673 XR 2,312,207 Cross Reference Search Room

UNITED STATES PATENT OFFICE

2,312,207

COMPOUNDED OIL

James O. Clayton and Bruce B. Farrington, Berkeley, Calif., assignors to Standard Oil Company of California, San Francisco, Calif., a corporation of Delaware

No Drawing. Application April 12, 1941, Serial No. 388,298

25 Claims. (Cl. 252—32)

This invention relates to a new and useful composition of matter comprising a hydrocarbon oil and a salt of an organic substituted arsenic compound. More particularly, the invention involves compounded oils containing an oxide, sulfide or selenide in which an oxygen, sulfur or selenium atom is directly attached to a metal and to an atom of arsenic.

The present invention involves the discovery that dispersion in hydrocarbon oils of oxides, sulfides or selenides containing the group—

(A) (X) (As) (R)

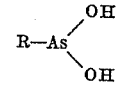
in which A represents a salt-forming element or radical, X is oxygen, sulfur or selenium, As is arsenic, and R is at least one organic radical, imparts new, unpredictable and desirable properties to the composition. These new properties render the compounded oil particularly useful for various purposes. Increased resistance to deterioration under oxidizing conditions, as indicated by greater stability to oxidation and enhanced color stability, comprise the principal advantages of the compounded oils of this invention, but it is to be understood that the invention is not limited to these features. Different compounds of the general type herein involved vary in their degree of effectiveness and may impart one or more other desirable properties to the composition. For example, certain of the compounds may reduce the amount of wear produced in lubrication of metal surfaces as compared with wear resulting with a straight uncompounded lubricating oil. The same or other compounds may inhibit corrosion of alloy bearings of the type represented by copper-lead or cadmium-silver bearing metals, or such compounds may impart enhanced film strength to the oil. In general, however, it has been discovered that the new compositions herein disclosed are more stable to deterioration by heat and oxidation than is a hydrocarbon oil with which the compositions are compounded. The new compounds of this invention are therefore useful where a stabilized oil is desired and resistance to deterioration is important. An example of such utility is their use as lubricating oils, particularly in internal combustion engines, to inhibit gumming of pistons, "varnish" formation, sticking of piston rings, sludge formation in the crankcase, and the like. The compositions are also useful as heat transfer fluids where it may be desirable to inhibit or prevent the formation of a deposit on the metal surfaces from or to which heat is being conveyed. Likewise, the increased resistance to oxidation imparted to the oils by the compounds of this invention finds various applications, such as in an insulating, switch or transformer oil.

Compounds of the type herein involved and containing the group—

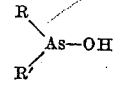
(A) (X) (As) (R)

as previously identified, may be regarded as salts of substituted acids of arsenic. Metal salts of substituted oxyacids of pentavalent arsenic are preferred compounding agents. Metals preferred as components of the salts utilized in this invention are metals selected from groups II, III, IV and VI of Mendeleeff's Periodic Table of the Elements. Specific examples of such metals are: calcium, strontium, barium, magnesium, zinc, cadmium, aluminum, zirconium, bismuth, tin, lead, chromium and molybdenum. Salts of iron, cobalt, nickel, manganese, vanadium, sodium, potassium, copper and silver comprise additional examples of metals falling within the broader aspects of the invention. Salt-forming radicals such as the ammonium and amine radicals are not precluded.

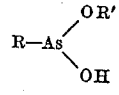
The compounds of this invention are derivatives of substituted acids such as exemplified by the following type formulae for substituted acids of arsenic:



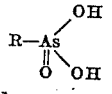
organo ortho-arsonous acid (arsine dihydroxides);



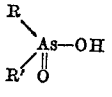
organo arsinous acid (diorgano substituted arsine hydroxide);



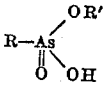
monoester of organo ortho-arsonous acid;



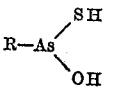
organo arsonic acid;



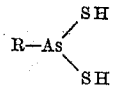
disubstituted organo arsinic acid;



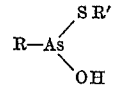
monoester of organo arsonic acid;



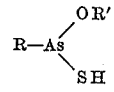
organo monothio-arsonous acid;



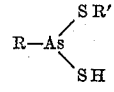
organo dithio-arsonous acid;



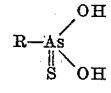
monothio-ester of organo arsonous acid;



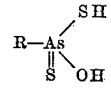
monoester of organo monothio-arsonous acid;



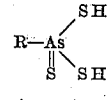
monoester of organo dithio-arsonous acid;



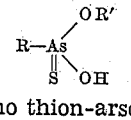
organo thion-arsonic acid;



