of a 45% oil solution of calcium petroleum sulfonate of 6.5% sulfate ash content, 75.5 grams (0.67 equivalent) of calcium phenate, 15.5 grams (0.17 equivalent) of phenol, and 90 grams of water were heated for 1 hour at 100° C. The temperature of the process mass was then elevated to 150° C. and CO_2 was blown through the reactants for 4 hours. The temperature was again elevated, this time to 190° C., and substantially all of the phenol liberated by the carbonation distilled out of the process mass. The residue was filtered, yielding (as filtrate) a brown, oil-soluble liquid having the following analyses:

Percent sulfur	2.68
Percent sulfate ash	14.1
Acid no	5.6
Metal ratio	2.12

Example 6

459 grams (4.88 equivalents) of phenol, 90.5 grams (2.44 equivalents) of $Ca(OH)_2$, and 244 grams of water were refluxed for 2 hours to form calcium phenate in situ and in the presence of excess phenol. 1046 grams (1.0 equivalent) of a 45% oil solution of calcium petroleum sulfonate were then added and the whole was heated to 125° C. to remove the bulk of the water and about 32 grams of phenol. The temperature was then elevated to 150° C. and CO_2 was blown through the mass for 2.5 hours. A distillate was collected which was found to consist of 18 grams of water and 42 grams of phenol. The process mass was then heated to 200° C. under reduced pressure, removing, as distillate, about 375 grams of phenol. Total phenol recovery was 449 grams or 98% of starting amount.

The residue on filtration yielded a brown, oil-soluble liquid having the following analyses:

Percent sulfate ash	18.3
Basic no	8.1
Metal ratio	3.07

Example 7

282 grams (3.0 equivalents) of phenol, 37 grams (1.0 equivalent) of $Ca(OH)_2$, and 100 ml. of water were stirred at 100°–105° C. for 2 hours to form calcium phenate in the presence of excess phenol. Thereafter, the process mass was elevated to 150° C., removing water and some of the excess phenol. 430 grams (0.41 equivalent) of a 45% oil solution of calcium petroleum sulfonate were added and the whole was CO_2 blown for 2 hours at 150° C. Thereafter, the process mass was heated to 215° C. under reduced pressure to remove substantially all of the excess phenol and the phenol which was liberated by the carbonation step.

The residue, on filtration, yielded a brown, oil-soluble liquid having the following analyses:

Percent sulfate ash	18.9
Acid no	7.7
Metal ratio	3.23

Example 8

1046 grams (1.0 equivalent) of a 45% oil solution of calcium petroleum sulfonate, 229 grams (2.4 equivalents) of phenol, 90.5 grams (2.44 equivalents) of a $Ca(OH)_2$, and 244 grams of water were stirred at 100°–105° C. for 2 hours to form calcium phenate in situ and in the absence of any excess phenol. The process mass was heated slowly to 120° C. to remove the bulk of the water and some phenol. CO_2 was then blown through the mass and the temperature was raised to 150° C. while CO_2 blowing was continued. After the whole had been maintained for 2 hours at 150° C. with CO_2 blowing, it was heated to 215° C. under reduced pressure to remove substantially all of the phenol liberated by the carbonation step. Total phenol recovery was 94%.

The residue was filtered to yield a brown, oil-soluble liquid having the following analyses:

Percent sulfate ash	18.2
Acid no	2.8
Metal ratio	3.06

Example 9

658 grams (7.0 equivalents) of phenol, 305 grams of low viscosity mineral oil, 130 grams (3.5 equivalents) of $Ca(OH)_2$, and 350 ml. of water were refluxed for 2 hours to form calcium phenate in the presence of excess phenol. 1050 grams (1.0 equivalent) of a 45% oil solution of calcium petroleum sulfonate were added and the process mass was heated for one hour at 100°–105° C. The temperature of the mass was then elevated to 150° C. and CO_2 was blown through it for one hour to render it substantially neutral to titre. Thereafter the whole was heated to 200° C. under 20 mm. Hg absolute pressure while a small current of CO_2 was bled through the residue. Substantially all of the phenol used was recovered.

Filtration of the residue yielded a brown, oil-soluble liquid having the following analyses:

Percent sulfate ash	18.2
Basic no	10.3
Metal ratio	4.02

Example 10

1285 grams (1.0 equivalent) of a 35% oil solution of barium petroleum sulfonate, 261 grams of low viscosity mineral oil, and 300 ml. of water were stirred together at 70° C. 301 grams (3.94 equivalents) of BaO and 94 grams (1.0 equivalent) of phenol were added and the whole was refluxed for 3 hours. The temperature of the process mass was then elevated to 150° C. and CO_2 was blown through the reactants until a substantially neutral titre was obtained on the mass (about 2 hours required). The process mass was then elevated to 200° C. and a vacuum was applied. Substantially all of the phenol used was recovered in the distillate.

The residue on filtration yielded a brown, oil-soluble liquid having the following analyses:

Percent sulfate ash	27.6
Basic no.	10.1
Metal ratio	4.46

Example 10a

A product similar to that described in Example 1 may be prepared by following the process described therein but omitting the step wherein the process is heated to 200° C. under reduced pressure to remove phenol.

In this instance the end-product retains a substantial proportion of the phenol originally used.

Example 10b

A product similar to that described in Example 10 may be prepared by following the process described therein but omitting the step wherein the process mass is heated to 200° C. under reduced pressure to remove phenol.

In this instance the end-product retains a substantial proportion of the phenol originally used.

Example 10c

A product similar to that described in Example 4 may be prepared using 2.44 equivalents of para-cresol in lieu of the 2.44 equivalents of phenol specified therein.

Example 10d

A product similar to that described in Example 4 may be prepared by using 2.44 equivalents of diisobutyl-phenol in lieu of the 2.44 equivalents of phenol specified therein.

Example 10e

A product similar to that described in Example 4 may be prepared by using 2.44 equivalents of 1-nitro-propane (an enolic compound) in lieu of the 2.44 equivalents of phenol specified therein.

Example 10f

A strontium complex similar to the barium complex described in Example 10 may be prepared by following the process described therein but using 1.0 equivalent of strontium petroleum sulfonate in lieu of the 1.0 equivalent of barium petroleum sulfonate, and 3.94 equivalents of $Sr(OH)_2$ in lieu of the 3.94 equivalents of BaO.

Example 10g

A product similar to that described in Example 9 may be prepared by using 1.0 equivalent of a 45% oil solution of mixture of equal molecular parts of calcium petroleum sulfonate and calcium di-isododecyl benzene sulfonate in lieu of the 1.0 equivalent of calcium petroleum sulfonate specified therein.

The salt complexes produced in accordance with the present invention can be employed in lubricants including oils and greases, and for such purposes as in crankcases, transmissions, gears, etc. as well as in torque converter oils. Other suitable uses for such complexes are in asphalt emulsions, insecticidal compositions, fire-proofing and stabilizing agents in plasticizers and plastics, paint driers, rust inhibiting compositions, pesticides, foaming compositions, cutting oils, metal-drawing compositions, flushing oils, textile treatment compositions, tanning assistants, metal cleaning compositions, emulsifying agents, antiseptic cleansing compositions, penetrating agents, gum solvent compositions, fat splitting agents, bonding agent for ceramics and asbestos, asphalt improving agents, flotation agents, improving agents for hydrocarbon fuels such as e. g., gasoline and fuel oil, etc.

More particularly, the complexes of this invention are especially adapted for the preparation of lubricants, paint driers and plastics, particularly the halogen bearing plastics. In these respects, the salt complex can be employed in the following concentrations based upon the weight of the total composition.

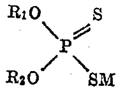
	Broad Range	Usual Range	Preferred Range
	Percent	*Percent*	*Percent*
Lubricant	0.01–20	0.2–15	0.5–10
Stabilizing Agent for Plastics	0.05– 5	0.1– 3	0.2– 2
Paint Drier	0.2 –25	0.5–20	1.0–15

LUBRICANT CONTAINING ORGANIC METAL COMPLEXES

While the metal complexes of the present invention are useful per se as improving agents for lubricating greases and oils, especially mineral lubricating oils intended for use in the crankcases of internal combustion engines, they are most advantageously employed in combination with one or more additional improving agents of the prior art such as, for example, the numerous prior art oxidation inhibitors, detergents, extreme pressure agents, rust inhibitors, and oiliness agents.

