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LUBRICATING COMPOSITIONS CONTAINING MIXED SALTS

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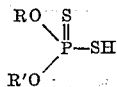
7 Claims. (Cl. 252—32.7)

This invention relates to lubricating compositions containing salts of dialkyl dithiophosphoric acid and to the process for making them. In particular, it relates to greases and lubricating fluids containing co-neutralized mixtures of salts of acetic acid, intermediate molecular weight carboxylic acids and a dialkyl dithiophosphoric acid and to their methods of preparation.

Mixed salts of low molecular weight carboxylic acids and intermediate or high molecular weight carboxylic acids or both which are useful in lubricating oils are known. These known mixtures have been used as grease thickeners and for imparting certain desirable properties to fluid type lubricants.

It has now been found that greases and lubricating fluids can be prepared from thickeners comprising mixtures of salts of a dialkyl dithiophosphoric acid, acetic acid, and intermediate molecular weight monocarboxylic acids. The salt mixtures are formed by co-neutralization of the corresponding acids with an alkaline earth metal base in situ in lubricating oil to form greases having higher load-carrying ability, reduced wear characteristics, and a lower degree of thixotropy than greases thickened with the aforementioned known mixtures. Furthermore, the presence of the dithiophosphoric acid salt in the co-neutralized mixtures acts as an oxidation inhibitor. Moreover, such low thixotropic greases are very plastic and are particularly useful in centralized lubrication systems because of their ease of pumping and their good slumping properties. Also, under high shearing stresses, the greases of the invention do not solidify or channel but flow readily to the gears. Moreover, because of the extreme plasticity of the thickeners, relatively large amounts can be incorporated into the grease to increase its extreme pressure properties without resulting in undue hardening. By using smaller amounts of the thickener of the invention, fluid lubricants are formed which have high load-carrying ability and reduced wear properties.

The dialkyl dithiophosphoric acids utilized in the present invention have the following general formula:



wherein R is an aliphatic hydrocarbon radical having either a straight or branched chain and containing from 3 to 8 carbon atoms. R' is the same or different from R and is also an aliphatic hydrocarbon radical having a straight or branched chain and containing from 3 to 8

2

carbon atoms. Examples of specific compounds which can be used include:

Di-n-propyl dithiophosphoric acid
Di-n-butyl dithiophosphoric acid
Dihexyl dithiophosphoric acid
Dioctyl dithiophosphoric acid
Propyl hexyl dithiophosphoric acid

The intermediate molecular weight monocarboxylic acids used as a component of the thickeners include those unsubstituted aliphatic monocarboxylic acids containing from 8 to 12 carbon atoms per molecule. For example, a mixture of caprylic, capric, and lauric acids which are obtained from coconut oil can be used.

The metal component of the thickeners of this invention are chosen from the alkaline earth metals such as calcium, strontium, and barium. Calcium is particularly preferred due to its low cost and availability. Mixtures of the above metals can be employed if desired. The metals are reacted with the acids in the form of metal bases such as the alkaline earth metal hydroxides, oxides, and carbonates.

The mol ratio of the dialkyl dithiophosphoric acid to the intermediate molecular weight monocarboxylic acids in the thickeners is in the range of 1:1 to 1:4. The mol ratio of the dialkyl dithiophosphoric acid and the intermediate molecular weight carboxylic acids combined to the acetic acid is in the range of from 1:2.5 to 1:15. In terms of parts by weight, excellent thickeners can be prepared from a mixture of 1 to 4 parts, preferably one part of dialkyl dithiophosphoric acid; 4 to 1 parts, preferably 2 to 1 parts of intermediate molecular weight monocarboxylic acids; and 10 to 1 parts, preferably 5 to 1 parts of acetic acid; with sufficient alkaline earth metal base to neutralize the mixture of acids.

