United States Patent Office 3,112,271 Patented Nov. 26, 1963

3,112,271

LIQUID HYDROCARBON COMPOSITION

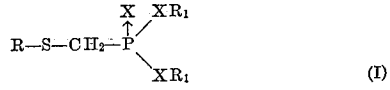
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5 Claims. (Cl. 252—46.6)

This invention relates to improved functional organic compositions and additives therefor. More particularly, the invention relates to compositions of the type of fuel and lubricant compositions having improved properties.

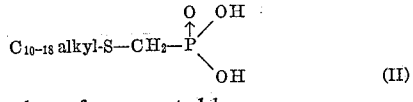
In general, hydrocarbon composition are doped with various oil-soluble compounds, namely, stabilizers and anti-oxidants, such as phenolic compounds, e.g., alkyl phenols and bisphenols; detergent and corrosion inhibitors such as organic salts such as carboxylates, phenates, phosphates, sulfonates and thiocarbamates; anti-wear and extreme pressure compounds such as esters of carboxylic acids or phosphorus acids such as partial esters of fatty acids and polyhydric alcohols or alkyl or aryl phosphites or phosphates, or free fatty acids and sulfur derivatives thereof such as C_{10-18} fatty acids (oleic or stearic acids) and sulfurized unsaturated fatty acids, e.g., sulfurized oleic acid. However, these compounds when used in liquid hydrocarbons, such as lubricating oil compositions which are subjected to high temperatures and pressures break down and fail to impart their expected desired properties under these extreme conditions.

It has now been discovered that liquid hydrocarbon compositions are improved with respect to stability, wear inhibition and extreme pressure properties and contribute to minimizing octane requirement increase when used in an internal combustion engine, and the like by incorporating therein a minor amount of an oil-soluble 2-thiaalkyl phosphorus-containing compound having the general formula:



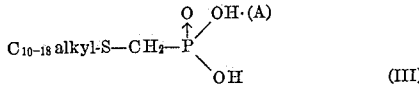
(I)

wherein R is an oil-soluble hydrocarbyl group, such as an alkyl, aryl, aralkyl, alkaryl or cycloalkyl radical having at least 6 and preferably a straight-chain alkyl radical having from 10 to 18 carbon atoms, the R_1's are the same or different groups selected from hydrogen, hydrocarbyl, or amine, preferably an alkylamine and the X's are independently chalcogen atoms having an atomic number of from 8 to 16, such as oxygen or sulfur. Preferred compounds of the general Formula I have the following formula:



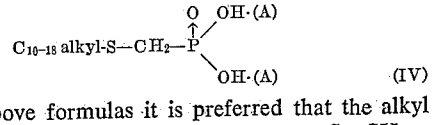
(II)

or the amine sals thereof represented by



(III)

or



(IV)

and of the above formulas it is preferred that the alkyl portion of the molecule be C_{10-18} alkyl $CHR_2—S—CH_2—$ and wherein R_2 is hydrogen or a short alkyl radical of 1–4 carbon atoms, A is an aliphatic amine, preferably a primary or secondary amine, such as C_{8-30} primary straight chain amines, e.g., octylamine, laurylamine,

stearylamine, etc., or branched chain primary aliphatic amines, e.g., t-C_{8-24} alkylamine, such as t-$C_8H_{17}NH_2$, t-$C_{12}H_{25}NH_2$ to t-$C_{15}H_3LNH_2$ or t-$C_{12}H_{25}NH_2$ to t-$C_{15}H_3LNH_2$ or C_{5-18} secondary aliphatic amines, such as diamylamine, di-2-ethylhexylamine, didecylamine, etc.