In addition to the above-named types of cooperating improving agents, the present invention also contemplates the inclusion, in the finished lubricant, of materials intended to modify the physical characteristics of the mineral lubricating oil base. Examples of such materials are foam inhibitors, pour point depressants, viscosity index improving agents, and odor improving agents. Since the types of materials useful as physical property improving agents are well known to those versed in the lubricant art, it is deemed unnecessary to lengthen the specification unduly by a recitation of the same.

Particularly effective lubricating oils for the crankcases of internal combustion engines can be made by incorporating, in suitable mineral lubricating oils, thiophosphate salt-esters and/or phosphorus sulfide treated unsaturated organic materials along with the metal complexes of the present invention. From the viewpoint of cost, effectiveness, and commercial utility, the most desirable thiophosphate salt-esters for use as oxidation and corrosion inhibitors along with materials of the present invention in lubricating oils are dithiophosphate salt-esters of the general formula



wherein R_1 and R_2 are the same or different organic radicals and M is one equivalent of a metal, especially a metal selected from Group II of the Mendeleef Periodic Table and most desirably either zinc or barium. In this connection reference may be made to the dithiophosphate salt-esters disclosed in U. S. Patents 2,261,047; 2,329,436; 2,344,392; 2,344,393; 2,344,394; 2,344,395; 2,342,572; 2,347,592; 2,361,746; 2,358,305; 2,364,283; 2,364,284; 2,365,938; 2,382,775; 2,386,207; 2,373,811; 2,410,650; 2,417,562; and 2,438,876.

Particularly useful in this respect are dithiophosphate salt-esters wherein R_1 and R_2 of the above formula are different organic radicals, which materials are the subject of pending applications Serial No. 250,959, filed October 10, 1951, and Serial No. 251,139, filed October 11, 1951, by Fred C. Goldsmith, and which applications have an assignee common to the instant application.

Where such salt ester materials, viz. those which contain dissimilar organic radicals, are used it is necessary only that the average number of carbon atoms per atom of phosphorus in the salt ester material be 7.6 or more. Thus it is not only possible, but entirely feasible to utilize such inexpensive alcohols as ethyl, propyl and butyl alcohols in the preparation of these dithiophosphate salt ester materials. The use of dithiophosphate salt ester materials in which R_1 and R_2 of the above general formula are the same requires the utilization of organic radicals containing a minium of six carbon atoms. Oil-solubility considerations govern the above minimum carbon atom contents.

Phosphorus sulfide treated unsaturated organic materials useful in conjunction with the metal complexes of the present invention include, for example, phosphorus sulfide treated acyclic and cyclic unsaturated hydrocarbons and phosphorus sulfide treated unsaturated esters, acids and ketones. Particularly valuable products may be obtained by reacting from 2 to 6 molds of at least one terpene hydrocarbon with at least one mole of phosphorus sulfide, especially P_2S_5. Particularly good results are secured by the employment of the products obtained by reacting about 3 to 5 moles of pinene and/or turpentine with one mole of P_2S_5 for about 1 to 6 hours, preferably about 4 hours, at about 100° C. to 160° C., preferably about 140° C. Such phosphorus sulfide treated materials may be further treated with reagents such as water, alcohols, phenols, or metallic bases to yield end products having enhanced lubricant improving properties for certain applications. All of the aforesaid phosphorus sulfide reaction products are well known in the lubricant improving agent field and have found application primarily as addition agents to reduce the corrosive action of lubricating compositions toward sensitive bearing metal alloys. Additional information on the preparation and utility of these materials may be had by reference to U. S. Patents 2,278,719; 2,315,529; 2,316,078; 2,316,079; 2,316,080; 2,316,084; 2,316,088; 2,316,089; 2,331,923; 2,356,073; 2,356,074; 2,367,468; 2,375,315; 2,377,955; 2,379,312; 2,379,313; 2,383,494; 2,383,495; 2,383,498; 2,392,252; 2,392,253; 2,406,575; 2,409,877; 2,409,878; 2,416,281; and 2,421,631.

In addition to thiophosphate salt-esters and phosphorus sulfide treated unsaturated organic materials, which products have been found to be of particular utility for use in conjunction with the metal complexes of the present invention in lubricants, it is also contemplated to use various other prior art improving agents belonging to the classes of materials known to be useful as detergents, corrosion inhibitors, oxidation inhibitors, and oiliness agents.

Many examples of prior art materials belonging to the classes of detergents, corrosion inhibitors, and oxidation inhibitors which may be used advantageously in combination with the metal complexes of this invention in lubricants may be found in articles by V. A. Kalichevsky (Petroleum Refiner, volume 28, No. 9, pages 88 to 93 inclusive, September 1949) and J. Harold Byers (National Petroleum News, February 10, 1937, pages 67 to 70 inclusive). In the interest of not lengthening the present specification unduly, it is intended that the improving agents therein disclosed be considered as forming a part of our disclosure.

The metal complexes of the present invention can also be used advantageously in combination with extreme pressure agents and optionally oiliness agents and rust inhibitors, for the preparation of compositions useful as lubricants in metal-working and wire-drawing operations and in the gears of automotive vehicles, industrial speed reducers, oil well drilling equipment, and the like, where relatively moving metal surfaces are subjected to high unit pressures which would normally tend to weld or score said metal surfaces.

The following table lists many types and specific examples of materials which have been found to be useful as extreme pressure agents. These materials either singly or in combination, may be used along with the metal complexes of the present invention and suitable lubricating oil bases for the preparation of improved extreme pressure lubricants.

Organic sulfur compounds: Thio derivatives of organic oxygen compounds:

- I. Classified according to nature of attachment of sulfur atom to the molecule:
  - A. Sulfur atom directly attached to one or more carbon atoms, as in the case of compounds containing the —SR— radicle where R is hydrogen or an organic radicle.
    - 1\. Thio-ethers and analogous compounds e. g.,
      - (*a*) Alkyl sulfides
        - Dibutyl sulfide
        - Diamyl sulfide
        - Dilauryl sulfide
        - Methyl lauryl sulfide
        - Dicyclohexyl sulfide
      - (*b*) Aryl sulfides
        - Naphthyl amyl sulfide
        - Phenyl ethyl sulfide
      - (*c*) Thio-acetals (mercaptals)
        - Thio-acetal
        - Acetone mercaptal
        - Phenyl benzyl thio-acetal
        - Di-amyl thio-acetal
        - Dimethyl benzene aldehyde thio-acetal
        - Dibenzyl aldehyde thio-acetal
      - (*d*) Thio-cyanates (R—S—CN)
      - (*e*) Aromatic substituted aliphatic sulfides
        - Benzyl sulfide
        - Xylyl sulfide

