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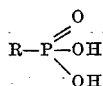
LUBRICATING COMPOSITIONS CONTAINING PHOSPHONIC ACID SALTS

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This invention relates to lubricating oil compositions containing salts of phosphonic acid. Particularly, the invention relates to lubricating fluids and greases improved in their oxidation resistance, load-carrying and anti-wear properties by certain metal salts of phosphonic acid.

It has been found that metal salts of high molecular weight hydrocarbon phosphonic acids containing 10 to 30 carbon atoms can be used to thicken lubricating oil to form greases having high dropping points. In addition to functioning as a thickening agent, these high molecular weight phosphonic acid salts serve as antioxidants which inhibit the degradation of the base oil, as well as imparting load-carrying and anti-wear properties to the lubricant. The metal salts of lower molecular weight hydrocarbon phosphonic acids containing 1 to 10 carbon atoms, while having reduced oil thickening power, still impart load-carrying and anti-wear properties to the oil as well as serving as antioxidants. It has been further found that the phosphonic acid salts can also be used in combination with other thickening agents, such as metal carboxylates and metal sulphonates.

The phosphonic acids used in preparing the salts of the invention have the general formula:



wherein R may be any hydrocarbon group containing 1 to 30 carbons. Such hydrocarbon groups may be saturated or unsaturated, aliphatic, aromatic, or cyclic, e.g., alkyl, aryl, cycloalkyl or alkenyl radicals. Specific examples of these phosphonic acids will include cetane phosphonic acid, dodecane phosphonic acid, ethane phosphonic acid, benzene phosphonic acid, toluene phosphonic acid, cyclohexane phosphonic acid, cyclopentane phosphonic acid, cetene phosphonic acid and octadecene phosphonic acids.

The metal component of the phosphonic acid salt can be any metal used in the grease-making art, e.g., aluminum. However, it is preferably an alkali metal such as sodium, lithium, potassium or an alkaline earth metal, such as calcium, barium, strontium and magnesium.

The phosphonate salt is formed by neutralizing the phosphonic acid with a metal base such as hydroxide, or oxide of the desired metal constituent, e.g., $\text{Ca}(\text{OH})_2$. The reaction mixture is then heated to dehydrate and to remove the water of reaction.

While the preformed phosphonates may be directly added to oil and grease compositions, it is more advantageous to form the salt in situ in at least a portion of the lubricating oil to thereby obtain a finer dispersion of the salt in oil. Thus, the phosphonic acid, if oil insoluble, may be first dissolved in hot water, oil added and then the metal base (generally also in a water solution) added.

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However, if the phosphonic acid is oil-soluble, then it may, of course, be directly dissolved in the oil and neutralized. Generally, the phosphonic acids having eight or more carbon atoms will be oil-soluble, while those having less than eight carbon atoms will be oil-insoluble. In either case, the reaction mixture is next heated to a temperature of about 212 to 600° F., in order to complete the reaction and to dehydrate the mixture. After dehydration, the oil-salt product may then be further blended with other oil or grease materials to form a finished lubricant. The finished lubricant, particularly if it is a grease, can then be homogenized by passing it through a Travis mill, a Morehouse mill or a Gaulin homogenizer in order to obtain a smoother product.

Metal salts of phosphonic acids can be used in combination with metal salts of C_1 to C_{30} fatty acids as well as metal sulphonates. In general, phosphonic acid salts may be utilized with metal salts of: low molecular weight C_1 to C_6 fatty acids, intermediate molecular weight C_6 to C_{12} fatty acids, high molecular weight C_{12} to C_{30} fatty acids, as well as the metal salts of high molecular weight sulphonic acids. One of the main advantages of these mixed-salt systems is that a higher molecular weight salt tends to maintain lower molecular weight salts stably suspended in oil. Thus, ethane phosphonate by itself, will tend to eventually settle out of oil. However, if a higher molecular weight salt (e.g. a stearate) is also present, a stable dispersion is obtained. Thus, if one component of the mixed-salt is a low molecular weight phosphonate (i.e. C_6 or less) then one of the other salts present preferably will have at least six or more carbon atoms. Of course, the lower molecular weight phosphonate may be stably suspended in oil by other means, such as other thickening agents, e.g. polyethylene and carbon black, as well as other dispersing agents.