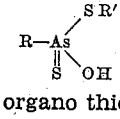
organo thion-monothiol-arsonic acid;



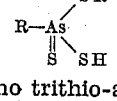
organo trithio-arsonic acid;



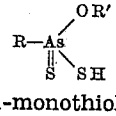
monoester of organo thion-arsonic acid;



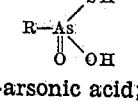
monothio-ester of organo thion-arsonic acid;



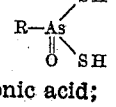
monoester of organo trithio-arsonic acid;



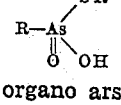
monoester of thion-monothiol-arsonic acid;



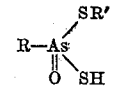
organo monothiol-arsonic acid;



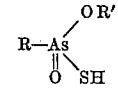
organo dithiol-arsonic acid;



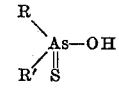
monothio-ester of organo arsonic acid;



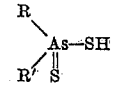
monothio-ester of organo thiol-arsonic acid;



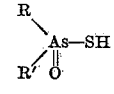
monoester of organo thiol-arsonic acid;



diorgano substituted thion-arsinic acid;



diorgano substituted dithio-arsinic acid;



diorgano substituted thiol-arsinic acid;

where R and R′ are radicals of hydrocarbon structure. It is understood that we do not preclude R and R′ having substituents, such as the polar radicals OH, SH, Cl, NH_2 and COOH. Likewise, by the term "radicals of hydrocarbon structure" it is intended to include radicals containing ether, sulfide and ester groups. Examples of preferred type acids are alkyl or alkaryl arsonic acids having at least twelve carbon atoms in the molecule. However, it is to be understood that the broader aspects of the invention include the use of derivatives of other types of organic substituted acids of arsenic.

It should be borne in mind that in the foregoing type formulae, all of the acids listed may not exist as such and that it is the salt-like derivatives thereof with which the present invention is concerned. Accordingly, existence of the free acid in a stable form is not a prerequisite to the preparation of the derivatives thereof contemplated herein.

Salts of acid arsenite esters and of acid arsenate esters, i. e. of partially esterified arsenous and arsenic acids, are highly useful. The following are type formulae of the acid esters from which the salts may be derived:



monoester of arsenous acid;



diester of arsenous acid;



monothio-ester of arsenous acid;



monothio-ester of monothio-arsenous acid;

Cross Reference Search Room



monoester of trithio-arsenous acid; (monothio-ester of dithio-arsenous acid)



monothio-diester of arsenous acid;



dithio-diester of arsenous acid;



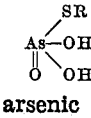
monothio-diester of monthio-arsenous acid;



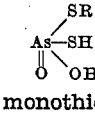
monoester of arsenic acid;



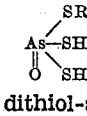
diester of arsenic acid;



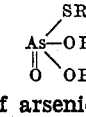
monothio-ester of arsenic acid;



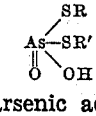
monothio-ester of monothiol-arsenic acid;



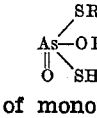
monothio-ester of dithiol-arsenic acid;



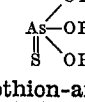
monothio-diester of arsenic acid;



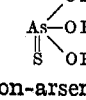
dithio-diester of arsenic acid;



monothio-diester of monothiol-arsenic acid;



monoester of monothion-arsenic acid;



diester of monothion-arsenic acid;



monothio-ester of monothion-arsenic acid;



monothio-ester of thion-monothiol-arsenic acid;



monothio-ester of tetrathio-arsenic acid;



monothio-diester of thion-arsenic acid;



dithio-diester of thion-arsenic acid;



monothio - diester of thion - monothiol - arsenic acid;

In all of the foregoing formulae, R and R′ are radicals of hydrocarbon structure. Throughout the specification and claims the term "radical of hydrocarbon structure" includes:

(*a*) Alkyl radicals, such as amyl, isoamyl, hexyl, heptyl, octyl, the isomeric octyls, lauryl, dodecyl (normal or branched chain), tetradecyl and cetyl (normal or branched chain) radicals;

(*b*) Aryl, such as the phenyl, diphenyl and naphthyl, radicals;

(*c*) Aralkyl, such as phenyl-octadecyl and similar alkyl radicals connected to the arsenic atom and having an aryl group as a substituent in the alkyl chain;

(*d*) Alkaryl, such as methylphenyl, cetylphenyl, and other radicals where the aryl group is connected to the arsenic atom and is substituted with an alkyl group;

(*e*) Cyclic nonbenzenoid radicals, such as cyclohexyl or other alicyclic radicals;

(*f*) Oxy radicals such as those in which the hydrogen of an hydroxyl group has been replaced by esterification, etherification, neutralization with a metal, or the like;

(*g*) Radicals containing thio, amino, halogen or other groups.