- 2\. Compounds containing the —C—SH radicle, e. g.
  - (*a*) Thio-alcohols and thiophenols (mercaptans)
    - Alkyl mercaptans, such as:
      - The amyl mercaptans
      - The heptyl mercaptans
      - The octyl mercaptans
        - n-Octyl mercaptan
        - Capryl mercaptan
        - 2-ethyl hexyl mercaptan
      - Lauryl mercaptan
      - Cetyl mercaptan
      - Methyl cyclohexyl mercaptan
      - Cyclohexyl mercaptan
      - Amyl cyclohexyl mercaptan
      - Cyclohexyl methyl mercaptan
    - Aryl mercaptans, such as:
      - Phenyl mercaptan
      - Diethyl phenyl mercaptan
      - The naphthyl mercaptans
      - Ethyl naphthyl mercaptan
      - Methyl naphthyl mercaptan
      - Capryl naphthyl mercaptan
      - Wax naphthyl mercaptan
    - Aromatic substituted aliphatic mercaptans, such as:
      - Benzyl mercaptan
      - Phenyl ethyl mercaptan
      - Ethyl phenyl ethyl mercaptan
      - Diphenyl methyl mercaptan
      - Triphenyl methyl mercaptan
  - (*b*) Dithio-alcohols and tithio-phenols (dimercaptans)
    - Dimercapto butane
    - Amyl dimercapto naphthalene
  - (c) Mercapto acids
    - Mercapto stearic acid
    - Mercapto lauric acid
- 3\. Compounds containing the C=S radicle, e. g.,
  - (*a*) Thio-aldehydes, e. g.
    - Thio-stearaldehyde
    - Thio-lauraldehyde
    - Thio-benzaldehyde
    - Thio-ethyl benzaldehyde
    - Thio-salicylaldehyde
    - Thio-carpryl salicylaldehyde
    - Thio-furfuraldehyde
    - Thio-tetrahydrofurfuraldehyde
  - (*b*) Thio-ketones, e. g.
    - Di-amyl thio-ketone
    - Di-lauryl thio-ketone
    - Thiobenzophenone
    - Thioacetophenone
  - (*c*) Thio-organic acids, and esters and salts of them; such as
    - Thio-fatty acids, e. g.
      - Thio-stearic (thiolic and thionic)
      - Thio-oleic (thiolic and thionic)
      - Dithio-stearic
      - Dithio-oleic
      - Thio ricinoleic (thiolic and thionic)
    - Thio-aromatic acids, e. g.
      - Thio-benzoic acid
      - Thio-salicylic acids
      - Thio-phthalic acids
      - Dithio phthalic acids
    - Esters of the above acids, e. g.,
      - Amyl thio-acetate
      - Lauryl thio-acetate
      - Ethyl dithio-benzoate
      - Methyl thio-stearate
      - Amyl thio-benzoate
      - Lauryl thio-benzoate
      - Lauryl thio-salicylate
      - Dicapryl thio-phthalate
      - Dilauryl thio-phthalate
      - Methyl mercapto-stearate
      - Ethyl mercapto-stearate
    - Salts of the above acids, e. g.,
      - Sodium dithio-benzoate
      - Sodium dithio-propionate
      - Calcium thio-stearate
    - Esters and salts of thio-carbonic acids, e. g.
      - Diethyl dithiocarbonate
      - Diphenyl thiocarbonate
      - Diphenyl tri-thiocarbonate
      - Diamyl tri-thiocarbonate
      - n-Octyl xanthate
      - 2-ethyl hexyl xanthate
      - Capryl xanthate
      - Lauryl xanthate
      - Ethyl phenyl xanthate
      - Benzyl xanthate
      - Stearyl xanthate
      - Sodium xanthate
      - Potassium xanthate
      - Calcium xanthate
    - Organic thio-cyanates and iso-thio-cyanates, such as:
      - Benzyl thiocyanate
      - Benzyl isothiocyanate
      - Butyl thiocyanate
      - Butyl isothiocyanate
      - Lauryl thiocyanate
      - Lauryl isothiocyanate
  - (d) Thio-amides, thio-anilides, and thio-ureas, e. g.
    - Thio-acetamide
    - Thio-acetanilide
    - Thio-stearanilide
    - Thio-benzanilide
    - Thio-carbanilide
    - Thio-urethane
    - Phenyl thio-urethane
    - Thio-urea
    - Di-amyl thio urea
    - Amyl diphenyl thiocarbamate

- (e) Compounds in which the C=S group is included in a ring structure, e. g.
  - Thio-quinone
  - Thio-naphthaquinones
  - Thio-anthraquinone
  - Thio-phthalic anhydride
  - Thio-diphenic anhydride
  - Diphenylene thioketone (thio-fluorenone)
  - Thio-camphor
- (*f*) Carbon bisulfide

4. Compounds in which the —S— radicle forms a part of an organic ring structure, e. g.
   - Thiophene alcohols
   - Thiophene carboxylic acids, and esters and salts of them,
     - Lauryl thenoate
     - Phenyl thenoate
     - Benzyl thenoate
   - Thiophene sulfonic acids, and esters and salts of them
     - Methyl thiophenes
     - Dimethyl thiophene (thioxene)
   - Thianthrene (diphenylene disulfides) and related compounds, such as homologues thereof
   - Diphenylene sulfide
   - Thiazole and derivatives, e. g.
     - Benzothiazole
     - Phenyl benzothiazole
     - Mercapto benzothiazole
   - Thiazine derivatives, e. g. methyl benzothiazine ("Bio-phen")
5. Sulfur atom attached in the form of an inorganic radicle, e. g.
   - Thio-arsenite
   - Thio-phosphite
     - Tri-thio-lauryl phosphite
   - Thio-phosphate
   - Thio-sulfonic acid, and esters and salts
   - Thio-sulfinic acid, and esters and salts

B. Sulfur attached to molecule through means of some other atom, i. e., in the form of an inorganic radicle, e. g.
   - Thio-arsenate
   - Thio-phosphate
   - Thio-sulfate
   - Thio-sulfite
   - Sulfate
   - Sulfite
   - Thio-sulfonate

Of the organic sulfur compounds which do not have stable analogous oxygen counter parts are those included in the following table:

A. Sulfones
   - Sulfoxides
   - Sulfonic acids, and esters and salts of them
   - Sulfinic acids, and esters and salts of them
   - Sulfenic acids, and esters and salts of them

B. Polysulfides, containing the —Sn— radicle, notably
   1. Alkyl polysulfides, e. g.,
      - Dibutyl disulfide
      - Dibutyl trisulfide
      - Dibutyl tetrasulfide
      - Diamyl disulfide
      - Diamyl trisulfide
      - Dilauryl disulfide
      - Dilauryl trisulfide
      - Cyclohexyl disulfide
   2. Aryl polysulfides, e. g.
      - Diphenyl disulfide
      - Diphenyl trisulfide
      - Chlor diphenyl trisulfide
      - Dinaphthyl disulfide
   3. Aromatic substituted aliphatic polysulfides, e. g.
      - Dibenzyl disulfide
      - Chlor dibenzyl disulfide
      - Xylyl disulfide
      - Chlor xylyl disulfide
      - Dibenzyl trisulfide
      - Dibenzyl tetrasulfide
   4. Mixed alkyl-aryl polysulfides, e. g.
      - Amyl benzyl disulfide
      - Amyl benzyl trisulfide
   5. Higher polysulfides, e. g. those formed from the above (or from sulfides) by the addition of an —S— group or groups.

- Organic halogen compounds
  - Halogenated aliphatic hydrocarbons
    - Pentachloroethane
    - Heptachloropropane
    - Hexachlorobutadiene
    - Chlorinated neohexane containing 75% chlorine
    - Chlorinated diisobutylene containing 60% chlorine
    - Chlorinated kerosene containing 45% chlorine
    - Chlorinated hexadecane containing 55% chlorine
    - Chlorinated octadecane containing 50% chlorine
    - Chlorinated eicosane containing 50% chlorine
    - Chlorinated docosane containing 50% chlorine
    - Chlorinated foots oil containing 40% chlorine
    - Chlorinated mineral oil containing 40% chlorine
    - Chlorinated paraffin wax containing 40% chlorine
    - Chlorinated petrolatum containing 40% chlorine
  - Halogenated aliphatic acids
    - Dichlorostearic acid
    - Dichlorolauric acid
    - Dichloropalmitic acid
  - Halogenated aliphatic esters
    - Alkyl dichlorolaurates
    - Alkyl dichloropalmitates
    - Alkyl dichlorostearates
  - Halogenated aromatic compounds
    - Dichlorobenzene
    - Trichlorobenzene
    - Dichloronaphthalene
    - Trichloronaphthalene
    - Polychloronaphthalenes
    - Hexachlorodiphenyl ether
    - Hexachlorodiphenyl sulfide
    - Hexachlorobenzophenone

Specific examples of oil-soluble organic phosphorus acids which may be used in the practice of this invention include the following:

