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3,583,915

LOAD CARRYING ADDITIVES

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Int. Cl. C10m 1/44, 1/48
U.S. Cl. 252—46.6 11 Claims

ABSTRACT OF THE DISCLOSURE

Industrial fluid compositions containing in additive amounts an admixture of (1) a dialkyl or dialkaryl hydrogen phosphonate, wherein the alkyl or alkenyl group has 14 carbon atoms or more, and (2) an active sulfur compound have unexpectedly improved load carrying properties. The phosphonates having at least 18 carbon atoms and sulfurized alkylene hydrocarbons are the preferred components.

BACKGROUND OF THE INVENTION

Field of the invention

This invention relates to lubricant compositions containing improved load carrying additives and in particular, it relates to a mixture of a phosphorus compound and a sulfur compound in lubricants.

Description of the prior art

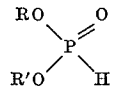
U.S. Pat. No. 3,115,465 deals with combinations of phosphorus compounds and hindered phenols in organic compositions for inhibition of oxidative deterioration of the organic base medium. In U.S. 3,088,917, phosphite esters are disclosed as scavengers for purifying alcohols. U.S. 3,329,742, discloses a method of preparing diaryl hydrogen phosphonates. None of these references show the use of dialkyl or dialkenyl hydrogen phosphonates as having utility as load carrying agents. U.S. 2,708,199 shows the use of organic polysulfides as extreme pressure agents in lubricants. The sulfides contain at least 12 carbon atoms. U.S. 3,278,432 discloses the combination of sulfur compounds with alkaline earth metal carboxylates which combination enhances extreme pressure properties of lubricants.

SUMMARY OF THE INVENTION

It has now been discovered that the combination of a di(organo)hydrogen phosphonate, in which at least one organo group is an aliphatic group containing at least 14 carbon atoms, in admixture with an active sulfur compound evidences synergistic load carrying properties in organic base media.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The di(organo)phosphonates of this invention have the structure



wherein R and R' are individually alkyl or alkenyl from 1 to 30 carbon atoms and at least one of which is an aliphatic group of at least 14 carbon atoms, and preferably over 16 carbon atoms. These groups may have the same number of carbon atoms or different, and one may be further substituted by the presence of alkoxy, hydroxy and halogen substituents. Dioctadecyl and dioleyl phosphonates are of particular interest. The phosphonates used in this invention may be produced by known methods of synthesis.

The second co-additive for the compositions of this invention may be designated as an active sulfur compound. The compounds of this class include organic sulfides and sulfurized hydrocarbons having up to 65% sulfur. Encompassed in this class are those compounds wherein the sulfur is "loosely-bound," and the non-corrosive or "firmly-bound" sulfur compounds. More specifically, such compounds include sulfurized animal and vegetable oils and fats and mineral oils containing at least 1% and up to 20% sulfur; up to about 10% for "firmly-bound" and from about 10% to 20% or more for "loosely-bound." A sulfurized mineral oil, for example, may be used as the base medium, thus supplying the sulfur necessary to achieve the effect described in this invention. Other sulfur-containing oils which may be used are sulfurized lard oil, palm oil, sperm oil, and other natural fats and oils. Also included in the category of active sulfur compounds are alkyl and aryl sulfides and polysulfides, having from 1 to about 30 carbon atoms and preferably about 3 to 15. The sulphur compounds described in U.S. Pat. Nos. 2,993,858 and 3,278,432 are those which may be employed in this invention.

The preferred example of the sulfur additive used in this invention are the polysulfurized alkylene hydrocarbons, particularly those derived from olefins having from 2 to 6 carbon atoms or their polymers. Suitable examples of such organic polysulfides are the polysulfides of ethylene, propylene, butylene, amylene, and the like. Sulfurized alkylene compounds, such as sulfurized isobutylene containing from about 30% to about 65% sulfur, and preferably from 35% to 50% sulfur, are used herein.

The preferred sulfurized alkylene compounds may be prepared by known means. One of the suitable routes for obtaining this additive is through the reaction of a mercaptan with a sulfur halide to form an organosulfenyl halide. This halide is then reacted with an olefin, whereby the sulfur atoms are added to the carbon atoms on either side of the double bond. The product so formed is a thioethyl halide. Further reaction of this compound with a sulfur-containing metal or ammonium salt, such as a metal sulfide, adds another sulfur atom to the product. Another means of obtaining polysulfurized alkylene compounds involves reacting the sulfur halide, such as sulfur monochloride, with an excess of olefin, such as isobutylene. This product is reacted with an alkali metal sulfide in the presence of free sulfur. The resulting product is then neutralized with an inorganic base, such as sodium hydroxide. In these reactions, the use of butylene as the olefin is preferred. The products contain a high percent of sulfur which has been found to be non-corrosive to metal parts of engines.

The compositions of this invention are effective in fluid compositions in which the base is a petroleum product, such as a mineral lubricating oil, or a synthetic fluid. Such synthetic oils as hydrocarbon fluids derived from either long chain alkanes or olefin polymers, ester lubricants obtained from polyhydric alcohols and monocarboxylic acids, or monohydric alcohols and dicarboxylic acids, polyglycol ethers, polyphenyl ethers, polysiloxane fluids, and the like may be used as the base medium for this invention.

The additive concentration may vary from about 0.05% to about 10% for each additive, preferably, the range is from 0.5% to 5% by weight. Optimum performance characteristics are evidenced when the fluid composition contains from about 0.005% to 0.25%, and especially 0.1%, phosphorus and from about 0.5% to 1.5%, and especially 0.9%, sulfur.

The following examples illustrate several embodiments of this invention. Parts and percentages are on a weight basis.