The lubricating compositions of the invention comprise from 50 to 98 wt. percent of a lubricating oil and from about 2 to 50 wt. percent of the thickener. When a grease is desired, the composition will contain about 15 to 50 wt. percent, preferably 20 to 40 wt. percent of the thickener and about 50 to 85 wt. percent, preferably 60 to 80 wt. percent lubricating oil; while for fluid lubricants the composition will contain from about 2 to 15 wt. percent, preferably 5 to 10 wt. percent of the thickener, and about 85 to 98 wt. percent lubricating oil.

The choice of lubricating oil used as a menstruum for co-neutralization of the acids with an alkaline earth metal base depends on the particular use contemplated for the finished lubricant. A wide variety of mineral as well as synthetic lubricating oils can be used. In general, the lubricating oil has a viscosity within the range of about 60 to 2500 S.S.U. at 100° F. and about 35 to 200 S.S.U. at 210° F., a pour point of about +20 to -75° F. and a flash point of about 350° to 650° F. Oils having a viscosity index of 100 or higher are usually desirable, though oils having a low viscosity index can be employed. As previously mentioned, synthetic as well as mineral lubricating oils can be employed as part or all of the liquid phase of the grease, and they include synthetic lubricating oils of the hydrocarbon, hydrocarbon polymer, ester, complex ester, formal, mercaptal, polyalkylene oxide, silicone, and similar types. Synthetic oils such as the simple diesters can also be used, e.g. di-2-ethylhexyl sebacate, di-isooctyl azelate and the complex esters formed from

glycols or alcohols or both with dicarboxylic acids or monocarboxylic acids or both.

The dialkyl dithiophosphoric acids of the invention are prepared by reacting phosphorus pentasulfide with an appropriate aliphatic alcohol or alcohols by techniques known to the art.

The reaction temperatures utilized for the co-neutralization of the acetic acid, intermediate molecular weight monocarboxylic acids and the dialkyl dithiophosphoric acid in a lubricating oil menstruum are in the range of about 150° to 350° F. However, when temperatures in the lower end of this temperature range are utilized, the heat of reaction will generally increase the temperature of the reaction mixture. The temperature of reaction is not critical, except that temperatures much above 350° F. should not be employed.

The reaction can take place by intimately mixing the metal base and lubricating oil and slowly adding with agitation a blend of the three acids. The agitation can be continued and the temperature allowed to drop to room temperature. However, the reaction temperature preferably is maintained for about ½ to 4 hours to insure completion or the salt formation. The mixture can then be cooled, and a conventional additive added, if desired. The mixture can then be homogenized such as by passing through a Gaulin homogenizer or a Charlotte Mill.

The lubricating compositions of the invention can be prepared by co-neutralizing the acids in all the lubricating oil which is required in the finished lubricating composition. Alternatively, the co-neutralization can take place in less than all but in at least a dispersing portion of the lubricating oil used in the finished composition and then additional lubricating oil blended therewith to form the finished product.

The invention will be better understood by reference to the following examples which include the preferred embodiments of the invention.

EXAMPLE I

A grease was prepared by dispersing 7.8 wt. percent of

of dihexyl dithiophosphoric acid was then added to the lime-oil dispersion slowly with agitation over 1 hour. No external heating was applied but the temperature rose to 160° F. during the addition. The mixture was then allowed to cool and the agitation continued until the temperature had subsided to about 100 to 120° F. The grease was then passed through a Gaulin homogenizer and inspected.

EXAMPLE II

A grease was prepared by first dispersing 4.75 wt. percent of hydrated lime in 86.25 wt. percent of a mineral lubricating oil having a viscosity of 1200 S.S.U. at 100° F. Then a blend of 6.00 wt. percent of glacial acetic acid, 1.50 wt. percent of Wecoline AAC acids, and 1.50 wt. percent of dihexyl dithiophosphoric acid was added to the mineral oil at a temperature of 320° F. The resulting product was agitated, allowed to cool, and then passed through a Gaulin homogenizer.

