

UNITED STATES PATENT OFFICE

2,685,567

LUBRICANT COMPOSITION CONTAINING
ALKYL-MERCAPTOALKYL PHOSPHITESDenham Harman, Orinda, Calif., assignor to Shell
Development Company, Emeryville, Calif., a
corporation of DelawareNo Drawing. Application November 29, 1951,
Serial No. 259,015

17 Claims. (Cl. 252—33.4)

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This invention relates to lubricants having improved stability and lubricating properties. More particularly, this invention pertains to compounded lubricants having incorporated therein an additive agent possessing outstanding wide temperature anti-oxidant and extreme pressure properties.

Various lubricants whether of natural and/or synthetic origin such as petroleum hydrocarbons, fixed fats and oils and fractions thereof as well as synthetic lubricants derived from olefinic polymers, organic esters and the like, are generally affected by oxygen, air or under various oxidizing conditions resulting in the formation of undesirable products and deleterious reactions which markedly decrease the useful life of such products or render them useless within a relatively short period of time for their intended purpose such as lubrication of engine parts. Additionally this phenomenon alters both the chemical and physical properties of both the additives and base lubricant and in the case of the additives possessing extreme pressure properties, such properties are altered rapidly or dissipate, resulting at the best only in a temporary solution to extreme pressure lubrication.

One object of this invention is to impart extreme pressure properties to base lubricants and inhibit their oxidation over a wide temperature range. Another object of this invention is to prevent oxidation of base lubricants. Still another object of this invention is to produce an improved lubricant of outstanding stability and extreme pressure properties by incorporating in said base lubricant a particular type of additive free from objectionable odors. Other objects of this invention will be apparent from the following description of this invention.

It has now been discovered that stable, excellent extreme pressure lubricants can be prepared by incorporating into a base lubricant minor amounts of a particular type of organo phosphites characterized by the presence of non-oxygen chalkogen atoms solely in the form of non-oxy ether groups in replacing hydrogen atoms of the hydroxy groups of phosphorous acids. The preferred class of compounds comprises the alkyl-mercaptoalkyl phosphites, which are aliphatic phosphites in which the aliphatic radicals replacing the hydrogen atoms of the hydroxyl groups of phosphorous acid, are of the general formula $-RX_y-R'$, in which R and R' are polar or non-polar substituted non-aromatic hydrocarbyl radicals and preferably represent mono and divalent C_1-C_{15} hydrocarbon radicals

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formed by the removal of hydrogen atoms from saturated aliphatic hydrocarbons; X is a non-oxygen chalkogen element, preferably sulfur and y is an integer of from 1 to 4.

Additive agents of this invention can be prepared by any suitable means such as the methods employed in the copending application, Serial No. 381,561 filed July 13, 1948 and which has matured into U. S. Patent No. 2,587,616 of which this application is a continuation-in-part, are particularly preferred.

Illustrative examples of additive agents of this invention include:

- 3-amymercaptopropyl phosphite
- Bis(3-amymercaptopropyl) phosphite
- Tris(3-amymercaptopropyl) phosphite
- 5-pentadecylmercaptopentyl phosphite
- Bis(5-pentadecylmercaptopentyl) phosphite
- Tris(5-pentadecylmercaptopentyl) phosphite
- 3-amymercapto-2-methylpropyl phosphite
- Bis(3-amymercapto-2-methylpropyl) phosphite
- Tris(3-amymercapto-2-methylpropyl) phosphite
- 3-octylmercapto-2-propylbutyl phosphite
- Bis(3-octylmercapto-2-propylbutyl) phosphite
- Tris(3-octylmercapto-2-propylbutyl) phosphite
- 3 - (1,1,3 - trimethylbutylmercapto) - 2 - methylpropyl phosphite
- Bis[3 - (1,1,3 - trimethylbutylmercapto) - 2 - methylpropyl] phosphite
- Tris[3 - (1,1,3 - trimethylbutylmercapto) - 2 - methylpropyl] phosphite
- 3-cyclohexylmercaptopropyl phosphite
- Bis(3-cyclohexylmercaptopropyl) phosphite
- Tris(3-cyclohexylmercaptopropyl) phosphite
- 3-cyclopentylmercapto-2-methylpropyl phosphite
- Bis(3 - cyclopentylmercapto - 2 - methylpropyl) phosphite
- Tris(3 - cyclopentylmercapto - 2 - methylpropyl) phosphite
- 3-amyrselenylpropyl phosphite
- Bis(3-amyrselenylpropyl) phosphite
- Tris(3-amyrselenylpropyl) phosphite
- Tris[3 - isobutylmercapto - 2,3 - dimethylbutyl] phosphite
- Octyl bis(3-amymercaptopropyl) phosphite
- Benzyl bis(3-amymercaptopropyl) phosphite
- Diethyl 3-octylmercapto-2-propylbutyl phosphite
- Dicyclohexyl 3 - cyclohexylmercaptopropyl phosphite
- Di-2-ethylhexyl 3-amyrselenylpropyl phosphite
- 3 - amymercaptopropyl dithio dicyclohexyl phosphite
- Chlorobenzyl bis(3-amymercaptopropyl) phosphite