EXAMPLE 1

To a solvent-refined mineral lubricating oil were added 2% by weight of dioctadecyl phosphonate and 2% by weight of a sulfurized isobutylene containing from about 45% to about 47% of sulfur. Both components were prepared by known means.

The composition was tested in the Timken Load Test. This test is a known test used to determine the load carrying properties of additives in lubricating oil compositions. The test is conducted by placing a steel test cup on a shaft which can be rotated at 800 r.p.m. Just below the cup and in contact with it is a small stationary steel block. A load is placed on these parts by means of a lever arm which pushes the block upwards against the rotating cup, which acts as a roller bearing, while the lubricant flows between the two surfaces. The load is gradually increased at 10-minute intervals until failure occurs. Failure is determined by visual inspection during the running period. Load usually varies from 0 to 80 pounds. The load for a pass result is the highest load which does not produce scoring of the contacting test surfaces. The fail rating is the lowest load at which such scoring occurs.

The result for the oil composition of Example 1 was over 60 pounds pass. The results for two compositions, one containing 5% by weight of dioctadecyl phosphonate and one containing 5% of the sulfurized isobutylene, were pass loads of 25 pounds and 30 pounds, respectively.

EXAMPLES

Other oil compositions were tested in the Timken Load Test, and the results, along with those of Example 1, are tabulated in the following table. The results for components used alone are also included in this table.

Example	Lubricant additive	Conc., percent by wt.	Percent P	Percent S	Timken load, lbs. Pass	Timken load, lbs. Fail
(a)	Dioctadecyl phosphonate	5	0.22		25	30
(b)	Dioleyl phosphonate	5	0.22		20	25
(c)	Sulfurized isobutylene	5		2.2	30	35
(d)	Tert-butyl trisulfide	4.5		2	30	35
(e)	Oleyl-2-chloroethyl phosphonate.	2.5	.2		15	20
1(a+c)	Dioctadecyl phosphonate	2	0.1		>60	
	Sulfurized isobutylene	2		0.9		
2(b+c)	Dioleyl phosphonate	2	0.1		>70	
	Sulfurized isobutylene	2		0.9		
3(b+d)	Dioleyl phosphonate	2	0.1		>60	65
	Tert-butyl trisulfide	2		0.9		
4(e+c)	Oleyl-2-chloroethyl phosphonate.	1.25	0.1		55	
	Sulfurized isobutylene	2		0.9		60
5	Dioleyl phosphonate	2	0.1		>70	
	Sulfurized fat [1]	2		0.9		
6	Dioleyl phosphonate	2	0.1		50	55
	Di-tert butyl disulfide	2.5		0.9		
7	Dioleyl phosphonate	2	0.1		60	65
	Di-tert butyl trisulfide	2.0		0.9		

[1] Sulfurized sperm oil containing 9% to 10% sulfur.

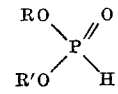
As evidence of the unusual effect of the compositions of this invention, it has been found that phosphonates of lower carbon content do not respond as do the higher phosphonates. A mixture of 1.4% by weight of di-n-dodecyl phosphonate (0.1% phosphorus) and 2% sulfurized isobutylene, Example C (0.9% sulfur) in the same mineral oil used previously had a Timken Load result of 35 and 40. This result is almost as poor as the sulfurized isobutylene alone.

From the results, it is seen that the combination of additives described in this invention is unexpectedly better than the individual additives in providing lubricant compositions with load carrying properties. Comparison with the results for the individual additives evidences unexpected cooperative activity. The lower alkyl phosphonates alone or in combination with the sulfur compound do not show this type of response as do the phosphonates in which at least one aliphatic group having at least 14 carbon atoms is present.

The combined additives of this invention may be used alone or in the presence of other additives, such as detergents, antioxidants, pour point depressants, and the like.

Having described my invention, I claim:

1. A fluid composition having increased load carrying properties comprising a major proportion of a lubricating oil and an amount sufficient to provide the said load carrying properties of a synergistic mixture of (1) a di(organo)phosphonate of the formula



wherein R and R′ are selected from the group consisting of alkyl and alkenyl, each having from 14 to 30 carbon atoms, and (2) an organic sulfur compound selected from the group consisting of sulfurized animal and vegetable oils and fats, a sulfurized monoolefin having from 2 to 6 carbon atoms, and an alkyl polysulfide, wherein said alkyl contains from 1 to about 30 carbon atoms.

2. The composition of claim wherein the sulfur compound is sulfurized sperm oil.

3. The composition of claim 1 wherein the sulfurized monoolefin contains from 30% to 65% sulfur.

4. The composition of claim 1 wherein the total concentration of phosphorus therein is 0.1% and the total concentration of sulfur is 0.9%.

5. The composition of claim 1 wherein the sulfur compound is di-tert-butyl disulfide.

6. The composition of claim 1 wherein the sulfur compound is di-tert-butyl trisulfide.

7. The composition of claim 1 wherein at least one of the organo groups of the phosphonate has over 16 carbon atoms.

8. The composition of claim 7 wherein the phosphonate is dioctadecyl phosphonate.

9. The composition of claim 7 wherein the phosphonate is dioleyl phosphonate.

10. The composition of claim 1 wherein the organic sulfur compound is a sulfurized isobutylene.

11. The composition of claim 10 wherein the sulfurized isobutylene is in admixture with a phosphonate selected from the group consisting of dioctadecyl phosphonate and dioleyl phosphonate.

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U.S. Cl. X.R.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,583,915 Dated June 8, 1971

Inventor(s) HERBERT MYERS

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

In column 4, Claim 2, after the word "claim", insert -- 1 --.

Signed and sealed this 9th day of November 1971.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Acting Commissioner of Patents