- Organic phosphorus compounds
  - Dithiophosphoric acids
    - Diamyl dithiophosphoric acid
    - Dihexyl dithiophosphoric acid
    - Diheptyl dithiophosphoric acid
    - Dioctyl dithiophosphoric acid
    - Dinonyl dithiophosphoric acid
    - Didecyl dithiophosphoric acid
    - Didodecyl dithiophosphoric acid
    - Ditetradecyl dithiophosphoric acid
    - Dihexadecyl dithiophosphoric acid
    - Dioctadecyl dithiophosphoric acid
    - Di(paraffin wax) dithiophosphoric acid
    - Dieicosyl dithiophosphoric acid
    - Dipentenyl dithiophosphoric acid
    - Dioctenyl dithiophosphoric acid
    - Didecenyl dithiophosphoric acid
    - Dihexadecenyl dithiophosphoric acid
    - Di(methyl-benzyl) dithiophosphoric acid
    - Di-(octylbenzyl) dithiophosphoric acid
    - Di-(phenyloctadecyl) dithiophosphoric acid
    - Di-(xenylhexyl) dithiophosphoric acid
    - Di-(phenoxyoctyl) dithiophosphoric acid
    - Di-(butoxy-ethyl) dithiophosphoric acid
    - Bis-(3,5-dichloro-n-octyl) dithiophosphoric acid
    - Bis-(2,6-dibromo-n-decyl) dithiophosphoric acid
    - Dicyclopentyl dithiophosphoric acid
    - Bis-(dimethylcyclopentyl) dithiophosphoric acid
    - Dicyclohexyl dithiophosphoric acid
    - Di-(methyl-cyclohexyl) dithiophosphoric acid
    - Di-(isopropylcyclohexyl) dithiophosphoric acid
    - Bis-(diisobutylcyclohexyl) dithiophosphoric acid
    - Dinaphthenyl dithiophosphoric acid
    - di-(hydroabietyl) dithiophosphoric acid
    - Dicyclopentenyl dithiophosphoric acid
    - Di-(methylcyclohexenyl) dithiophosphoric acid
    - Diabietyl dithiophosphoric acid
    - Di-(tert-amyl-phenyl) dithiophosphoric acid
    - Di-(2,4-di-tert-amyl-phenyl) dithiophosphoric acid
    - Di-(paraffin wax-phenyl) dithiophosphoric acid
    - Di-(lauroxyphenyl) dithiophosphoric acid
    - Di-(caprylxenyl) dithiophosphoric acid
    - Methyl octadecyl dithiophosphoric acid
    - Butyl hexyl dithiophosphoric acid
    - Isopropyl sec-amyl dithiophosphoric acid
  - Monothiophosphoric acids
    - Diheptyl thiophosphoric acid
    - Dioctyl thiophosphoric acid
    - Dinonyl thiophosphoric acid
    - Didodecyl thiophosphoric acid
    - Dihexadecyl thiophosphoric acid
    - Dioctadecyl thiophosphoric acid
    - Di-(paraffin wax) thiophosphoric acid
    - Dihexenyl thiophosphoric acid
    - Didecenyl thiophosphoric acid
    - Dihexadecenyl thiophosphoric acid
    - Diphenethyl thiophosphoric acid
    - Di-(butyl-benzyl) thiophosphoric acid
    - Di-(octadecylphenyl) thiophosphoric acid
    - Diphenoxydecyl thiophosphoric acid
    - Di-(butoxyphenyl) thiophosphoric acid
    - Di-(nitrophenyloctyl) thiophosphate acid
    - Dicyclopentyl thiophosphoric acid
    - Dicyclohexyl thiophosphoric acid
    - Di-(methyl-cyclohexyl) thiophosphoric acid
    - Thiophosphoric acid
    - Dinaphthenyl thiophosphoric acid
    - Dicyclohexenyl thiophosphoric acid
    - Butyl hexyl thiophosphoric acid
    - Amyl cyclohexyl thiophosphate acid
    - Isopropyl cyclohexyl thiophosphoric acid
  - Phosphoric acids
    - Dihexyl phosphoric acid
    - Dioctyl phosphoric acid
    - Didecyl phosphoric acid
    - Diundecyl phosphoric acid
    - Didodecyl phosphoric acid
    - Dioctadecyl phosphoric acid
    - Dihexenyl phosphoric acid
    - Dioctenyl phosphoric acid
    - Didecenyl phosphoric acid
    - Dioctadecenyl phosphoric acid
    - Dicyclopentyl phosphoric acid
    - Dicyclohexyl phosphoric acid
    - Di-(methylcyclohexyl) phosphoric acid
    - Dicyclopentenyl phosphoric acid
    - Dicyclohexenyl phosphoric acid
    - Di-(methyl-cyclohexenyl) phosphoric acid
    - Di-(phenylbutyl) phosphoric acid
    - Di-(naphthylethyl) phosphoric acid
    - Di-(chlorophenyloctyl) phosphoric acid
    - Di-(propylphenyl) phosphoric acid
    - Di-(methyl-naphthyl) phosphoric acid
    - Methyl decyl phosphoric acid
    - Ethyl dodecyl phosphoric acid
    - Ethyl methylcyclohexyl phosphoric acid
  - Dithiophosphinic acids
    - Dihexyl dithiophosphinic acid
    - Dioctyl dithiophosphinic acid
    - Dinonyl dithiophosphinic acid
    - Ditetradecyl dithiophosphinic acid
    - Didecenyl dithiophosphinic acid
    - Dihexadecenyl dithiophosphinic acid
    - Dicyclohexyl dithiophosphinic acid

- Di-(methyl-cyclohexyl) dithiophosphinic acid
- Dicyclohexenyl dithiophosphinic acid
- Diphenyl dithiophosphinic acid
- Ditolyl dithiophosphinic acid
- Dinaphthyl dithiophosphinic acid
- Amyl hexyl dithiophosphinic acid
- Isopropyl heptyl dithiophosphinic acid
- Ethyl methylcyclohexyl dithiophosphinic acid

Phosphorous acids
- Mono-(paraffin-wax) phosphorous acid
- Mono octadecyl phosphorous acid
- Mono dodecyl phosphorous acid
- Mono octyl phosphorous acid
- Methylcyclohexyl phosphite acid
- Di-(methylcyclohexyl) phosphite acid
- Capryl phosphite acid
- Dicapryl phosphite acid

In addition to the above specific examples of phosphorus acids, the metal salts of each such acid may be regarded also as further specific examples of materials which may be used as starting materials in the practice of this invention.

While the metal complexes of the present invention find their widest application in the preparation of lubricants intended for use in the crankcases of internal combustion engines, they are also useful in the preparation, as above indicated, of improved extreme pressure lubricants. In addition to these particular applications, the metal complexes of this invention may also be used in the preparation of improved lubricants for specialized uses, such as jet aviation, top cylinder, steam cylinder, steam locomotive, railway car, gas engine, refrigerating machine, hydraulic, compressor, turbine, spindle, and torque converter lubricants.

The lubricating oil base in which the metal complexes of the present invention and, optionally, certain additional improving agents are incorporated may be of synthetic, vegetable, animal, or mineral origin. Because of their low cost, availability, and desirable properties, the mineral oils, i. e., those derived from petroleum, find the widest application in the lubricant field.

This invention as heretofore described also relates to various types of lubricant improving agents and lubricating compositions. There is, at the present time, sundry mineral oils, each best suited from the standpoint of viscosity and other properties for different uses and environments. The oil base of a lubricating composition of the present invention designed for a particular use and enviornment will preferably comprise a lubricating oil having the characteristics now well recognized as best suited for such use and environment.

In the following tables, particular characteristics of refined mineral lubricating oils best suited for many types of use and climate are disclosed.

The actual upper limit of preferred viscosity index is infinite for most uses. The values given in the following tables indicate the present commercial maximum values.

