

1

2,837,481

METAL ALKYL PHOSPHONATE THICKENED LUBRICATING OILS

Bruce W. Hotten, Orinda, and Frederick O. Johnson, Berkeley, Calif., assignors to California Research Corporation, San Francisco, Calif., a corporation of Delaware

No Drawing. Application March 31, 1955
Serial No. 498,436

13 Claims. (Cl. 252—32.5)

This patent application is directed to grease compositions thickened with metal salts of certain phosphonic acids.

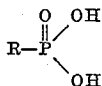
Grease thickening agents which are useful in the preparation of multipurpose grease compositions are continually being sought. Multipurpose greases are those which can be used in a number of services rather than merely one or two. Heretofore, it has been customary to use one particular grease for each particular service. For example, it is well known that as many as nine different types of greases have been used in the lubrication of automotive chassis. The over-all cost of greasing operations is increased by the necessity of using nine different types of greases for automotive lubrication. A large inventory is required for each one of the several grease compositions, and it is time-consuming for a grease operator to change his operations from a grease gun containing one type of grease to one containing a second type of grease composition.

In addition to having high resistance to emulsification in water, the grease compositions embodied herein have greater work stability and greater resistance to oxidation than the usual metal soaps of fatty acids which are so prevalently used in grease compositions at the present time.

These greases have a wide variety of applications, particularly where it is advantageous to use greases which are resistant to emulsification in water and which have greater stability to oxygen than presently used grease compositions. Such greases are particularly effective in lubricating steel mill motors and transfer table bearings, paper mill roller bearings, automotive wheel bearings under winter and wet conditions, including use in amphibious military vehicles, exposed controls of surface bearings for aircraft, etc.

According to the present invention, it has been discovered that oxidation-resistant, and water-resistant grease compositions are obtained by the use of metal salts of certain phosphonic acids as thickening agents.

These phosphonic acids can be represented by the formula:



wherein R represents straight-chain or branched-chain, saturated or unsaturated hydrocarbon radicals having from 12 to 40 carbon atoms; that is, R represents an aliphatic radical containing from 12 to 40 carbon atoms.

Examples of "R" radicals of the above formula include aliphatic radicals derived from dodecane, dodecene, tetradecane, tetradecene, hexadecane, hexadecene, octadecane, octadecene, eicosane, tetracosane, triacontane; radicals obtained from mixtures of hydrocarbons found in petroleum oil, such as diesel fuel oil, petroleum wax, etc. The "R" radicals can be derived from pure hydrocarbons (including pure alkanes and pure alkenes)

2

or mixtures of hydrocarbons having molecular weights ranging from about 150 to about 500.

When used herein, the term "hydrocarbon phosphonates" (or "phosphonic acids") means that the "R" groups of the phosphonates can be saturated or unsaturated, branched-chain or straight-chain radicals.

Because the greases prepared therefrom have higher dropping points, it is preferred that the "R" radicals contain from 12 to 18 carbon atoms. Based on the molecular weights, it is preferred that the average molecular weights of the "R" radicals range from about 150 to about 300.

The metals which can be used in the formation of the grease thickeners herein include the metals of groups I, II, III, and IV of Mendeleeff's periodic table. Particular metals include lithium, sodium, potassium, silver, magnesium, calcium, zinc, strontium, cadmium, and barium. Because of the improved characteristics of the grease compositions prepared therefrom, it is preferred to use lithium and sodium.

Examples of the metal phosphonates herein include sodium dodecane phosphonate, sodium tetradecane phosphonate, sodium hexadecane phosphonate, sodium eicosane phosphonate, sodium docosane phosphonate, sodium triacontane phosphonate, sodium tetracontane phosphonate, sodium petroleum hydrocarbon phosphonate; lithium dodecane phosphonate, lithium tetradecane phosphonate, lithium hexadecane phosphonate, lithium eicosane phosphonate, lithium docosane phosphonate, lithium triacontane phosphonate, lithium tetracontane phosphonate, lithium petroleum hydrocarbon phosphonate; calcium dodecane phosphonate, calcium octadecane phosphonate, calcium eicosane phosphonate, calcium tetracosane phosphonate, calcium tetra-triacontane phosphonate, calcium tetracontane phosphonate, calcium diesel fuel oil phosphonate, calcium petroleum wax phosphonate.

Lubricating oils which are useful in the preparation of grease compositions of this invention include a wide variety of lubricating oils, such as naphthenic base, paraffin base, and mixed base, other hydrocarbon lubricants, e. g., lubricating oils derived from coal products, and synthetic oils, e. g., alkylene polymers (such as polymers of propylene, butylene, etc., and mixtures thereof), alkylene oxide-type polymers, dicarboxylic acid esters, liquid esters of acids of phosphorus, alkylbenzene polymers, polymers of silicon, etc. Synthetic oils of the alkylene oxide-type polymers which may be used include those exemplified by the alkylene oxide polymers (e. g., propylene oxide polymers) and derivatives, including alkylene oxide polymers prepared by polymerizing the alkylene oxides, e. g., propylene oxide, in the presence of water or alcohols, e. g., ethyl alcohol, esters of ethylene oxide-type polymers, e. g., acetylated propylene oxide polymers prepared by acetylating propylene oxide polymers containing hydroxyl groups; polyethers prepared from alkylene glycols, e. g., ethylene glycol, etc.