EXAMPLE III

A grease prepared in accordance with Example I was heated to 320° F. in a steam kettle at 100 lbs. per square inch of steam pressure and the resultant semi-fluid material was Gaulin homogenized and blended with an equal quantity of a lubricating oil having a viscosity of 177.8 S.S.U. at 100° F. and a viscosity index of 110. The resulting blend was again Gaulin homogenized at 5,000 lbs. per square inch.

EXAMPLE IV

A grease prepared according to Example I was heated to 320° F. in a steam kettle at 100 lbs. per square inch of steam pressure and then Gaulin homogenized. The homogenized material was then blended with an equal quantity of a mineral lubricating oil having a viscosity of 1200 S.S.U. at 100° F. The resulting blend was again Gaulin homogenized at 5,000 lbs. per square inch.

The characteristics of the above lubricants and greases are shown in the following Table I.

Table I

Properties	Example I	Example II	Example III	Example IV
Appearance	Smooth uniform grease.	Smooth uniform fluid.	Uniform fluid lubricant.	Uniform fluid lubricant.
Dropping Point, ° F.	500+			
Consistency:				
Penetrations, 77° F., mm./10—				
Unworked	310			
Worked 60 strokes	320			
Worked 100,000 strokes	325			
Viscosity, S.S.U.:				
100° F.		1900.0	186.3	1395.
210° F.		128.0	46.2	90.8.
Extreme pressure properties:				
Almen test—				
Gradual loading:				
Wt. Carried	15.	15.	15.	15.
Pin Condition	Excellent polished	Excellent polished	Excellent polished	Excellent polished.
Shock loading:				
Wt. Carried	15.	15.	15.	15.
Pin Condition	Excellent polished	Excellent polished	Excellent polished	Excellent polished.
Timken Test: 50 lbs. load				
4 Ball Wear Test: Scar Spot Diam., mm. (1,800 r.p.m.—10 kg.—1 hour—75° C.)	0.23	0.22	0.24	0.22.
Centrifuge Test: ¼ hour, 1,500 r.p.m., Percent Sediment.		1.5	0.75	0.5.

hydrated lime in 77.8 wt. percent of a mineral lubricating oil having a viscosity of 45.3 S.S.U. at 210° F., a viscosity of 177.8 S.S.U. at 100° F., and a viscosity index of 110. A blend of 10.0 wt. percent of glacial acetic acid, 2.4 wt. percent of Wecoline AAC acids,¹ and 2.0 wt. percent

¹ Wecoline AAC acids has the following composition: 20% lauric acid, 24% caprylic acid and 56% capric acid.

As previously noted, the acids making up the salt mixtures of the invention are co-neutralized in situ in mineral oil. It can be seen from the following Table II that the greases of this invention have unexpectedly good characteristics when compared to an analogous product containing calcium dialkyl dithiophosphate which was not formed by co-neutralization with the other acids.

Table II

LOAD-CARRYING TESTS ON GREASES CONTAINING CALCIUM DIHEXYL DITHIOPHOSPHATE

	Grease of Example I	Grease similar in composition to Example II but formed at 150° F. by separate addition of Calcium dihexyl dithiophosphate
Appearance.....	Uniform fluid Product..	Calcium dihexyl dithiophosphate tends to settle out even after Gaulin homogenization.
4 Ball Wear Test: Scar Spot, Diam., mm.....	0.23.....	0.34.
Almen Test:		
Gradual Loading—		
Weights carried.....	15.....	15.
Pin Condition.....	Excellent polished.....	Slight scratching.
Shock loading—		
Weights carried.....	15.....	10.
Pin Condition.....	Excellent polished.....	Sheared.

As seen from the above tables, excellent solid greases and fluid lubricants can be prepared wherein the thickener comprises a co-neutralized mixture of salts of acetic acid, intermediate molecular weight monocarboxylic acids and a dialkyl dithiophosphoric acid.