The type acids previously listed and the derivatives thereof with which the present invention is concerned may be classified into compounds containing trivalent arsenic, on the one hand, and compounds in which the arsenic is pentavalent, on the other hand. To illustrate the properties and general methods of preparation applicable to these two general groups of compounds, the following discussion is given:

Aryl arsine oxides may be regarded as the anhydride of arsonous acids. Arsonous acids are also called dihydroxy arsines. The unsubstituted oxides are readily obtained by treating the cor-

responding dihalogenated arsines with alkali hydroxides or carbonates in the reaction—

$$R—AsCl_2+Na_2CO_3 \rightarrow R—AsO+2NaCl+CO_2$$

They form white crystalline substances readily soluble in organic solvents, sparingly in alcohol, and insoluble in water. The arsine oxides are amphoteric, dissolving in concentrated aqueous caustic alkalies, and will form the disodium salt when such solutions are properly treated.

Although unsubstituted aryl dihydroxy arsines or arsonous acids corresponding to the formula—

$$R—As(OH)_2$$

have not been isolated, the esters may be successfully obtained; for example, by the interaction of phenyl dichloro arsine and sodium alcoholates or phenylates—

$$C_6H_5AsCl_2+2RONa \rightarrow C_6H_5As(OR)_2+2NaCl$$

In the case of the catechyl ester the lead salt of catechol is employed. These esters may be converted to the metal salt of the half ester or both hydrocarbon radicals of the ester group substituted with metal to obtain the compounding agents of this invention. More detailed descriptions of methods of preparing various salts will be given hereinafter.

Several methods are available for the preparation of aliphatic arsonic acids:

(1) Hydrolysis of the corresponding alkyl arsine oxyhalides or tetrahalides—

$$R—AsOCl_2+2H_2O \rightarrow R—AsO(OH)_2+2HCl$$
$$R—AsCl_4+3H_2O \rightarrow R—AsO(OH)_2+4HCl$$

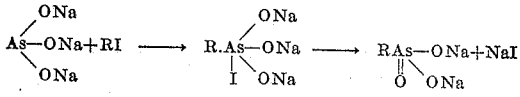
(2) Oxidation of primary aliphatic dihalogenated arsines by means of moist silver oxide or hydrogen peroxide—

$$R—AsCl_2+Ag_2O+2H_2O \rightarrow R—AsO(OH)_2+2HCl+2Ag$$
$$2R—AsCl_2+4H_2O_2 \rightarrow 2R—AsO(OH)_2+4HCl+O_2$$

(3) Oxidation of alkyl arsines by atmospheric oxygen—

$$2R—AsH_2+3O_2 \rightarrow 2R—AsO(OH)_2$$

(4) The reaction of alkyl halides with alkali arsenites is highly useful for present purposes because it yields directly an alkali salt of the arsonic acids according to the reaction—



These sodium salts may be converted to other metal salts by double decomposition, e. g., the calcium salts are precipitated by adding aqueous calcium chloride to aqueous solutions of the sodium salts. Dialkyl arsinic acids may be prepared from secondary trivalent aliphatic arsenicals by oxidation with oxygen or mercuric oxide; from alkyl dichloro arsines and bromine in the presence of water, or by the action of mercuric oxide upon alkyl arsine oxides. The lower members of this series of acids are highly stable and readily form metallic salts.

Thio-dialkyl arsinic acid salts are obtained by the action of hydrogen sulfide upon the respective metal dialkyl arsinates or from the dialkyl arsinic disulfides and metallic salts in alcoholic medium. The effectiveness of some of these thio-dialkyl arsinates may not be due primarily to the compounds themselves but rather to decomposition products thereof after addition to oil, as contemplated by the present invention.

An additional example of the preparation of thio compounds utilizes the aryl arsine sulfides and sesquisulfides as starting materials. The arsine sulfides may be obtained by the action of hydrogen sulfide upon the corresponding arsonic acids:

$$R—AsO(OH)_2+2H_2S \rightarrow R—AsS+S+3H_2O$$

These compounds form sulfo-salts with either alkali polysulfides or alkali sulfides and sulfur:

$$R—AsS+M_2S+S \rightarrow R—AsS(SM)_2$$

where M is an alkali metal. The aryl arsine sesquisulfides also dissolve in alkali polysulfides, forming sulfo-salts:

$$R_2—As_2S_3+M_2S_2+M_2S \rightarrow 2R—AsS(SM)_2$$

There are also a number of methods by which aryl or alkaryl arsonic acids may be prepared. The following are exemplary:

(1) Diazotizing aryl or alkaryl amines and treating the resulting diazo or isodiazo compounds with sodium arsenite in either alkaline or neutral solution, the reaction proceeding according to the equation:

$$RN=NX+Na_3AsO_3 \rightarrow RAsO(ONa)_2+NaX+N_2$$

The reaction with normal diazo compounds is facilitated by the use of catalysts, such as metallic copper, cuprous hydroxide or copper salts in the absence of free alkali;

(2) By oxidizing aryl arsines with nitric acid—

$$RAsH_2+3O \rightarrow RAsO(OH)_2$$

(3) By oxidizing arsine oxides, e. g., with hydrogen peroxide in alkaline solution—

$$RAsO+O+H_2O \rightarrow RAsO(OH)_2$$

The metal salts are readily formed from these acids.

Esters may be prepared from sodium alkoxides and aryl arsine oxychlorides:

$$C_6H_5AsOCl_2+2RONa \rightarrow C_6H_5AsO(OR)_2+2NaCl$$

or by double decomposition between alkyl iodides and silver arsonates, e. g.:

$$C_6H_5AsO(OAg)_2+2RI \rightarrow C_6H_5AsO(OR)_2+2AgI$$

These esters in turn may be partially hydrolyzed and the sodium or other metal salts of the half ester obtained.

Hydroxy aryl arsonic acids may be obtained by directly heating phenol arsenates (Béchamp reaction) or from amino arsonic acids by diazotizing and replacing the diazo group with a hydroxyl in the usual manner.

It should be observed that the straight phenyl substituted acids of arsenic and their salts are, in general, relatively insoluble in organic solvents such as hydrocarbon oils. Accordingly, it is preferred to utilize an aryl radical containing an alkyl substituent since it is found that such substituted aryl radicals impart greater oil solubility to the final compounds. However, it is to be understood that oil solubility is not an absolute prerequisite for utility of the present invention in its broader aspects, as will be explained in more detail hereinafter.

In general, salts and preferably metal salts of organic derivatives of acids of arsenic or their anhydrides are suitable for use in the compositions of this invention in its broadest aspects. By way of summary, the arsenic compounds from which the addition agents of this invention may

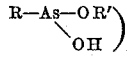
100 Cross Reference Search Room

be derived are as follows: alkyl arsine hydroxides or oxides, alkyl arsine sulfides, dialkyl arsine hydroxides or oxides, dialkyl arsine sulfides, aryl arsine hydroxides or oxides, alkaryl arsine hydroxides or oxides, aryl or alkaryl arsine sulfides and sesquisulfides, diaryl arsine hydroxides or oxides, dialkaryl arsine hydroxides or oxides, diaryl or dialkaryl arsine sulfides, alkyl arsonic acids, alkyl arsine disulfides, alkyl arsinic acids, aryl arsonic acids, aryl di-arsonic acids, halogenated aryl arsonic acids, nitro-aryl arsonic acids, amino aryl arsonic acids, hydroxy aryl arsonic acids, carboxy aryl arsonic acids, alkaryl arsonic acids, alkaryl diarsonic acids, halogenated alkaryl arsonic acids, aryl arsinic acids, alkaryl arsinic acids, aryl trithio-arsonic acids, alkaryl trithio-arsonic acids, aryl arsine disulfides, and alkaryl arsine disulfides.

Heterocyclic substituted acids of arsenic are also contemplated within the scope of the invention: thienyl-2-arsonic acid or oil-soluble derivatives thereof, and methyl benzodiazole arsonic acids are exemplary.

The preferred acids are substituted acids of pentavalent arsenic and the preferred salts comprise the oil-soluble magnesium, aluminum, calcium, barium, tin and chromium salts of these acids. Examples of such salts are:

Partially esterified arsonous acids (type formula of salt-forming acid,



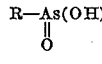
are exemplified by: magnesium, aluminum, calcium, barium, tin and chromium hexyl, octyl, decyl, tetradecyl, cetyl and benzyl, phenylarsonites, as well as magnesium, aluminum, calcium, barium, tin and chromium cetyl or cetylphenyl, cetylphenylarsonites.

Salts of dialkyl arsinic acids,



are exemplified by: magnesium, aluminum, calcium, barium, tin and chromium di-isoamyl, dihexyl, dioctyl, didecyl, didodecyl, ditetradecyl and dicetyl, arsinates.

Salts of alkaryl arsonic acids,



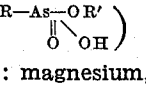
are exemplified by: magnesium, aluminum, calcium, barium, tin and chrominum amylphenyl, decylphenyl, dodecylphenyl, tetradecylphenyl and cetylphenyl, arsonates.