The polymeric products prepared from the various alkylene oxides and alkylene glycols may be polyoxy-alkylene diols or polyalkylene glycol derivatives; that is, the terminal hydroxy group can remain as such, or one or both of the terminal hydroxy groups can be removed during the polymerization reaction by esterification or etherification.

Synthetic oils of the dicarboxylic acid ester type include those which are prepared by esterifying such dicarboxylic acids as adipic acid, azelaic acid, suberic acid, sebacic acid, alkenyl succinic acid, fumaric acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dibasic (dicarboxylic) acid ester synthetic oils

include dibutyl adipate, dihexyl sebacate, di-2-ethylhexyl sebacate, di-N-hexylfumaric polymer.

Synthetic oils of the alkylbenzene type include those which are prepared by alkylating benzene (e. g., dodecylbenzene, tetradecylbenzene, etc.).

Synthetic oils of the type of polymers of silicon include the liquid esters of silicon and the polysiloxanes. The liquid esters of silicon and the polysiloxanes include those exemplified by tetraethyl silicate, tetraisopropyl silicate, tetra(methyl-2-butyl) silicate, tetra(4-methyl-2-penta) silicate, tetra(1-methoxy-2-propyl) silicate, hexyl (4-methyl-2-pentoxy) disiloxane, poly(methylsiloxane), poly(methylphenyl) siloxane, and poly(siloxyglycols), etc.

The above base oils may be used individually as such, or in various combinations, wherever miscible or wherever made so by the use of mutual solvents.

When the alkylene oxide-type polymers or polymers of silicon are the base oils, it is preferable that the grease gel structure be formed first in a hydrocarbon solvent, e. g., toluene, after which the alkylene oxide-type polymer, or the polymer of silicon is added, and the solvent removed by distillation or other means. An alcohol may be added to the hydrocarbon solvent to form a blend (e. g., a petroleum thinner and ethyl alcohol blend).

Lithium salts of phosphonic acids containing from 4 to 22 carbon atoms are used in amounts of 0.5% to 5% to enhance the oxidation and work stability characteristics of grease compositions comprising polybasic organic acid esters (e. g., di(2-ethylhexyl sebacate)) thickened with lithium soaps of fatty acids (e. g., lithium stearate). However, in contrast thereto, amounts of 7% to 50% of metal phosphonates of the present invention are not compatible with grease compositions thickened with soaps of fatty acids. Grease compositions containing such a combination of thickening agents gradually lose their grease gel structure.

The metal phosphonates of the present invention are admixed with lubricating oils in amount sufficient to form grease compositions, that is, sufficient to thicken the oil to the consistency of a grease. Although from 7% to 50% by weight of these grease thickening agents may be incorporated in grease compositions, it is preferred to use amounts of from about 10% to 30%.

A process which can be used in preparing the phosphonic acids is described in Jensen-Clayton U. S. Patent No. 2,683,168. According to this process, a hydrocarbon is reacted with phosphorus trichloride in the presence of oxygen, forming a phosphonyl dichloride, which is then hydrolyzed to yield the corresponding phosphonic acid. The acid can then be neutralized by a metal oxide or metal hydroxide to form the desired salt.

The examples hereinbelow illustrate the preparation of phosphonate grease thickening agents and greases therefrom.

Example 1.—Preparation of the calcium salt of diesel fuel oil phosphonic acid

A diesel fuel oil having a viscosity of 35 SSU at 100° F. and having an ASTM D-158 distillation 10% point at 425° F. and end point at 690° F., was desulfurized by washing with fuming sulfuric acid. A mixture of 538 grams of the desulfurized fuel oil and 560 grams of phosphorus trichloride was placed in a glass tube having a porous gas inlet at the bottom. Oxygen was bubbled through this mixture for a period of 3 hours. During the reaction the temperature varied from room temperature to 100° F. When the phosphonation reaction was complete, the temperature returned to room temperature. The resulting phosphonyl dichloride was hydrolyzed to the phosphonic acid. The water-washed product had a neutralization number of 187.

100 grams of this phosphonic acid was treated with 30 grams of potassium hydroxide to obtain the potassium

phosphonate, which was then reacted with 34 grams of calcium chloride in aqueous solution to form the calcium hydrocarbon phosphonate, which precipitated from solution. This precipitate was water washed and dried.

Example 2.—Preparation of grease thickened by a calcium diesel fuel oil phosphonate

A mixture consisting of 30 grams of the calcium phosphonate of Example 1 and 80 grams of a California naphthenic base oil having a viscosity of 450 SSU at 100° F. was heated with agitation to 400° F. to disperse the phosphonate in the oil. The resulting grease had a dropping point of 336° F., and an ASTM worked penetration of 298 at 77° F.