Chlorophenyl bis(3-amymercaptopropyl) phosphite

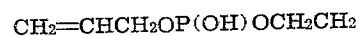
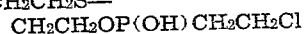
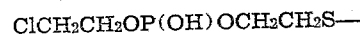
Diallyl 5-pentadecylmercaptopentyl phosphite

Dioleyl 3-octylmercapto-2-propyl phosphite

Mono - 3 - octyl mercapto-2-propyl dithio octyl phosphite

Tris(3-amyldimercaptopropyl) phosphite

Poly phosphites can be used and include such compounds as:



Metal and nitrogen base salts of the acidic phosphorous esters of this invention can also be used as oil improving agents such as the Na, K, Li, Ca, Ba, Al, Zn and Pb as well as the amine salts of any of the above esters or mixtures thereof. Included among the preferred salts are:

Na, Ca and Pb salts of bis(3-amymercaptopropyl) phosphite

Na, Ca, Zn and Al salts of cyclohexyl mercaptopropyl phosphite

Di-2-ethylhexylamine salt of bis(3-amymercaptopropyl) phosphite

Dicyclohexylamine salt of cyclohexylmercaptopropyl phosphite

Morpholine salt of 3-octylmercaptopropyl phosphite

The non-oxygen chalkogen ether containing phosphites of this invention can be used to improve base lubricants, in concentrations varying from 0.001% to 20% and preferably from 0.1% to 5% by weight.

To illustrate the pronounced superiority of additives of this invention as anti-oxidants, the following lubricating compositions were prepared and evaluated by the Dornte Oxidation Stability Test as described in the National Petroleum News, September 17, 1941, pages R294-296, and in the High-Temperature Oxidation Apparatus of H. Diamond et al., which is fully described in the general papers presented before the Division of Petroleum Chemistry at the meeting of the American Chemical Society (September 18-23, 1949, Atlantic City, New Jersey) on pages 31-45 of the reprints. Results of such tests are presented below.

[Base: Refined Mineral Lubricating Oil]

	Dornte Oxidation Test (150° C; 150 cc. (hr.))		High Temperature Test, 260° C., 250 cc. (min.)	
	Cu Cat.	Crankcase Cat.	Cu Cat.	Crankcase Cat.
None	10	5	5	6.5
1.6% tri-octyl phosphite	13	19	32	28
1.84% tris(3-amymercaptopropyl) phosphite	50	120	36	40

Compositions of this invention can be combined with other additives such as blooming agents, pour-point depressors, and/or viscosity improvers, anti-foaming agents, and the like. Among the specific additives for lubricating purposes which can be used are oil-soluble detergents which include oil-soluble salts of various bases with detergent-forming acids. Such bases include metal-containing as well as organic bases. Metallic bases include those of alkali metals, Ca, Mg, Cu, Sr, Ba, Zn, Cd, Al, Sn, Pb, Cr, Mn, Fe, Ni,

Co, etc. Organic bases include various nitrogen bases as primary, secondary, tertiary amines and quaternary ammonium compounds, e. g., benzyl trimethyl ammonium hydroxide.

Examples of detergent-forming acids are the fatty acids of say, 10 to 30 carbon atoms, tall-oil acids, rosin acids, wool-fat acids, paraffin-wax acids (produced by oxidation of paraffin wax), chlorinated fatty acids, aromatic hydroxy fatty acids, paraffin-wax benzoic acids, various alkyl salicylic acids, phthalic acid monoesters, aromatic keto acids, aromatic ether acids, diphenols such as di-(alkylphenol) sulfides and disulfides, methylene bis-alkyl phenols; sulfonic acids such as may be produced by treatment of alkyl aryl hydrocarbons or high-boiling petroleum oils with sulfuric acid; sulfuric acid monoesters; phosphoric, arsonic and antimony acid mono- and diesters, including the corresponding thiophosphoric and arsonic acids and the like.

Additional detergents are the alkaline earth phosphate di-esters, including the thiophosphate di-esters; the alkaline earth diphenolates, specifically, the calcium and barium salts of diphenol mono- and poly-sulfides.

Non-metallic detergents include compounds such as the phosphatides (lecithin and cephalin), certain fatty oils such as rapeseed oils, "Volto-lized" fatty or mineral oils and the like.

An excellent detergent for the present purpose is the calcium salt of oil-soluble petroleum sulfonic acids. This may be present advantageously in the amount of about 0.025% to 0.2% sulfate ash. Also, alkaline metal salts of alkyl phenol-aldehyde condensation products are excellent detergents.