Salts of aryl arsonic acids,



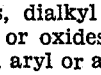
are exemplified by: magnesium, aluminum, calcium, barium, tin and chromium naphthyl or hydroxyphenyl, arsonates.

Salts of partially esterified aryl arsonic acids (type formula of salt-forming acid,



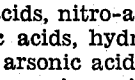
are exemplified by: magnesium, aluminum, calcium, barium, tin and chromium hexyl, octyl, decyl, tetradecyl, cetyl and benzyl, phenylarsonates.

Salts of alkyl arsonic acids,



are exemplified by: magnesium, aluminum, calcium, barium, tin and chromium dodecyl, tetradecyl, cetyl, octadecyl, n-propyl and allyl, arsonates.

Salts of partially esterified alkyl arsonic acids (type formula of salt-forming acid,



are exemplified by. magnesium, aluminum, calcium, barium, tin and chromium decyl, dodecyl, tetradecyl and cetyl, propylarsonates.

In general, the alkali metal salts are the easiest prepared, and the other desired metal salts utilized in this invention may be obtained from aqueous or aqueous alcoholic solutions of the alkali metal salts by adding an aqueous solution containing the desired metal ion. For example, solutions of the sodium salts of arsonic acids may be prepared by neutralization of the free acid.

Example 1.—Aqueous calcium chloride is added to an aqueous solution of sodium allyl arsonate to precipitate the calcium allyl arsonate. The precipitate is filtered, washed and dried or it may be taken up immediately upon precipitation by dissolving in an organic solvent such as a hydrocarbon mineral oil.

Example 2.—To prepare the zinc salt, aqueous zinc chloride solution is added to the sodium allyl arsonate solution.

Example 3.—To prepare the magnesium salt, aqueous magnesium chloride or magnesium sulfate solution is added to the sodium allyl arsonate solution.

Example 4.—To prepare the aluminum salt, aqueous aluminum chloride or aluminum sulfate solution is added to the sodium allyl arsonate solution.

Example 5.—To prepare the tin salt, aqueous tin chloride solution is added to the sodium allyl arsonate solution.

Example 6.—To prepare the lead salt, aqueous lead acetate solution is added to the sodium allyl arsonate solution.

Example 7.—To prepare the chromium salt, aqueous chromic sulfate or chrome alum solution is added to the sodium allyl arsonate solution.

Example 8.—To prepare the manganese salt, aqueous manganese sulfate solution is added to the sodium allyl arsonate solution.

Example 9.—To prepare the nickel salt, aqueous nickel chloride solution is added to the sodium allyl arsonate solution.

Example 10.—To prepare the cobalt salt, aqueous cobalt chloride solution is added to the sodium allyl arsonate solution.

Salts of other alkyl arsonic acids are prepared in a similar manner. Where the alkali metal salt of the parent acid is insufficiently water-soluble to give a suitable dispersion (complete water-solubility is unnecessary in many instances), auxiliary solvents may be mixed with the water to aid solution of the sodium salt. Alcohol is an example of an auxiliary solvent.

Salts of the partially esterified arsonic acids may be prepared by partially hydrolyzing the ester, e. g. with sodium hydroxide to obtain the sodium salt of the partial ester. Other salts may be prepared by double decomposition in ac-

cordance with the methods described in the foregoing examples.

Among the improvements which the compounding agents of this invention may impart to hydrocarbon oils is increased resistance to oxidation or absorption of oxygen at superatmospheric temperatures. In the tests whose results are reported below the oils referred to were subjected to the "Oxidator test" particularly described in the Journal of Industrial & Engineering Chemistry, vol. 28, page 26, 1936. This test is carried out at 340° F. (except where otherwise noted), which conditions are extremely severe. The results of the tests are reported in cubic centimeters of oxygen absorbed per 100 grams of the respective oils.

Test 1

Oil	Paraffinic type S. A. E. 30					
Hours at 400° F	0.5	1.0	1.5	2.0	2.5	3.5
Cc. oxygen absorbed per 100 gms	114	228	359	504	702	1051

Test 2

Oil	Paraffinic type S. A. E. 30+0.5% calcium allyl arsonate		
Hours at 400° F	0.3	0.45	1.3167
Cc. oxygen absorbed per 100 gms	31	67	282

Test 3

Oil	Acid refined naphthenic base S. A. E. 30				
Hours at 340° F	0.5	1.0	2.0	3.0	4.0
Cc. oxygen absorbed per 100 gms	70	150	283	410	590

Test 4

Oil	Acid refined naphthenic base S. A. E. 30+0.5% calcium benzyl arsonate		
Hours at 340° F	0.9	2.15	2.55
Cc. oxygen absorbed per 100 gms	10	45	65