Suitable low molecular weight acids for forming the above described salt compositions include saturated and unsaturated, substituted and unsubstituted aliphatic monocarboxylic acids and their anhydrides having about 1 to 6 carbon atoms per molecule. These acids include fatty acids such as acetic, propionic, and similar acids including their hydroxy derivatives such as lactic acid, or their anhydrides, e.g., acetic acid anhydride. Acetic acid or acetic acid anhydride is preferred.

The intermediate molecular weight fatty acids operable for the salt formation include those aliphatic, saturated or unsaturated, unsubstituted monocarboxylic acids containing 7 to 12 carbon atoms per molecule, e.g., capric, caprylic, nonanoic, lauric acids, etc.

The high molecular weight fatty acids or aliphatic monocarboxylic acids useful for forming the salt thickeners of the invention include naturally-occurring or synthetic, substituted and unsubstituted, saturated and unsaturated, fatty acids having about 12 to 30, e.g., 16 to 22, carbon atoms per molecule. Examples of such acids include palmitic, stearic, 12-hydroxy stearic, dihydroxy stearic, behenic, montanic, linolinic, linoleic, arachidic, ricinoleic, oleic, hydrogenated fish oil, tallow acids, etc.

The sulphonic acids used in forming metal salts as oil thickeners are generally the high molecular weight (e.g. 300 to 650) alkyl aryl sulphonic acids. One source of these acids is by the treatment of petroleum oils of the lubricating oil range with fuming sulphuric acid. Such sulphonic acids and their salts have been described in numerous patents as, for example, U.S. 2,467,176. The

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metal sulphonates can also be prepared from relatively pure alkyl aryl sulphonic acids having from about 10 to 33 carbon atoms per molecule. For example, sulphonated products of alkylated aromatics, such as benzene, toluene, xylene, etc., alkylated with olefins or olefin polymers of the type of polypropylene, polyisobutylene, etc. can be used. Specific examples of such sulphonates include: petroleum sulphonic acid, C_8 alkyl benzene sulphonic acid, C_9 alkyl benzene sulphonic acid and C_{16} alkyl benzene sulphonic acid.

The metal component of salts of the above fatty acids and sulphonic acids can be any of those previously described as operable in forming the phosphonate. Generally, alkali and alkaline earth metals will be used. Again, such carboxylates and sulphonates may be pre-formed and then dispersed in the oil composition, or they too can be formed in situ in the oil by neutralizing the acid with a metal base.

The lubricating oil used in the compositions of the invention may be a mineral lubricating oil, a synthetic lubricating oil, or mixtures thereof. Synthetic lubricating oils which may be used include esters of dibasic acids (e.g., di-2-ethyl hexyl sebacate); esters of glycols (e.g., C_{13} Oxo acid diester of tetraethylene glycol); complex esters (e.g., the complex ester formed by reacting one mole of sebacic acid with two moles of tetraethylene glycol and two moles of 2-ethyl-hexanoic acid); formals, silicones, carbonates, polyglycols and other synthetic lubricating oils known in the art.

Various other additives may also be added to the lubricating composition in amounts of about 0.1 to 10.0 weight percent, based on the total weight of the composition. Examples of such additives include: viscosity index improvers such as polyisobutylene; corrosion inhibitors such as sorbitan monooleate; pour depressants; detergents; dyes, and the like.