The 2-thiaalkylphosphonic compounds are prepared by reacting a mercaptan or mercaptide having at least 6 carbon atoms with a halomethylphosphono compound such as chloromethylphosphonic acid or chloromethylphosphonate or their thioderivatives in a suitable solvent, such as an aqueous alcoholic solution, at reflux temperature and under inert conditions until the reaction is completed which normally requires from 1 to about 5 days. The mercaptans include aliphatic mercaptans, such as hexyl, octyl, decyl, dodecyl, octadecyl mercaptans, cycloalkyl mercaptans, such as cyclohexyl mercaptan, dicyclohexyl mercaptan, aralkyl mercaptan; such as phenyldecyl mercaptan, benzyl mercaptan and the like. Instead of the mercaptans, the mercaptides can be used such as the alkali metal (Na or K) mercaptides of the above compounds. Suitable halomethylphosphonic compounds include chloromethylphosphonic acid, mono or dihydrocarbyl chloromethylphosphonates, e.g., mono or dibutyl chloromethylphosphonate, mono or di-2-ethylhexyl chloromethylphosphonate, mono or dilauryl chloromethylphosphonate, mono or diphenyl chloromethylphosphonate, mono or dicyclohexyl chloromethylphosphonate, mono or dibenzyl chloromethylphosphonate, dibutyl dithiochloromethylphosphonate, diphenyl chloromethyl dithiophosphonate, dibutyl chloromethyltrithiophosphonate, alkali metal salts such as Na and K salts of chloromethylphosphonic acid, Na and K salts of monobutyl chloromethylphosphonic acid, Na and K salt of monodecyl chloromethylphosphonic acid and the like.

A preferred method of making the 2-thiaalkylphosphonates is to react a suitable mercapto compound, such as an alkali metal (Na or K) C_{10-18} alkyl mercaptide with an alkali metal (Na or K) salt of chloromethylphosphonic acid in an alcoholic solution under reflux conditions and under an inert atmosphere to form the alkali metal salt of an alkylmercaptomethylphosphonic acid. The salt is then treated with a strong acid such as hydrochloric acid to spring the free alkylmercaptomethylphosphonic acid, which can be converted into desired partial or full esters or polyvalent metal salts or amine salts for use as oil, fuel and grease additives as well as other uses.

The following examples illustrate the preparation of additives for use in accordance with the present invention.

EXAMPLE I

Stoichiometric amounts of the potassium salt of decyl mercaptan and monochloromethylphosphonic acid were dispersed in an aqueous solution of ethyl alcohol and the mixture was refluxed at 78° C. under a nitrogen atmosphere for about 1 day. The potassium decylmercaptomethylphosphonate was then treated with strong hydrochloric acid to spring the free phosphonic acid which was recovered by extraction with ether. The final product decylmercaptomethylphosphonic acid analyzed as follows:

	Percent C	Percent H	Percent S	Percent P	Equiv. Wt. 1st Hydrogen	Equiv. Wt. Both Hydrogens
Found	49.1	9.4	12.0	11.2	261	132
Expected	49.2	9.4	11.94	11.54	268.3	134.1

EXAMPLE II

The procedure of Example I was followed except that potassium salt of phenylmercaptan was used instead of potassium salt of decylmercaptan and the final product was phenylmercaptomethylphosphonic acid.

EXAMPLE III

The dibutyl ester of decylmercaptomethylphosphonic acid of Example I was prepared by treating decylmercaptomethylphosphonic acid with butyl alcohol in an alcoholic solution at about 60° and extracting the ester with ether.

EXAMPLE IV

Di-2-ethylhexylamine salt of decylmercaptomethylphosphonic acid (2-thiadodecylphosphonic acid) was prepared by reacting the product of Example I with di-2-ethylhexylamine in an amount sufficient to completely neutralize both acid groups, at about 50° C. in an alcoholic solution and thereafter recovering the amine salt from the alcoholic solution.

EXAMPLE V

Following the procedure of Example IV, the tert-octadecylamine salt of decylmercaptomethylphosphonic acid was prepared using tertoctadecylamine, available commercially under the trade-name of Primene JM–R, instead of di-2-ethylhexylamine.