Various other additives can also be added to the lubricating compositions, such as detergents, oxidation inhibitors, viscosity index improvers, corrosion inhibitors, pour depressants, dyes, other grease thickeners, and the like, as known to those skilled in the art.

What is claimed is:

1. A lubricating composition comprising from 50 to 98 wt. percent of a lubricating oil having a viscosity in the range of 60 to 2500 S.S.U. at 100° F., and from 2 to 50 wt. percent of a thickener comprising a co-neutralized mixture of alkaline earth metal salts of acetic acid, intermediate molecular weight monocarboxylic acids having from 8 to 12 carbon atoms per molecule and a dialkyl dithiophosphoric acid having from 3 to 8 carbon atoms per alkyl group, the mole ratio of dithiophosphoric acid to intermediate molecular weight monocarboxylic acid being about 1:1 to 1:4, the mole ratio of dithiophosphoric acid and intermediate molecular weight monocarboxylic acids combined to acetic acid being in the range of from 1:2.5 to 1:15, said mixture being prepared at a temperature of about 150° to 350° F.

2. A lubricating grease composition according to claim 1 wherein the composition has from 20 to 40 wt. percent thickener.

3. A fluid lubricating composition according to claim 1 wherein the composition has from 2 to 15 wt. percent thickener.

4. A lubricating composition comprising from 50 to 98 wt. percent of a lubricating oil having a viscosity in the range of 60 to 2500 S.S.U. at 100° F., and from 2 to 50 wt. percent of a thickener comprising a co-neutralized mixture of alkaline earth metal salts of 10 to 1 parts by weight of acetic acid, 4 to 1 parts by weight of intermediate molecular weight monocarboxylic acids having from 8 to 12 carbon atoms per molecule and 1 to 4

parts by weight of a dialkyl dithiophosphoric acid having from 3 to 8 carbon atoms per alkyl group, said mixture being prepared at a temperature of about 150° to 350° F.

5. A lubricating grease composition comprising a major proportion of a mineral lubricating oil and from 20 to 40 wt. percent of a co-neutralized calcium salt mixture of from 10 to 1 parts by weight of acetic acid, 4 to 1 parts by weight of coconut oil acids and 1 to 4 parts by weight of dihexyl dithiophosphoric acid, said mixture being prepared at a temperature of about 150° to 350° F.

6. A lubricating oil composition comprising a major proportion of a mineral lubricating oil and from 5 to 10 wt. percent of a co-neutralized calcium salt mixture of from 10 to 1 parts by weight of acetic acid, 4 to 1 parts by weight of coconut oil acids and 1 to 4 parts by weight of dihexyl dithiophosphoric acid, said mixture being prepared at a temperature of about 150° to 350° F.

7. The process of preparing a lubricating composition comprising co-neutralizing with an alkaline earth metal base, and in a dispersing portion of a lubricating oil having a viscosity in the range of 60 to 2500 S.S.U. at 100° F., a mixture of acetic acid, intermediate molecular weight monocarboxylic acids having from 8 to 12 carbon atoms per molecule, and a dialkyl dithiophosphoric acid having from 3 to 8 carbon atoms per alkyl group at a temperature in the range of 150° to 350° F., the mole ratio of dithiophosphoric acid and intermediate molecular weight monocarboxylic acids combined to acetic acid being in the range of from 1:2.5 to 1:15 and the mole ratio of dithiophosphoric acid to intermediate molecular weight monocarboxylic acid being about 1:1 to 1:4.

References Cited in the file of this patent

UNITED STATES PATENTS

2,252,985	Rutherford et al.	Aug. 19, 1941
2,343,213	Ashley	Feb. 29, 1944
2,344,392	Cook et al.	Mar. 14, 1944
2,364,283	Freuler	Dec. 5, 1944
2,364,284	Freuler	Dec. 5, 1944