The lubricant compositions of the invention will therefore comprise lubricating oil and about .05 to 30, e.g., 3 to 24, weight percent of the metal salt of the phosphonic acid material. The amount used, will depend largely upon its purpose. Thus, if a grease is desired and the phosphonate is to be used as the sole thickener, then generally about 10 to 30 weight percent of the total composition will be phosphonate, while .05 to 10 weight percent of the phosphonate material will generally suffice to impart antioxidant or load-carrying ability to a lubricant. The phosphonate may be used as the sole salt component of the lubricant, or it may be used in the form of a mixed-salt. Such mixed-salts, in turn, will generally comprise in a molar ratio about .1 to 100, e.g., 0.2 to 70 moles of phosphonate per mole of a carboxylate and/or sulphonate. The fatty acids used in forming the carboxylate may consist entirely of low molecular weight fatty acid, intermediate molecular weight fatty acid or entirely of high molecular weight fatty acid or blends of these three types of fatty acids in any proportion. Fluid lubricants containing the mixed-salts are best prepared by heating the mixed-salt material dispersed in oil to temperatures of about 300 to about 430° F., while the greases containing mixed-salts are best prepared by heating to about 430 to 700° F., where complexing occurs and optimum thickening power is obtained. However, the fluid lubricants can also be prepared at these higher temperatures, i.e., 430° F. and above, while the greases may also be prepared at the lower temperatures, i.e., less than 430° F.

The invention will be further understood by the following examples:

EXAMPLE I

19.3 grams of cetane (C_{16}) phosphonic acid in the form of a finely divided powder was dispersed in 20 grams of water to form a paste which was heated to 210° F. 77.4 grams of a mineral lubricating oil having a viscosity of 300 SUS at 100° F., and a viscosity index of 70 was then

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added slowly to the paste with constant stirring. Next, a water slurry containing 3.3 grams of lithium hydroxide monohydrate ($LiOH \cdot H_2O$) and 10.0 grams of water was added to the oil-phosphonic acid solution in order to neutralize the acid. Next, the grease was dehydrated by heating it on a hot plate for about 1 hour until a final temperature of 400° F. was reached. The grease was then cooled to about 150° F., and homogenized by passing through a Travis mill.

EXAMPLE II

A grease was prepared in a manner similar to that in Example I except that the phosphonic acid was dodecane phosphonic acid and the metal base was calcium hydroxide, i.e. $Ca(OH)_2$.

EXAMPLES III AND IV-A

Greases containing mixed phosphonates were prepared in the general manner of Examples I and II except that the phosphonic acid was a mixture of a low molecular weight phosphonic acid and a high molecular weight phosphonic acid and the grease composition was heated to a final temperature of 500° F.

EXAMPLE IV-B

The composition of Example IV-A was cut back by simple mixing with additional mineral oil to form a liquid lubricant containing 6 weight percent of the mixed phosphonate.

EXAMPLE V

A grease was prepared by dispersing 13.0 parts by weight of ethane phosphonic acid in water, heating to about 210° F., then adding 76.8 parts by weight of oil and 9 parts by weight of calcium hydroxide as a water slurry. Then, 1.2 parts by weight of a calcium sulphonate concentrate was added. The concentrate consisted of 30% by weight of petroleum sulphonate and 70 wt. percent mineral oil. The sulfonate had an average molecular weight of about 700. The composition was heated to dehydration and finally finished by heating to 500° F., then cooled.

EXAMPLE VI

A grease was prepared in the same manner as Example V except that 5.5 parts by weight of cetane phosphonic acid was added in place of the 13 parts by weight of ethane phosphonic acid and calcium acetate in an aqueous dispersion was added instead of the calcium sulphonate.

The compositions of several of the preceding examples were tested for water absorption as follows: 100 grams of grease is worked with 20 cc. of water for 300 strokes in an ASTM grease worker. This procedure is repeated again and again until free water is observed after the last 300 strokes. At this point, the test is stopped and the weight percent, based on the weight of dry grease, of water absorbed into the grease is determined. Greases having an ability to absorb large quantities of water, without losing their structure are particularly desirable since they may be used in applications where the grease is exposed to moisture.

Several of the preceding grease compositions were also tested for their oxidation resistance by packing 3.0 grams of the grease into a weighed ball-and-roller bearing, suspending the bearing in an oven maintained at 250° F. and periodically re-weighing the bearing to determine the weight loss of the grease.