Example 3.—Preparation of lithium paraffin wax phosphonate

A mixture of 320 grams of a paraffin wax having an average molecular weight of 422 and having a melting point ranging from 143° F. to 150° F., and 410 grams of phosphorus trichloride was heated to 160° F. in a glass tube having a porous gas inlet at the bottom. Air was charged to this mixture for a period of 6 hours at temperatures ranging from 150° F. to 160° F., forming the paraffin wax phosphonyl dichloride, which was hydrolyzed to form the acid.

Example 4.—Preparation of grease thickened with lithium paraffin wax phosphonate

The paraffin wax phosphonic acid of Example 3 was neutralized with lithium hydroxide, forming the lithium paraffin wax phosphonate. A mixture of 15 grams of this lithium phosphonate and 85 grams of the base oil of Example 2 hereinabove was heated to 500° F. to disperse the lithium phosphonate in the oil. After milling, the resulting grease had a dropping point of 132° F., an unworked ASTM penetration of 334 at 77° F., and a worked ASTM penetration of 380.

When the hydrocarbon radicals are branched-chain radicals, it is understandable that there is a greater possibility for more than one reactive branched alkyl group on that molecule. It is these branched alkyl groups with which the PCl_3 reacts in the presence of oxygen to form the phosphonate bond. The degree of phosphonation of any one branched-chain hydrocarbon radical depends on the reaction time. The longer the time the greater the phosphonation of any one particular branched-chain hydrocarbon radical.

Besides being excellent thickening agents for lubricating oils, the thickening agents of this invention are suitable as agents in pigment manufacture, in dusting powders, in such materials as leather, textiles, wood and other fibrous or porous materials, for imparting greater water improvements etc. Also, the thickening agents herein are useful as gelling agents for plastigels.

In addition to the agents noted herein, the grease composition of this invention may contain oxidation inhibitors (e. g., dihydroxyanthraquinones, metal organo-dithiophosphates, etc.), rust inhibitors (e. g., metal petroleum sulfonates), lubricity agents (e. g., aromatic phosphates), color correctors, stringiness agents, etc.

We claim:

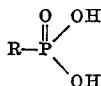
1. A grease composition comprising an oil of lubricating viscosity and, in an amount sufficient to thicken said oil to the consistency of a grease, a metal hydrocarbon phosphonate, wherein the hydrocarbon radical is an aliphatic radical containing from 12 to 40 carbon atoms, and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

2. A grease composition comprising a major proportion of an oil of lubricating viscosity and, in an amount sufficient to thicken said oil to the consistency of a grease, a metal hydrocarbon phosphonate, wherein the hydrocarbon radical contains more than one phosphonate group attached thereto, said hydrocarbon radical being an ali-

5

phatic radical containing from 12 to 40 carbon atoms and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

3. A grease composition comprising a major proportion of an oil of lubricating viscosity and, in an amount sufficient to thicken said oil to the consistency of a grease, a metal salt of a phosphonic acid of the formula:



wherein R is an aliphatic radical containing from 12 to 40 carbon atoms and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

4. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50% of a metal hydrocarbon phosphonate, wherein said hydrocarbon radical is an aliphatic radical containing from about 12 to about 40 carbon atoms and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

5. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50% of a metal alkane phosphonate containing at least one phosphonate radical per alkane radical, wherein said alkane radical contains from 12 to 40 carbon atoms and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

6. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 10% to about 30% of a metal alkane phosphonate containing at least one phosphonate radical per alkane radical, wherein said alkane radical contains from 12 to 18 carbon atoms and wherein said metal is a metal selected from the group consisting of alkali metals and alkaline earth metals.

7. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50%, by weight, of an alkaline earth metal hydrocarbon phosphonate, wherein said hydrocarbon radical is an aliphatic radical containing from 12 to 40 carbon atoms.

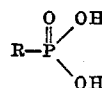
8. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50%, by weight, of a calcium alkane phosphonate, wherein said alkane radical is derived from a petroleum radical containing from 12 to 40 carbon atoms.

9. A grease composition comprising a major propor-

6

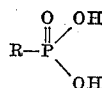
tion of an oil of lubricating viscosity and from about 10% to about 30%, by weight, of a calcium alkane phosphonate, wherein said alkane radical is derived from a petroleum radical containing from 12 to 40 carbon atoms.

10. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50%, by weight, of an alkali metal salt of a phosphonic acid of the formula:



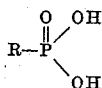
wherein R is an aliphatic radical containing from 12 to 40 carbon atoms.

11. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 10% to about 30%, by weight, of an alkali metal salt of a phosphonic acid of the formula:



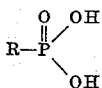
wherein R is an aliphatic radical having from 12 to 40 carbon atoms.

12. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 7% to about 50%, by weight, of a lithium salt of an alkane phosphonate of the formula:



wherein R is an alkane radical containing from 12 to 40 carbon atoms.

13. A grease composition comprising a major proportion of an oil of lubricating viscosity and from about 10% to about 30%, by weight, of a lithium salt of an alkane phosphonate of the formula:



wherein R is an alkane radical containing from 12 to 40 carbon atoms.

References Cited in the file of this patent

UNITED STATES PATENTS

2,628,949 Butcosk Feb. 13, 1953