Test 5

Oil	Acid refined naphthenic base S. A. E. 30+.5% calcium allyl arsonate		
Hours at 340° F	0.5	1.0	2.0
Cc. oxygen absorbed per 100 gms	5	25	80

Test 6

Oil	Acid refined naphthenic base S. A. E. 30+1% calcium cetyl arsonate			
Hours at 340° F	0.5	1.0	2.0	4.0
Cc. oxygen absorbed per 100 gms	35	80	170	380

Test 7

Oil	Acid renfied naphthenic base S. A. E. 30+1% calcium phenyl arsonate		
Hours at 340° F	0.5	1.0	2.0
Cc. oxygen absorbed per 100 gms	25	50	110

Test 8

Oil	Acid refined naphthenic base S. A. E. 30+1% calcium benzyl arsonate		
Hours at 340° F	0.5	1.0	2.0
Cc. oxygen absorbed per 100 gms	20	70	130

Test 9

Oil	Acid refined naphthenic base S. A. E. 30+1% calcium n-propyl arsonate		
Hours at 340° F	0.5	1.0	2.0
Cc. oxygen absorbed per 100 gms	45	100	190

Test 10

Oil	Acid refined naphthenic base S. A. E. 30+1% calcium n-amyl arsonate		
Hours at 340° F	0.5	1.0	2.0
Cc. oxygen absorbed per 100 gms	50	115	180

An additional example of the advantages of the compounds of this invention as additives for lubricating oils is illustrated by the non-corrosiveness of the compounds when added to a base oil of relatively low corrosivity. In fact, the addition agents actually reduced the low corrosivity of the base oil. Table I gives the data illustrating these properties.

In the tests whose results are summarized in Table I, thin sheets of the indicated bearing metals were cut into strips (copper-lead, $\frac{9}{16}$'' x 1¾'' x $\frac{3}{32}$''; cadmium-silver ½'' x 1⅜'' x $\frac{1}{16}$''), and these strips were immersed in the exemplified oils carried in 2'' x 20'' glass test tubes; these test tubes were carried in an oil bath maintained at 300° F. ±1° F. Each test tube contained approximately 300 cc. of oil, and air was bubbled through each tube at the rate of ten liters per hour. At the end of each of three 24-hour periods, the strips were removed from the oils, washed with petroleum ether and carefully wiped with a soft cotton cloth; weight losses of the strips were measured in connection with the weight of each individual strip. The duration of the tests was 72 hours.

Table I

Oil	Weight loss in milligrams					
	Copper-lead			Cadmium-silver		
	24 hours	48 hours	72 hours	24 hours	48 hours	72 hours
Paraffinic type S. A. E. 30	0.6	0.9	1.5	0.1	0.1	0.2
Paraffinic type S. A. E. 30+0.5% calcium allyl arsonate	0.5	1.2	1.3	0.0	0.2	0.2
Paraffinic type S. A. E. 30+0.5% calcium benzyl arsonate	+0.2	0.2	0.9	0.0	0.0	0.0

Among the beneficial effects which flow from the incorporation of the compounds herein described in a hydrocarbon oil of the lubricating oil class is enhanced resistance to deterioration and sludge formation as indicated by increased

Cross Reference

color stability. Table II gives data illustrating this property.

Table II

Oil	Color change
Paraffinic type S. A. E. 30	43
Paraffinic type S. A. E. 30+0.5% calcium allyl arsonate	24.5
Paraffinic type S. A. E. 30+0.5% calcium benzyl arsonate	8
Paraffinic type S. A. E. 30+0.5% calcium n-propyl arsonate	18.5

The color stability measurements given in Table II were determined by heating weighed amounts of the oils under carefully controlled conditions followed by a determination of the oil darkening in an electrically operated colorimeter. The heating was carried out in 50 ml. beakers resting in cups in a heavy copper block setting on a hot plate. The copper block was 18 cm. in diameter, 8½ cm. high, and weighed 12.4 kg. It contained seven holes drilled 4½ cm. deep and of such diameter that the beakers fitted loosely in them. The holes were symmetrically arranged around a center one. The temperature distribution throughout the block was quite uniform so that all the beakers in a block were at substantially the same temperature. The beakers used were of uniform cross-section so that when a given quantity of oil was added to each, the level was the same distance below the top in every beaker. The apparatus was protected from stray drafts so that still air was always in contact with the heated oil surface. The surface of the oil was not disturbed in any manner. These precautions are necessary to obtain reproducible results. It is also necessary to acid-wash the beakers before each determination in order to destroy catalysts or inhibitors adsorbed on the surface of the glass.