Type of Climate	Crankcase			Jet Aviation	Top Cylinder	Steam Cylinder
	Gasoline	Diesel	Aviation			
Arctic						
Preferred viscosity range [1]	90–120/130° F	90–120/130° F	60–90/210° F	25–55/100° F	50–150/100° F	80–120/210° F.
Flash pt. preferably no lower than	300° F	320° F	340° F	225° F	275° F	400° F.
Pour pt. preferably no higher than	−50° F	−50° F	−50° F	−70° F	−50° F	0° F.
Temperate						
Preferred viscosity range [1]	110–400/130° F	110–400/130° F	80–130/210° F	25–55/100° F	50–150/100° F	100–190/210° F.
Flash pt. preferably no lower than	325° F	340° F	360° F	225° F	300° F	500° F.
Pour pt. preferably no higher than	0° F	0° F	−10° F	−70° F	0° F	50° F.
Tropical						
Preferred viscosity range [1]	250–400/130° F	250–400/130° F	120–150/210° F	25–55/100° F	50–150/100° F	100–190/210° F.
Flash pt. preferably no lower than	350° F	360° F	380° F	225° F	300° F	500° F.
Pour pt. preferably no higher than	20° F	20° F	10° F	−70° F	20° F	50° F.
Preferred V. I. (Dean and Davis)	85–120	35–120	95–130	80–150		35–120.

[1] Expressed in Saybolt Universal seconds at indicated temperature.

Type of Climate	Steam Locomotive	Railway Car	Gas Engine	Refrigerating Machine	Hydraulic	Compressor
Arctic						
Preferred viscosity range [1]	25–45/210° F	40–60/210° F	30–60/210° F	40–80/100° F	90–150/100° F	100–800/100° F.
Flash pt. preferably no lower than	350° F	350° F	350° F	300° F	300° F	325° F.
Pour pt. preferably no higher than	−20° F	−20° F	−20° F	−40° F	−40° F	−40° F.
Temperate						
Preferred viscosity range [1]	35–60/210° F	50–70/210° F	40–80/210° F	80–180/100° F	125–300/100° F	200–500/100° F.
Flash pt. preferably no lower than	375° F	350° F	375° F	325° F	325° F	350° F.
Pour pt. preferably no higher than	0° F	0° F	0° F	−25° F	0° F	10° F.
Tropical						
Preferred viscosity range [1]	35–60/210° F	50–70/210° F	40–80/210° F	80–180/100° F	200–1,000/100° F	300–600/100° F.
Flash pt. preferably no lower than	375° F	350° F	375° F	350° F	350° F	350° F.
Pour pt. preferably no higher than	20° F	15° F	20° F.	−25° F	20° F	20° F.
Preferred V. I. (Dean and Davis)	35–120	35–120	85–120	85–150	85–120	85–120.

[1] Expressed in Saybolt Universal seconds at indicated temperature.

Type of Climate	Turbine	Spindle	Torque Converter	Gear	
				Automotive	Industrial
Arctic					
Preferred viscosity range [1]	120-500/100° F	35-100/100° F	20-80/100° F	30-80/210° F	30-1,000/210° F.
Flash pt. preferably no lower than	375° F	275° F	275° F	300° F	300° F.
Pour pt. preferably no higher than	−20° F	−50° F	−50° F	−30° F	10° F.
Temperate					
Preferred viscosity range [1]	125-500/100° F	70-200/100° F	30-250/100° F	50-140/210° F	50-2,000/210° F.
Flash pt. preferably no lower than	400° F	275° F	300° F	325° F	325° F.
Pour pt. preferably no higher than	0° F	0° F	−30° F	0° F	20° F.
Tropical					
Preferred viscosity range [1]	125-500/100° F	150-300/100° F	30-300/100° F	80-200/210° F	80-2,000/210° F.
Flash pt. preferably no lower than	400° F	300° F	300° F	350° F	325° F.
Pour pt. preferably no higher than	20° F	10° F	0° F	20° F	30° F.
Preferred V. I. (Dean and Davis)	85-120	75-120	100-160	75-120	35-120.

[1] Expressed in Saybolt Universal seconds at indicated temperature.

As indicated earlier, our metal complexes find their widest application in the preparation of lubricants intended for use in the crankcases of internal combustion engines, particularly in combination with other improving agents such as, in the preferred instance, dithiophosphate salt-esters and/or phosphorus sulfide treated unsaturated organic materials.

It is common practice in the lubricant additive industry to prepare a liquid, homogeneous concentrate containing one or more separate improving agents and, optionally, a minor proportion of a mineral oil, preferably one of low viscosity. Such liquid concentrates dissolve more readily in lubricating oil bases than do solid improving agents and, in addition, minimize the problems usually associated with the processing, handling, and transportation of solid materials.

Thus the present invention contemplates not only the preparation of finished lubricants containing the metal complexes of our invention, but also the preparation of lubricant improving agents, i. e. concentrates, which when dissolved in suitable lubricating oil bases will yield finished lubricants containing our metal complexes, and, optionally, such other improving agents as are desired.

From an examination of the specification it will be noticed that our metal complexes vary widely in metal content, such metal content usually being expressed, for convenience, as percent metal sulfate ash. As a matter of actual practice in the compounding of lubricants from our metal complexes, we have found that the amount of metal in combined form in the lubricant due to the presence of our complex is the critical factor to be considered. Since it has been shown that our metal complexes may differ very substantially in metal content, it follows that in the preparation of a lubricant having a certain fixed proportion of metal due to our complex, one would use less of a metal complex of high metal content than a similar metal complex of lower metal content. To illustrate this point more specifically, 10 parts by weight of a complex of 40% sulfate ash content dissolved in 90 parts by weight of lubricating oil would yield a lubricant having the same metal content as one prepared by dissolving 40 parts by weight of a complex of 10% sulfate ash content in 60 parts by weight of lubricating oil.

It becomes apparent then that we can properly define the amounts of our metal complexes desirably present in lubricant improving agents, and lubricants only in terms of metal content or a proportional equivalent thereof, for example, metal sulfate ash content. Furthermore, it should be pointed out that the desirable range of such metal or metal sulfate ash content will differ substantially in going from one metal complex to a complex of a different metal. This situation exists because different metals have different chemical combining weights, and are perforce present in different weight percentages in complexes of our invention wherein the organic acid and promoter material have been fixed both as to identity and amount.

As a consequence of a large number of tests performed on lubricants containing metal complexes of our invention, we have been able to determine the operable ranges of metal content and metal sulfate ash content (due to the presence of our complexes) for both lubricant improving agents and finished lubricants.

RANGES FOR WEIGHT PERCENT OF METAL SULFATE ASH AND METAL (DUE TO METAL COMPLEX) IN LUBRICANT IMPROVING AGENTS AND LUBRICANTS

	Range		
	broad	intermediate	preferred
In lubricant improving agent:	*Percent*	*Percent*	*Percent*
Metal sulfate ash due to metal complex.	0.38 to 40	0.64 to 30	1.28 to 20.
Metal due to metal complex.	0.07 to 23.5	0.13 to 17.5	0.27 to 12.
In lubricant:			
Metal sulfate ash due to metal complex.	0.002 to 8	0.005 to 6	0.01 to 4.
Metal due to metal complex.	0.001 to 5	0.0011 to 3.5	0.02 to 2.5.

A wide variety of oil-soluble, phosphorus- and sulfur-bearing organic materials are available and are preferred for use in combination with our oil-soluble, metal complexes in preparing lubricant improving agents and lubricants.

By this statement we do not mean that all oil-soluble, phosphorus-and-sulfur-bearing organic materials are of equal efficacy for use in lubricant compositions. Some are more effective than others; for example, dithiophosphate salt-diesters and phosphorus sulfide treated unsaturated organic materials (especially P_2S_5-treated terpene hydrocarbons) have been found to be of particular utility.