The compositions of Examples I to VI in terms of their original ingredients and some of the physical properties of these compositions are summarized in the following table:

Table I

Composition (wt. percent)	Example						
	I	II	III	IV-A	IV-B	V	VI
Cetane phosphonic acid.....	19.3	15.2	3.5	4.0	1.10	-----	5.5
Dodecane phosphonic acid.....	-----	-----	8.7	10.0	2.75	13.0	-----
Ethane phosphonic acid.....	3.3	4.8	7.8	7.8	2.15	9.0	1.3
LiOH.H ₂ O.....	-----	-----	-----	-----	-----	1.2	-----
Ca(OH) ₂	-----	-----	-----	-----	-----	-----	18.2
Calcium sulphonate (sol. of 80 wt. percent sulphonate in oil).....	-----	-----	-----	-----	-----	-----	80.0
Calcium acetate.....	77.4	80.0	80	78.2	94.0	78.8	80.0
Mineral Oil (50 SUS at 210° F.).....	400	400	500	500	500	500	500
Max. Temp. of manufacture, °F.....	-----	-----	-----	-----	-----	-----	-----
Properties — ASTM worked penetration — 60 strokes:	-----	-----	-----	-----	-----	-----	-----
77° F.—mm./10.....	274	335	397	288	fluid	348	314
10,000 strokes penetration.....	-----	-----	-----	306	-----	-----	-----
Dropping Point, °F.....	500+	500+	500+	500+	-----	500+	408
Water absorption before saturated (wt. percent based on wt. of grease).....	50.0	-----	-----	105	-----	-----	-----
Oxidation Resistance (wt. percent loss)—	-----	-----	-----	-----	-----	-----	-----
300 hours.....	9.0	-----	-----	5.0	-----	-----	12.0
600 hours.....	13.0	-----	-----	10.0	-----	-----	17.0
900 hours.....	21.0	-----	-----	13.0	-----	-----	20.0
1,200 hours.....	23.0	-----	-----	15.0	-----	-----	-----
Falex load-carrying, lbs.....	-----	-----	-----	-----	4,500	-----	-----
4-ball Wear Test (1 hr.—1,800 r.p.m.—15 Kg.—77° F.) Wear Scar dia., mm.....	-----	-----	-----	0.366	-----	-----	0.428

As seen from the above table, the phosphonates of the invention may be used as the sole thickening agent to form greases having high dropping points, good stability in the presence of water, low wear characteristics and high load-carrying ability as well as fluid lubricants (see Examples I to IV-B). Examples V and VI illustrate the use of other salts as a supplemental thickening aid. The oxidation resistance of the phosphonate greases tested (Examples I, IV-A and VI) was exceptionally good, since by comparison a commercial grease thickened with lithium-calcium soap of 12-hydroxy stearic acid showed a weight percent loss of 18% at 300 hours; 53 weight percent loss at 600 hours and 57 weight percent loss at 900 hours; whereas the product of Example VI containing only about 7 weight percent of phosphonate showed only 20.0 weight percent loss after 900 hours. By the same token, the wear scar diameters of 0.366 mm. and 0.428 mm. for the greases of Examples IV-A and VI respectively compared well to a wear scar diameter of 0.426 mm. for the previously mentioned commercial grease.

To illustrate the use of synthetic oils as the base oil, the following grease was prepared.

EXAMPLE VII

A grease composition was prepared from 5 grams of cetane phosphonic acid, 15 grams of ethane phosphonic acid, 12 grams of Ca(OH)₂ and 68 grams of a methyl phenyl silicone oil having a viscosity at 100° F. of 73 centistokes. The grease was prepared in the general manner of Example I, except that the maximum temperature employed was 300° F. After cooling and homogenization, a smooth light colored grease was obtained having an ASTM—worked 60 strokes penetration of about 250 mm./10 at 77° F.