The following additional compounds were prepared: octylmercaptomethylphosphonic acid, dodecylmercaptomethylphosphonic acid, cyclohexylmercaptomethylphosphonic acid, benzylmercaptomethylphosphonic acid, phenylmercaptomethylphosphonic acid, dibutyl decylmercaptomethylphosphonate, phenyldecylmercaptomethyl acid phosphonate, dithiobutyl dodecylmercaptomethylphosphonate, dibutyl phenylmercaptomethylphosphonate, dithiooctyl cyclohexylmercaptomethylthiophosphonate, dioctylamine dodecylmercaptomethylphosphonate, dioctadecylamine phenylmercaptomethylphosphonate, tert-octadecylamine dodecylmercaptomethylphosphonate and mixtures thereof.

The additives of this invention are believed to be novel compounds. They are oil-soluble and can be used in amounts of from about 0.1% to about 25%, preferably from about 0.5% to about 5.0% by weight.

Mercaptomethylphosphono compounds of this invention are outstanding additives for various liquid hydrocarbon products, such as natural and synthetic hydrocarbon lubricating oils, greases, fuels (gasoline, kerosene, gas oil, burner fuel oil), asphalts, waxes, slushing oils, industrial oils, e.g., metal working and drawing oils, quenching oils, textile oils, hydraulic oils, dielectric compositions and other industrial oils. They are particularly outstanding when added in small amounts to lubricating oils and lubricating compositions to impart extreme pressure and anti-wear properties to such materials. Also, these additives are useful additives for gasoline, fuel oils, and other light oil products.

Lubricating oils useful for the preparation of compositions of this invention can be one or more of a variety of synthetic oils or natural hydrocarbon oils having a viscosity range of from 50 SUS at 100° F. to 250 SUS at 210° F. (SAE viscosity number ranging from SAE 10W to SAE 90). The natural hydrocarbon oils can be obtained from paraffinic naphthenic, asphaltic or mixed base crudes, and/or mixtures thereof. Synthetic oils include polymerized olefins, alkylated aromatics, isomerized waxes, copolymers of alkylene glycols and alkylene oxides (Ucon fluids) which are described in U.S. Patents 2,425,755, 2,425,845 and 2,774,733 such as Ucon 50HB170, Ucon 50HB660 or Ucon LB550X and which are copolymers of ethylene and 1,2-propylene oxides, the mono and diols, as well as their ester derivatives; organic esters of aliphatic dibasic acids such as di-2-ethylhexyl sebacate or di-2-ethylhexyl adipate and the like. The hydrocarbon oils may be blended with fixed oils such as castor oil, lard oil and the like and/or synthetic oils as mentioned or silicone polymers and the like. Two typical

oils A and B are paraffinic and naphthenic in character, respectively, having the following properties:

	(A) (SAE 10W)	(B) (SAE 30)
Pour point, ° F	−10	−5
Flash, ° F	390	415
Viscosity, SUS at 210° F	44	58
Viscosity Index	90	60

Other suitable oils are the gas turbine lube oils having the following properties:

Grade	1010	1065
Flash, COC, ° F	300	465
Pour, ° F	−10	0
Viscosity, SUS at 100° F	59.4	530
Neutral Number	0.02	0.01
Ash	None	None

The following compositions are illustrative of the invention, the percentages being by weight, of the indicated additive or additives with the remainder being essentially the base.