The colorimeter used for comparing the oxidized samples contained 2 glass cells, 50 mm. square by 7 mm. thick, set equidistant from a light source consisting of a small electric light. The light from the source impinged on two photoelectric cells after passing through the oil samples contained in the glass cells. These two photoelectric cells were mounted in two arms of a Wheatstone bridge so that differences in the two photoelectric currents could be determined. The oil before oxidation was placed in one glass cell and the oil after oxidation was placed in the other. The difference in light transmission through the two oils was thus measured on the Wheatstone bridge and the reading of the bridge dial directly recorded as the color change given in Table II.

The following table gives the relation between the Wheatstone bridge readings and A. S. T. M. color standards.

Table III

Dial readings	A. S. T. M. colors
7	3.
10	4−.
15	5−.
20	5½.
30	7.
40	3+ dilute.
50	3½+dilute
60	4 dilute.
70	5 dilute.
90	7 dilute.

Various of the compounds may be utilized to inhibit piston ring sticking or "varnish" formation in internal combustion engines as, for example, in Diesel engines or in aircraft spark or compression ignition engine operations.

Amine salts of the acids disclosed in this specification fall within the broader aspects of the invention. Examples of suitable amines are the alkyl amines, such as triethyl amine; the alkylol amines, like triethanol amine; and the aromatic amines, such as aniline. Nitrogen bases obtained from petroleum, and especially reduced nitrogen bases such as homologues of piperidine, are also included as an amine with which the salts of this invention may be made.

Reference has previously been made to the derivatives of halogenated organo arsonic acids. These compounds are useful particularly where, in addition to the properties previously disclosed herein, enhanced film strength, oiliness or reduction of wear is desired. Examples of halogenated organo-arsonic acids, the derivatives of which may be utilized in accordance with this invention, are: 2-chloro phenyl arsonic acid, 4-chloro phenyl arsonic acid, and half esters of these acids. Polyvalent metal salts such as magnesium, aluminum, calcium, barium, tin and chromium salts of the half esters are preferred. Likewise, these salts of the chlorinated thio-acids corresponding to the above are particularly useful.

The proportion of the addition agents herein disclosed which may be added to hydrocarbon oils according to the principles of the present invention may vary widely, depending upon the uses involved and the properties desired. As little as 0.05% by weight of various of the compounds gives measurable improvements. From approximately 0.1% to 2% of the compounds may be added to lubricants where enhanced stability under oxidizing conditions is desired. More than 2% of the compounds may be utilized for various purposes, e. g. for preparing lubricating greases and concentrates capable of dilution with mineral lubricating oils and the like. Concentrates containing high percentages of the addition agents comprise a convenient method of handling the ingredients and may be marketed as such as addition agents for lubricants in general as well as for other purposes.

The compounded hydrocarbon oils herein disclosed may have one or more advantages depending upon the particular compounding agents selected, the proportions utilized and the environment or use which the compounded oil is to encounter. It should be observed, for example, that even though a compounded oil may be somewhat corrosive to copper-lead or cadmium-silver bearing metals, Babbitt bearings may be little if at all affected by such corrosive action. Hence, compounded oils which may not be particularly desirable for lubrication of copper-lead or cadmium-silver bearings at high temperatures where corrosion becomes a factor of importance may be highly useful and extremely advantageous in conjunction with operations where bearings of Babbitt or other corrosive-resistant bearing metals are utilized. Likewise, compounded oils in which the addition agent is not sufficiently powerful to stabilize the oil against deterioration by oxidation under the most severe conditions may be highly useful in those applications where the temperatures or oxidizing conditions encountered are not so severe, e. g. in a transformer oil. The present invention in its broader aspects is therefore not limited to the particular ingredients having all or the greatest number of advantages obtainable, but embraces various of

the less advantageous addition agents which will find utility in particular applications where all the possible improvements in the properties may not be required or where the standard of performance may not be so high.

In the preparation of either the finished oils of the invention or the bases or concentrates referred to, complete or clear and homogeneous solution is not always necessary. Blending agents or homogenizers may be employed, if desirable, to prevent sedimentation of the less oil-soluble agents but it has been found that the possible detrimental effect of the presence of filterable insoluble materials of this character, if present, is determined largely by the particular conditions attending the contemplated use and that with those addition agents of limited oil-solubility the presence of additional oil-insoluble agents is not in all cases deleterious to the function of the compositions in their intended manner.

The preferred hydrocarbon oil is a mineral lubricating oil fraction such as a moderately acid refined naphthenic base lubricating oil. Other base oil stocks for the compounded oils involved herein may be utilized, e. g. paraffinic oil stocks or highly refined naphthenic oils, as well as synthetic hydrocarbon oils. It is to be understood that the broader aspects of the invention are not limited to any particular base stock since the advantages herein disclosed may be obtained, at least to some degree, with various oils, the selection of which will be determined by conditions and service which the product is to encounter.