EXAMPLE VIII

2.9 wt. percent of the neutral sodium salt of 1-dodecane phosphonic acid was mixed with 97.1 wt. percent of a base grease. This addition was carried out by adding a water solution of the phosphonate to the grease (which had been preheated to 300° F.). This mixture was maintained at 300° F. until dry, then heated to 420° F. and next allowed to cool to 140° F. while stirring. After reaching 140° F., the mixture was allowed to cool without stirring. The base grease used above consisted of 1 wt. percent of phenyl-alpha-naphthylamine, 23 wt. percent of sodium 12-hydroxy stearate, 1.8 wt. percent of a sodium petroleum sulfonate of about 375 molecular weight, and 74.2 wt. percent of mineral oil of 500 SUS viscosity at 100° F. and a V.I. of 90. The phosphonate containing grease composition was next tested for oxidation resistance by packing 5 grams of the composition into a bearing, and hanging the bearing in an oven maintained at 300° F. After 3,000 hours, the grease composition had reached a micropenetration of 5, which indicated the extent of its useful lubricating life, and had suffered a weight loss of 42%. The base grease without the phosphonate, had an indicated useful lubricating life of only 1,100 hours in the same test, and a weight loss of 48% at the end of the 1,100 hours. The use of 3 wt. percent trisodium phosphate with the base grease increased its life to only 1,500 hours. It is thus seen the strong antioxidant effect of even minor amounts of the phosphonates of the invention.

EXAMPLE IX

Example VIII was repeated but using 2.0 wt. percent of the neutral sodium salt of ethane phosphonic acid with 98.0 wt. percent of the same base grease. This composition had a useful lubricating life of 1,500 hours, which was a considerable improvement over the 1,100 hour life of the base grease.

To further illustrate the invention, a lubricant may be prepared in the manner of Example I but using benzene phosphonic acid in place of the cetane phosphonic acid and Al(OH)₃ in place of the LiOH.H₂O.

In summary, this invention relates to oil compositions, either fluids or greases, containing the neutral metal salts of a C₁ to C₃₀ hydrocarbon phosphonic acid. The preferred form of the hydrocarbon group of the phosphonate will vary widely according to the intended use of the phosphonate. Thus, the hydrocarbon group is preferably a straight chain alkyl group when the phosphonate is used primarily as a thickening agent, since this form will give the maximum thickening effect. Although when the phosphonate is utilized because of its other properties, e.g. as an antioxidant, then the nature of the hydrocarbon group is of less importance, and straight or branched, saturated or unsaturated, alkyl, aromatic, alicyclic and other hydrocarbon configurations will give about the same result. However, in this latter case, i.e. when the phosphonate is used primarily because of its antioxidant or E.P. properties, then it is generally preferred to use the lower molecular weight hydrocarbon phosphonates, i.e. containing 10 carbon atoms or less. The reason for this preference being that for properties other than thickening, the effective functional portion of the phosphonate is centered about the phosphorus atom. Thus, lower molecular weight phosphonates can be incorporated in a greater molar proportion into oil than the higher molecular weight phosphonates.

phonates to thereby achieve maximum effectiveness. The phosphonates of the invention can also be used in lubricant compositions supplemented with other thickening agents. Thus, lubricating compositions can be prepared containing 0.5 to 30.0 wt. percent of total mixed-salt materials, a portion of said mixed-salt being a phosphonate and the remainder being carboxylates and/or sulfonates as previously described, or other additive or thickening agents.

What is claimed is:

1. A lubricating oil composition comprising a major amount of mineral lubricating oil and about 0.5 to 30 wt. percent of a neutral metal salt of ethane phosphonic acid, said metal being selected from the group consisting of alkali metals and alkaline earth metals.

2. A lubricating oil composition comprising a major amount of mineral lubricating oil and a thickening amount of a mixture of neutral metal salts, one salt being a metal salt of ethane phosphonic acid and another salt being a salt of a C_{10} to C_{30} alkyl phosphonic acid, said

metal being selected from the group consisting of alkali metals and alkaline earth metals and wherein the amount of salt of the ethane phosphonic acid is about 0.5 to 30.0 wt. percent of the total composition.

3. A lubricating oil composition comprising a major amount of mineral lubricating oil and about 0.5 to 30 wt. percent of a mixed salt material, said material comprising about 0.2 to 70 molar proportions of a neutral metal salt of ethane phosphonic acid and about one molar proportion of a metal salt of alkyl aryl sulfonic acid of 300 to 650 molecular weight and wherein said metals are selected from the group consisting of alkali metals and alkaline earth metals.

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