	Percent
Composition A:	
Example I additive	2
1010 mineral oil	Balance
Composition B:	
Example II additive	2
1010 mineral oil	Balance
Composition C:	
Example III additive	2
1010 mineral oil	Balance
Composition D:	
Example IV additive	2
1010 mineral oil	Balance
Composition E:	
Example II additive	1
SAE 30 mineral oil	Balance
Composition F:	
Example I additive	2
SAE 90 mineral oil	Balance
Composition G:	
Example I additive	2
Lauric acid	2
SAE 90 mineral oil	Balance
Composition H:	
Example I additive	5
Ucon 50HB660 (polyethylene-propylene glycol having a SUS viscosity at 100° F. of 660)	Balance
Composition I:	
Example I additive	2
Di-2-ethylhexyl sebacate	Balance
Composition J:	
Example I additive	1
Leaded gasoline (3 cc. of TEL)	Balance
Composition K:	
Example I additive	0.1
Fuel oil (No. 2)	Balance

Compositions of this invention were evaluated for their extreme pressure properties on a spur-gear machine. The machine consists essentially of two geometrically similar pairs of gears connected by two parallel shafts. The gear pairs are placed in separate gear boxes, which also contain the supporting ball bearings. One of the shafts consists of two sections connected by a coupling. Loading is accomplished by locking one side of the coupling and applying torque to the other. The conditions of the test were:

Speed ——— r.p.m.	3200
Oil temperature ——— ° C.	100
Oil flow-rate ——— cc./sec.	10

Load in increments 5 min. at each setting.

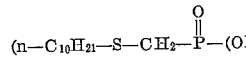
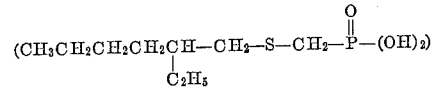
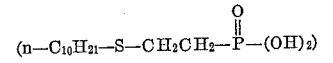
Results of the evaluations are given in Table I and for the purpose of comparison, the results obtained from the use of the base oil alone and with other known extreme pressure compositions are also given.

Table I

Composition:	Score load, lbs./in.
A through I	5,600
1010 mineral oil+2% C_{16} alkenyl succinic acid	1,400
1010 mineral oil+2% malonic acid	2,800
1010 mineral oil+2% 3-hexadecyl adipic acid	1,400
1010 mineral oil+2% dodecylmercapto succinic acid	1,400
1010 mineral oil+10% glycerol monooleate	1,800
1010 mineral oil+2% $C_{13}H_{27}OH$ ("Oxo" process)	600
1010 mineral oil	600

The following compositions were also tested for stability in the Dornté oxidation test described in the Natural Petroleum News, September 17, 1941, pages 294–6, under the following conditions: 302° F., iron catalyst, mineral white oil base and additive amount in each example was about 1% by weight and the results are shown in Table II.

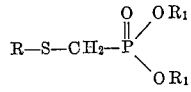
Table II

Additive	Induction period (hrs.)
(1) n-Decylmercaptomethylphosphonic acid 	140
(2) 2-Ethylhexylmercaptomethylphosphonic acid 	80
(3) n-Decylmercaptoethylphosphonic acid 	14

The mercaptomethylphosphono compounds of this invention are useful also for providing superior load-carrying properties for lubricating oils which contain minor amounts of other agents, such as silicone anti-foaming agents, alkylphenol anti-oxidants, polyacrylate ester viscosity-index improvers, long chain fatty acids such as lauric and oleic acids, oiliness agents and the like.

I claim as my invention:

1. A lubricating oil composition comprising a major amount of lubricating oil and a minor amount, sufficient to impart extreme pressure properties to the lubricating oil, of an oil-soluble alkylmercaptomethylphosphono compound having the general formula



wherein R is a C_6–C_{18} saturated alkyl radical, the R_1's are selected independently from the group consisting of hydrogen, and C_1–C_4 saturated alkyl radical.

2. A lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.1% to about 5% of a C_{10-18} alkylmercaptomethylphosphonic acid.

3. A lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.1% to about 5% of an ester of C_{10-18} alkylmercaptomethylphosphonic acid.

4. A lubricating oil composition consisting essentially of a major amount of mineral lubricating oil and from about 0.1% to about 5% of decylmercaptomethylphosphonic acid.

5. A lubricating oil composition consisting essentially a major amount of mineral lubricating oil and from about 0.1% to about 5% of an ester of decylmercaptomethylphosphonic acid.

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