By way of illustration, a number of oil-soluble, phosphorus-and-sulfur-bearing organic materials are given, one or more of which may be used along with our metal complexes in producing lubricant compositions:

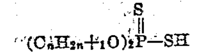
I. Esters and salt-esters of inorganic thioacids of phosphorus, for example
    (1) Esters of thiophosphorus acids, e. g.:
        S-n-octyl monothiophosphite
        S,S-di-n-hexyl dithiophosphite
        Tri-amyl trithiophosphite
        Lauryl diethyl trithiophosphite
        O,O-di-n-hexyl monothiophosphite
        O,S-di-n-octyl dithiophosphite
        Di-lauryl trithiophosphite
        S-cetyl monothiophosphite
    (2) Salt-esters of thiophosphorous acids, e. g.:
        Barium S-cetyl monothiophosphite
        Strontium O,S-dilauryl dithiophosphite
        Calcium di-lauryl trithiophosphite
        Zinc S-octadecyl monothiophosphite
        Copper S,S-di-decyl dithiophosphite

(3) Esters of thiophosphoric acids, e. g.:
Triamyl trithiophosphate
Tri-lauryl dithiophosphate
Tri-cetyl monothiophosphate
Tri-(tert-butyl-phenyl) dithiophosphate
Tri-(methyl-cyclohexyl) dithiophosphate

(4) Salt-esters of thiophosphoric acids, e. g.:
(*a*) Monothiophosphate salt-esters, e. g.:
Barium di-lauryl thionophosphate
Zinc di-(methyl-cyclohexyl) thionophosphate
Cadmium mono-cetyl thionophosphate
Nickel di-lauryl thiolphosphate
Magnesium di-cetyl thiolphosphate

(*b*) Dithiophosphate salt-esters, for example, the sodium, lithium, potassium, calcium, strontium, barium, magnesium, zinc, cadmium, nickel, copper, and cobalt salts of the following dithiophosphoric acid-diesters (the zinc and barium salts being preferred):

(i) Di-alkyl dithiophosphoric acids, e. g.:
Di-amyl dithiophosphoric acids, e. g.:
Di-n-amyl dithiophosphoric acid
Di-sec-amyl dithiophosphoric acid
Di-iso-amyl dithiophosphoric acid
Di-hexyl dithiophosphoric acids, e. g.:
Di-n-hexyl dithiophosphoric acid
Di-sec-hexyl dithiophosphoric acid
Di-(2, 2-dimethyl-butyl-3) dithiophosphoric acid
Di-(4-methyl-pentyl-2) dithiophosphoric acid
Di-(2-methyl-pentyl-1) dithiophosphoric acid
Di-(3-methyl-pentyl-2) dithiophosphoric acid
Di-heptyl dithiophosphoric acids, e. g.:
Di-n-heptyl dithiophosphoric acid
Di-sec-heptyl dithiophosphoric acid
Di-(2,3-dimethyl-pentyl-3) dithiophosphoric acid
Di-(2,4-dimethyl-pentyl-2) dithiophosphoric acid
Di-(3-ethyl-pentyl-2) dithiophosphoric acid
Di-(2-methyl-hexyl-2) dithiophosphoric acid
Di-octyl dithiophosphoric acids, e. g.:
Di-n-octyl dithiophosphoric acid
Di-(2-ethyl-hexyl) dithiophosphoric acid
Di-capryl dithiophosphoric acid
Bis-(diisobutyl) dithiophosphoric acid
Di-nonyl dithiophosphoric acids, e. g.:
Di-(3,5,5-trimethyl-hexyl) dithiophosphoric acid
Di-(2,4,4-trimethyl-hexyl) dithiophosphoric acid
Di-n-nonyl dithiophosphoric acid
Di-decyl dithiophosphoric acids, e. g.:
Di-n-decyl dithiophosphoric acid
Di-(3,6,6-trimethyl-heptyl) dithiophosphoric acid
Di-dodecyl dithiophosphoric acids, e. g.:
Di-lauryl dithiophosphoric acid
Bis-(triisobutyl) dithiophosphoric acid
Di-tetradecyl dithiophosphoric acids, e. g.: di-myristyl dithiophosphoric acid
Di-hexadecyl dithiophosphoric acids, e. g.:
Di-cetyl dithiophosphoric acid
Di-(3,6-diethyl-dodecyl-2) dithiophosphoric acid
Di-alkyl dithiophosphoric acids of the general formula



$$(C_nH_{2n+1}O)_2\overset{\overset{\displaystyle S}{\|}}{P}-SH$$

where *n* is an integer of from about 18 to about 40, e. g.:
Di-octadecyl dithiophosphoric acids, e. g.: di-stearyl dithiophosphoric acid
Di-(paraffin-wax) dithiophosphoric acids
Di-eicosyl dithiophosphoric acids
Di-tetracosyl dithiophosphoric acids
Di-hexacosyl dithiophosphoric acids, e. g.: di-cery dithiophosphoric acid
Di-triacontyl dithiophosphoric acids
Di-hentriacontyl dithiophosphoric acids, e. g.: di-myricyl dithiophosphoric acid
Di-hexatriacontyl dithiophosphoric acids

(ii) Di-aralkyl dithiophosphoric acids, e. g.:
Di-(methyl-benzyl) dithiophosphoric acid
Di-(octyl-benzyl) dithiophosphoric acids, e. g.:
Di-(capryl-benzyl) dithiophosphoric acids
Bis-(diisobutyl-benzyl) dithiophosphoric acids
Di-(phenyl-octadecyl) dithiophosphoric acids, e. g.: di-(phenyl-stearyl) dithiophosphoric acids
Di-(naphthyl-octyl) dithiophosphoric acids, e. g.: di-(alpha-naphthyl-diisobutyl) dithiophosphoric acids
Di-(xenyl-hexyl) dithiophosphoric acids

(iii) Di-cycloalkyl dithiophosphoric acids, e. g.:
Di-cyclopentyl dithiophosphoric acid
Di-(methyl-cyclopentyl) dithiophosphoric acids
Bis-(di-methyl-cyclopentyl) dithiophosphoric acids
Bis-(di-ethyl-cyclopentyl) dithiophosphoric acids
Di-cyclohexyl dithiophosphoric acid
Di-(methyl-cyclohexyl) dithiophosphoric acids
Di-(ethyl-cyclohexyl) dithiophosphoric acids
Bis-(di-methyl-cyclohexyl) dithiophosphoric acids
Di-(isopropyl-cyclohexyl) dithiophosphoric acids
Di-(tert-amyl-cyclohexyl) dithiophosphoric acids
Bis-(diisobutyl-cyclohexyl) dithiophosphoric acids
Di-(cetyl-cyclohexyl) dithiophosphoric acids
Di-(naphthenyl) dithiophosphoric acids
Di-(hydroabietyl) dithiophosphoric acids

(iv) Aromatic dithiophosphoric acids, substituted and unsubstituted, for example:
Di-phenyl dithiophosphoric acid
Di-cresyl dithiophosphoric acids
Di-xylyl dithiophosphoric acids
Di-mesityl dithiophosphoric acids
Di-(ethyl-phenyl) dithiophosphoric acids
Bis-(di-ethyl-phenyl) dithiophosphoric acids
Di-(isopropyl-phenyl) dithiophosphoric acids
Di-(tert-butyl-phenyl) dithiophosphoric acids
Di-(tert-amyl-phenyl dithiophosphoric acids
Bis-(2,4-ei-tert-amyl-phenyl) dithiophosphoric acid
Bis-(diisobutyl-phenyl) dithiophosphoric acids
Di-(cetyl-phenyl) dithiophosphoric acids
Di-(paraffin wax-phenyl) dithiophosphoric acids
Di-(nitro-phenyl) dithiophosphoric acids
Di-(chloro-phenyl) dithiophosphoric acids
Bis-(di-chloro-phenyl) dithiophosphoric aicds
Di-(acetyl-phenyl) dithiophosphoric acids
Di-(lauroxy-phenyl) dithiophosphoric acids
Di-(carbohexoxy-phenyl) dithiophosphoric acids
Di-(thiolauroxy-phenyl) dithiophosphoric acids
Di-(selenohexoxy-phenyl) dithiophosphoric acids
Bis-(triethyl-silico-phenyl) dithiophosphoric acids
Di-(phenoxy-phenyl) dithiophosphoric acids
Bis-(trichloro-phenoxy-phenyl) dithiophosphoric acids
Di-(xenyl) dithiophosphoric acids
Di-(capryl-xenyl) dithiophosphoric acids
Di-(ethyl-naphthyl) dithiophosphoric acids
Di-(lauryl-naphthyl) dithiophosphoric acids
Di-(cetyl-phenanthryl) dithiophosphoric acids
and mixtures of two or more of any of the acids given in i, ii, iii, and iv above.