The addition agents of this invention may be utilized in hydrocarbon oils containing other compounding agents, such as pour point depressants, oiliness agents, extreme pressure addition agents, blooming agents, compounds for enhancing the viscosity index of the hydrocarbon oil, and auxiliary stabilizing agents such as metal alcoholates, metal salts of phenols containing organic substituents and the like. Further, thickening agents and/or metal soaps in grease-forming proportions or in amounts insufficient to form grease may be utilized in combination with the addition agents of this invention.

While the character of the invention has been described in detail and numerous examples of the compounds given, this has been done by way of illustration only and with the intention that no limitation should be imposed upon the invention thereby. It will be apparent to those skilled in the art that numerous modifications and variations of the illustrative examples may be effected in the practice of the invention which is of the scope of the claims appended hereto.

We claim:

1. A composition comprising a hydrocarbon oil and a small amount of a salt of an organic substituted arsenic compound, said small amount being at least about 0.05% by weight.

2. A composition comprising a hydrocarbon oil containing from about 0.1% to about 2% by weight of a salt of a substituted compound of arsenic having an organic substituent.

3. A composition comprising a hydrocarbon oil containing from about 0.1% to about 2% by weight of a metal salt of a substituted compound of arsenic having an organic substituent.

4. A composition comprising a hydrocarbon oil containing from about 0.1% to about 2% by weight of a polyvalent metal salt of a substituted compound of arsenic having an organic substituent.

5. A composition comprising a hydrocarbon oil containing from about 0.1% to about 2% by weight of an ammonium salt of a substituted compound of arsenic having an organic substituent.

6, A composition comprising a hydrocarbon oil containing from about 0.1% to about 2% by weight of an amine salt of a substituted compound of arsenic having an organic substituent.

7. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a compound containing the group—

(A) (X) (As) (R)

in which A is a metal, X is selected from the group consisting of oxygen, sulfur and selenium, As is arsenic, and R is an organic radical.

8. A composition as defined in claim 7 in which A is a polyvalent metal.

9. A composition comprising a hydrocarbon oil and at least about 0.05% by weight of a salt of an acid ester of an acid of arsenic.

10. A composition comprising a hydrocarbon oil and at least about 0.05% by weight of a metal salt of an acid ester of an acid of arsenic.

11. A composition comprising a hydrocarbon oil and at least about 0.05% by weight of a polyvalent metal salt of an acid ester of an acid of arsenic.

12. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of an oxyacid of arsenic containing an organic substituent.

13. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of a sulfur-containing acid of arsenic having an organic substituent.

14. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of an oxyacid of pentavalent arsenic containing an organic substituent.

15. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of a sulfur-containing acid of pentavalent arsenic having an organic substituent.

16. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of an organo arsonic acid.

17. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of an organo arsinic acid.

18. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of a monobasic acid of arsenic containing an organic substituent.

19. A composition comprising a hydrocarbon oil and from about 0.1% to about 2% by weight of a salt of a dibasic acid of arsenic containing an organic substituent.

20. A compound lubricant comprising a lubricating oil subject to deterioration at elevated temperatures and a salt of an acid of arsenic containing an organic substituent, said salt being present in a small amount sufficient substantially to inhibit said deterioration.

21. A compounded lubricant comprising a hydrocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.05% by weight based on the oil of a salt of an acid of arsenic containing an organic substituent.

22. A compounded lubricant as defined in claim 21, in which said salt is a polyvalent metal salt.

23. A compounded lubricant comprising a hy-

252. COMPOSITIONS.
100
Cross Reference
Search Room

drocarbon oil with the properties of such composition affecting its use as a lubricant improved by incorporating therein at least 0.05% by weight based on the oil of a salt of an organic acid ester of an acid of arsenic.

24. An addition agent capable of inhibiting deterioration of lubricating oils which comprises a concentrated solution in oil of a salt of an organic substituted arsenic compound, said concentrated solution containing more than 2% by weight based on the oil of said salt and being capable of dilution with mineral lubricating oil to form a homogeneous mixture containing from approximately 0.05% to 2% by weight of said salt.

25. An addition agent capable of inhibiting deterioration of lubricating oils which comprises a concentrated solution in oil of a polyvalent metal salt of an acid of arsenic containing an organic substituent, said concentrated solution containing more than 2% by weight based on the oil of said salt and being capable of dilution with mineral lubricating oil to form a homogeneous mixture containing from approximately 0.05% to 2% by weight of said salt.

JAMES O. CLAYTON.
BRUCE B. FARRINGTON.