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

Additional ingredients may comprise oil-soluble urea or thiourea derivatives, e. g., urethanes, allophanates, carbazides, carbazones, etc., polyisobutylene polymers, unsaturated polymerized esters of fatty acids and monohydric alcohols and other high-molecular-weight oil-soluble compounds.

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

I claim as my invention:

1. An improved lubricant comprising a mineral lubricating oil base having incorporated therein from 0.01 to 5% by weight of tri(3-amymercaptopropyl) phosphite.

2. An improved lubricant comprising a mineral lubricating oil base having incorporated therein from 0.01 to 5% by weight of bis(3-amymercaptopropyl) phosphite.

3. An improved lubricant comprising a mineral lubricating oil base having incorporated therein from 0.01 to 5% by weight of tris(3-cyclohexylmercaptopropyl) phosphite.

4. An improved lubricant comprising a mineral lubricating oil base having incorporated therein from 0.01 to 5% by weight of 5-pentadecylmercaptopentyl phosphite.

5. An improved lubricant comprising a mineral lubricating oil base having incorporated therein from 0.01 to 5% by weight of 3-cyclophenylmercapto-2-methylpropyl phosphite.

6. An improved lubricant comprising a mineral oil base having incorporated therein a minor amount sufficient to stabilize said oil base against oxidation deterioration of tris(3-amymercapto-propyl) phosphite.

7. An improved lubricant comprising a mineral oil base having incorporated therein a minor amount sufficient to stabilize said oil base against oxidation deterioration of bis(3-amymercapto-propyl) phosphite.

8. An improved lubricant comprising a mineral oil base having incorporated therein a minor amount sufficient to stabilize said oil base against oxidation deterioration of tris(3-cyclohexylmercapto-propyl) phosphite.

9. An improved lubricant comprising a mineral oil base having incorporated therein a minor amount sufficient to stabilize said oil base against oxidation deterioration of 5-pentadecyl mercapto-pentyl phosphite.

10. An improved lubricant comprising a mineral oil base having incorporated therein a minor amount sufficient to stabilize said oil base against oxidation deterioration of 3-cyclopentylmercapto-2-methylpropyl phosphite.

11. An improved lubricant comprising a petroleum hydrocarbon base having incorporated therein in an amount sufficient to stabilize said base against oxidation deterioration of an alkylmercaptoalkyl ester of phosphorous acid in which at least two hydrogen atoms of the acid are replaced by alkylmercaptoalkyl radicals.

12. An improved lubricant comprising a petroleum hydrocarbon base having incorporated therein in an amount sufficient to stabilize said base against oxidation deterioration of an organic ester of phosphorous acid in which the organic radicals which replace hydrogen atoms from the hydroxyl groups of the acid have the formula $-R-S-R'$ in which R and R' are saturated aliphatic hydrocarbon radicals, R and R' containing from 1 to 15 carbon atoms.

13. An improved lubricant comprising a mineral oil base having incorporated therein in an amount sufficient to stabilize said base against oxidation deterioration of an organic ester of phosphorous acid in which the organic radicals which replace hydrogen atoms from the hydroxyl groups of the acid have the formula $-R-S-R'$ in which R and R' are saturated aliphatic hydrocarbon radicals, R and R' containing from 1 to 15 carbon atoms.

14. An improved lubricant comprising a petroleum hydrocarbon base having incorporated therein in an amount sufficient to stabilize said base against oxidation deterioration of an organic ester of phosphorous acid in which the organic radicals which replace hydrogen atoms from the hydroxyl groups of the acid have the formula $-R-X-R'$ in which R and R' each are saturated aliphatic hydrocarbon radicals, R and R' contain from 1 to 15 carbon atoms, X is an element selected from the group consisting of sulfur and selenium.

15. An improved lubricant comprising a liquid hydrocarbon lubricant base having incorporated therein in an amount sufficient to stabilize said base against oxidation deterioration of an organic ester of phosphorous acid in which the organic radicals which replace hydrogen atoms from the hydroxyl groups of the acid have the formula $-R-X-R'$ in which R and R' each are saturated nonaromatic hydrocarbon radicals containing from 1 to 15 carbon atoms, X is an element selected from the group consisting of sulfur and selenium.

16. An improved lubricant comprising a mineral lubricating oil base, from about 0.01% to about 5%, by weight, of tris(3-amymercapto-propyl) phosphite, and from about 0.01% to about 2% of an oil-soluble calcium petroleum sulfonate.

17. An improved lubricant comprising a liquid hydrocarbon lubricant base, having incorporated therein, in an amount sufficient to stabilize said base against oxidation deterioration, an organic ester of phosphorous acid in which the organic radicals which replace hydrogen atoms of the hydroxyl groups of said acid have the formula $-R-X-R'$ in which R and R' each are saturated non-aromatic hydrocarbon radicals containing from 1 to 15 carbon atoms, X is an element selected from the group consisting of sulfur and selenium, and from about 0.01% to about 2% of an oil-soluble detergent.

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