(*c*) Trithiophosphate salt-esters, e. g.:
Zinc di-lauryl trithiophosphate
Barium di-cetyl trithiophosphate
Cadmium eicosyl trithiophosphate

II. Esters and salts of organic thioacids of phosphorus having at least one carbon-to-phosphorus bond, for example:
(1) Esters of thiophosphinic acids, e. g.:
Lauryl ester of di-hexyl dithiophosphinic acid
2-ethyl-hexyl ester of di-phenyl dithiophosphinic acid
n-Octyl ester of di-tolyl monothiophosphinic acid
Cyclohexyl ester of di-naphthyl monothiophosphinic acid
(2) Salts of thiophosphinic acids, e. g.:
Zinc di-(lauryl-phenyl) dithiophosphinate
Barium di-(2-ethyl-hexyl) dithiophosphinate
(3) Esters of thiophosphonic acids, e. g.:
Di-lauryl ester of phenyl mono-thiophosphonic acid
Di-n-hexyl ester of tolyl dithiophosphonic acid
(4) Salts of thiophosphonic acids, e. g.:
Barium lauryl-phenyl monothiophosphonate
Zinc cetyl-phenyl dithiophosphonate
Calcium di-octyl-naphthyl trithiophosphonate

III. Phosphorus-and-sulfur-bearing organic materials of undetermined structure produced by treating an organic material (preferably unsaturated) with at least one inorganic phosphorus-and-sulfur-bearing reagent; for example, the materials produced in accordance with the particulars of the following table, wherein the designated starting materials were reacted for about 2 to 4 hours at temperatures in the range of from about 80° C. to about 150° C.

UNSATURATED HYDROCARBONS

Example No.	Organic Material	Mols	Additional Reactant	Mols	Reagent	Mols	Analysis of Reaction Product	
							Percent Sulfur	Percent Phosphorous
11	Normal octene-1	4			P_4S_7	1	28.2	14.4
12	do	8			P_4S_7	1	20.6	11.1
13	Iso-octene	4			P_4S_7	1	25.8	15.8
14	do	10			P_4S_7	1	17.3	8.5
15	Di-isobutylene	6	Lorol (Du Pont)	4	P_4S_7	1	14.5	6.1
16	do	8	Oleic Acid	2	P_4S_7	1	12.8	3.6
17	do	4	Lorol (Du Pont)	4	P_4S_7	1	12.8	5.1
18	Caprylene	8			P_4S_7	1	10.8	6.3
19	Dipentene	8			P_4S_5 and P_4S_7	1	6.5	4.4
20	Hexadecene-1	8			P_4S_7	1	10.2	5.6
21	Cetene-1	8			P_4S_7	1		
22	Unsaturated Kerosene (C_{12})	8			P_4S_7	1	13.0	7.1
23	Turpentine	8			P_4S_7	1	15.7	7.3
24	do	4			P_4S_7	1	20.6	12.6
25	do	4			P_2S_5	1	19.5	8.03
26	Tri-isobutylene	8			P_4S_7	1	20.9	16.0
27	Wax Unsaturate	8			P_4S_7	1	9.03	4.7
28	do	8			P_4S_3	1	1.1	1.2

ALCOHOLS AND MERCAPTANS

Example No.	Organic Material	Mols	Additional Reactant	Mols	Reagent	Mols	Analysis of Reaction Product	
							Percent Sulfur	Percent Phosphorous
29	Capryl Alcohol	6	Oleic Acid	2	P_4S_7	1	12.2	6.4
30	do	4			P_4S_3	1	1.7	2.5
31	Oleyl Alcohol	6			P_4S_7	1	8.7	6.2
32	do	8			P_4S_7	1	5.4	4.5
33	Sulfurized Oleyl Alcohol	3			PCl_3	1	9.1	2.0
34	Amyl Mercaptan	3			PCl_3	1	29.2	9.5
ACIDS AND ESTERS								
35	Oleic Acid	8			P_4S_7	1	5.9	4.4
36	do	8			P_4S_3	1	0.9	0.93
37	Oleyl Oleate	4			P_4S_7	1	8.5	3.5
38	Cetyl Oleate	8			P_4S_7	1	3.9	1.6
39	Oleyl Salicylate	8			P_4S_7	1	6.9	3.6

SPECIFIC EXAMPLES OF LUBRICANT IMPROVING AGENTS AND EMPLOYING METAL COMPLEXES OF THE PRESENT INVENTION

Certain oil-soluble phosphorus-and-sulfur-bearing organic materials used in many of the lubricant compositions illustrated herein are designated as follows (unless otherwise stated, percentages given are in weight-percent of total improving agent):

Improving Agent	Description
A	product prepared by reacting about 4 moles of turpentine with 1 mole of P_2S_5 for about 4 hours at about 140° C; 61% solution in low viscosity mineral oil.
B	zinc di-(4-methyl-sec-amyl) dithiophosphate; 44% solution in low viscosity mineral oil.
C	mixture of 60 mole-percent zinc di-(4-methyl-sec-amyl) dithiophosphate and 40 mole-percent zinc di-isopropyl dithiophosphate; 40% solution in low viscosity mineral oil.
D	barium salt of the mixed dithiophosphate diester obtained by treating a mixture of 4-methyl-sec-amyl, n-hexyl, and capryl alcohols (3, 2, and 3 parts by weight, respectively) with P_2S_5; 39% solution in low-viscosity mineral oil.

For each of the specific lubricants shown hereinafter, the composition of the corresponding lubricant improving agent can be discerned by considering the weight percentages of the separate improving agents as parts by weight. For example, the lubricant improving agent corresponding to lubricant No. 1 would consist of 1 part by weight of improving agent B, plus 5 parts by weight of the complex of Example 1 (or 0.71 sulfate ash part by weight thereof). If the separate improving agents do not themselves contain a proportion of mineral oil, some may be added, if necessary, to secure a fully liquid, multi-component "concentrate" as discussed earlier in the section regarding improving agent concentrates.

The values in parentheses ( ) in the percent column below give the percent of metal sulfate ash present in the lubricant imparted by the amount and kind of metal complex employed therein.

Lubricant Number	Composition (weight percent)	
	Percent	Component
1	94.0	SAE 30 mineral oil.
	5.0 (0.71)	metal complex of Example 1.
	1.0	improving agent B.
2	90.0	SAE 30 mineral oil.
	8.0 (1.14)	metal complex of Example 1.
	2.0	improving agent C.
3	92.52	SAE 30 mineral oil.
	5.3 (0.75)	metal complex of Example 1.
	0.28	improving agent A.
	0.98	improving agent C.
	0.92	improving agent D.
4	93.84	SAE 30 mineral oil.
	3.98 (0.61)	metal complex of Example 2.
	0.28	improving agent A.
	0.98	improving agent B.
	0.92	improving agent D.
5	97.13	SAE 30 mineral oil.
	1.47 (0.22)	metal complex of Example 2.
	0.25	improving agent A.
	1.15	improving agent B.
6	96.83	SAE 30 mineral oil.
	1.65 (0.25)	metal complex of Example 2.
	0.2	improving agent A.
	0.88	improving agent B.
	0.44	improving agent D.
7	92.00	SAE 30 mineral oil.
	5.82 (0.82)	metal complex of Example 3.
	0.28	improving agent A.
	0.98	improving agent B.
	0.92	improving agent D.
8	93.94	SAE 30 mineral oil.
	3.88	metal complex of Example 3.
	0.28	improving agent A.
	0.98	improving agent B.
	0.92	improving agent D.
9	94.32	SAE 30 mineral oil.
	1.47	prior art viscosity index improver.
	2.74 (0.38)	metal complex of Example 3.
	0.2	improving agent A.
	0.83	improving agent B.
	0.44	improving agent D.
10	95.28	SAE 30 mineral oil.
	1.47	prior art viscosity index improver.
	1.78 (0.32)	metal complex of Example 4.
	0.2	improving agent A.
	0.83	improving agent B.
	0.44	improving agent D.
11	95.79	SAE 20 mineral oil.
	0.99	prior art viscosity index improver.
	1.75 (0.31)	metal complex of Example 4.
	0.2	improving agent A.
	0.83	improving agent C.
	0.44	improving agent D.
12	96.35	SAE 40 mineral oil.
	1.85 (0.33)	metal complex of Example 4.
	0.14	improving agent A.
	1.2	improving agent B.
	0.46	improving agent D.
13	95.05	SAE 40 mineral oil.
	3.15 (0.45)	metal complex of Example 5.
	0.14	improving agent A.
	1.2	improving agent B.
	0.46	improving agent D.
14	96.08	SAE 40 mineral oil.
	2.12 (0.3)	metal complex of Example 5.
	0.14	improving agent A.
	1.2	improving agent B.
	0.46	improving agent D.
15	94.97	SAE 30 mineral oil.
	3.4 (0.48)	metal complex of Example 5.
	0.49	improving agent A.
	1.14	improving agent C.
	(1)	silicone anti-foam agent.
16	94.44	SAE 30 mineral oil.
	3.38 (0.62)	metal complex of Example 6.
	0.28	improving Agent A.
	0.98	improving agent B.
	0.92	improving agent D.
17	88.9	SAE 10 mineral oil.
	10.0 (1.83)	metal complex of Example 6.
	0.5	zinc di-lauryl dithiophosphate.
	0.6	P and S bearing product of Example 11.

Lubricant Number	Composition (weight percent)	
	Percent	Component
18	92.5	SAE 10 mineral oil.
	6.0 (1.1)	metal complex of Example 6.
	1.0	magnesium di-n-octyl dithiophosphate.
	0.5	P and S bearing product of Example 33.
19	84.0	SAE 10 mineral oil.
	15.0 (2.84)	metal complex of Example 7.
	0.3	triamyl trithiophosphite.
	0.7	P and S bearing product of Example 15.
20	92.0	SAE 20 mineral oil.
	5.5 (1.04)	metal complex of Example 7.
	1.5 (0.27)	metal complex of Example 6.
	0.5	trilauryl trithiophosphate.
	0.5	P and S bearing product of Example 27.
21	95.0	SAE 20 mineral oil.
	4.0 (0.75)	metal complex of Example 7.
	0.8	calcium di-n-decyl dithiophosphate.
	0.2	P and S bearing product of Example 26.
22	96.5	SAE 20 mineral oil.
	2.5 (0.46)	metal complex of Example 8.
	0.5	zinc di-(lauryl-phenyl) dithiophosphinate.
	0.5	P and S bearing product of Example 35.
23	96.5	SAE 20 mineral oil.
	1.0 (0.18)	metal complex of Example 8.
	2.0 (0.38)	barium carbonate complex of Example 7.
	0.5	cobalt di-capryl dithiophosphate.
24	97.5	SAE 20 mineral oil.
	2.0	metal complex of Example 8.
	0.5	P and S bearing product of Example 38.
25	97.3	SAE 30 mineral oil.
	1.5 (0.27)	metal complex of Example 9.
	1.2	improving agent C.
26	93.3	SAE 30 mineral oil.
	6.0 (1.1)	metal complex of Example 9.
	0.5	nickel di-octadecyl dithiophosphate.
	0.2	P and S bearing product of Example 19.
27	96.2	SAE 30 mineral oil.
	3.0 (0.55)	metal complex of Example 9.
	0.5	tri-(tert-butyl-phenyl) dithiophosphate.
	0.3	P and S bearing product of Example 24.
28	91.5	SAE 30 mineral oil.
	8.0 (2.2)	metal complex of Example 10.
	0.5	P and S bearing product of Example 39.
29	95.25	SAE 30 mineral oil.
	4.0 (1.1)	metal complex of Example 10.
	0.75	improving agent A.
30	98.3	SAE 30 mineral oil.
	0.2 (0.055)	metal complex of Example 10.
	1.5	improving agent C.
31	81.0	SAE 30 mineral oil.
	15.0 (4.1)	metal complex of Example 10.
	2.0	zinc di-(methyl-cyclohexyl) dithiophosphate.
	2.0	P and S bearing product of Example 28.

[1] 2 parts per million.

Other modes of applying the principle of the invention may be employed, change being made as regards the details described, provided the features stated in any of the following claims, or the equivalent of such, be employed.

I therefore particularly point out and distinctly claim as my invention:

1. A process which comprises preparing and mixing a mass in which, at 50° C., at least 50% of the total mass is in the liquid state, and in which mass the active components consist of: A, at least one oil-soluble organic acid compound; B, at least one organic metal compound derived from a metal-free organic compound having: (*a*) an ionization constant in water of at least about 1×10^{-10} at about 25° C.; (*b*) a water solubility at 50° C. of at least about 0.0005%; and (*c*) in saturated aqueous solutions at about 25° C. a pH of not greater than about 7, the relative amounts of A and B used being in the range of from about one equivalent of A to about 10 equivalents of B to about 10 equivalents of A to about one equivalent of B; C, water, in an amount equal to at least about one-tenth mole per mole of B; maintaining the mass at a temperature and for a period of time sufficient to drive off substantially all free water and water of hydration which may be present; and then treating the mass with an acidic material of which the ionization constant is higher than the ionization constant of the organic compound from which was derived component B and in amounts sufficient to liberate a substantial proportion of said organic compound of component B.

2. The process of claim 1 further characterized in that component A is at least 1 sulphur acid compound.

3. The process of claim 1 further characterized in that component A is a phosphorus acid compound.

4. The process of claim 1 further characterized in that component A is a thiophosphorus acid compound.

5. The process of claim 1 further characterized in that component A is at least 1 sulphur acid compound and at least 1 phosphorus acid compound.

6. The process of claim 1 further characterized in that component A is at least 1 sulphur acid compound and at least 1 thiophosphorus acid compound.

7. The process of claim 1 further characterized in that component A is at least 1 sulphonic acid compound.

8. The process of claim 1 further characterized in that component A is at least 1 barium salt of an oil-soluble organic acid.

9. The process of claim 1 further characterized in that component A is the barium salt of at least 1 sulphur acid.

10. The process of claim 1 further characterized in that component A is the barium salt of at least 1 phosphorus acid.

11. The process of claim 1 further characterized in that component A is the barium salt of at least 1 thiophosphorus acid.

12. The process of claim 1 further characterized in that component A is a mixture of the barium salts of at least 1 sulfur acid and the barium salts of at least one phosphorus acid.

13. The process of claim 1 further characterized in that component A is a mixture of the barium salts of at least one sulfur acid and the barium salts of at least one thiophosphorus acid.

14. The process of claim 1 further characterized in that component A is at least one barium sulfonate.

15. The process of claim 1 further characterized in that component A is a mixture of at least one barium sulfonate and the barium salts of at least one phosphorus acid.

16. The process of claim 1 further characterized in that component A is a mixture of at least one barium sulfonate and the barium salts of at least one thiophosphorus acid.

17. The process of claim 1 further characterized in that component B is the metal salt of a phenolic compound.

18. The process of claim 1 further characterized in that component B is the metal salt of a phenol.

19. The process of claim 1 further characterized in that component B is the metal salt of a hydrocarbon substituted phenol in which the hydrocarbon substituents have not more than 16 carbon atoms.

20. The process of claim 1 further characterized in that component B is the metal salt of an alkyl phenol.

21. The process of claim 1 further characterized in that component B is the metal salt of an enolic compound.

22. The process of claim 1 further characterized in that the process is treated with CO_2 in amounts sufficient to liberate a substantial proportion of said organic compound of component B.

23. The process of claim 1 further characterized in that the component A is a mixture of petroleum mahogany sulphonic acid compounds and oil soluble alkyl aromatic sulphonic acid compounds.

24. The process of claim 1 further characterized in that the process mass is stripped of said liberated organic compound of component B.

25. The process of claim 1 further characterized in that said process mass is treated with CO_2 in amounts sufficient to liberate a substantial proportion of said organic compound of component B, and said liberated portions of said organic compound of component B are stripped from the process mass.

26. A product in accordance with the process of claim 1.

(References on following page)

References Cited in the file of this patent

UNITED STATES PATENTS

2,616,905	Asseff et al.	Nov. 4, 1952
2,616,906	Asseff et al.	Nov. 4, 1952
2,616,911	Asseff et al.	Nov. 4, 1952
2,616,924	Asseff et al.	Nov. 4, 1952
2,616,925	Asseff et al.	Nov. 4, 1952
2,617,049	Asseff et al.	Nov. 4, 1952