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GREASE COMPOSITION CONTAINING METAL SALT OF REACTION PRODUCT OF ALKYLPHENOL, FATTY ACID AND ALDEHYDE

Bruce W. Hotten, Orinda, Calif., assignor to California Research Corporation, San Francisco, Calif., a corporation of Delaware

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This invention relates to grease compositions which are particularly resistant to oxidation and emulsification in water.

Grease compositions thickened with sodium soaps of fatty acids (e.g., sodium stearate) have melting points in the range of approximately 250° F. to 300° F. Although fatty acid soap-thickened grease compositions are useful at such temperatures, such greases have a serious drawback in that they are readily emulsifiable in water; thus, the greases are readily washed from the surfaces to be lubricated, resulting in lubrication failure.

Thus, soda soap greases in general are known to have good high temperature characteristics, but very poor resistance to emulsification in water. It is also known that changing the metal of a fatty acid-soap grease thickening agent to calcium results in a grease-thickening agent forming grease compositions having good resistance to water. However, such greases have very low melting points.

Water resistant, oxidation resistant, high-melting greases (i.e., greases characterized by low solubility and low emulsibility in water and having high dropping points) are used for lubricating automotive wheel bearings, steel mill equipment, high speed motors, universal joints, rocker arms of airplane motors, water pumps, automotive chassis, valves, etc.

Therefore, it is an object of this invention to prepare oxidation resistant grease compositions having high melting points and high resistance to emulsibility in water.

In accordance with this invention, it has been found that high melting point, oxidation resistant, and water resistant grease compositions may be obtained by incorporating in a lubricating oil a thickening agent which is a metal salt of a condensation product obtained by reacting an alkylphenol with a fatty acid and formaldehyde. Briefly, the improved composition of the present invention comprises a lubricating oil and a grease thickening agent obtained by forming a metal soap of an alkylphenol-fatty acid-formaldehyde condensation product.

In addition to the attributes noted hereinabove, the grease compositions of this invention have high work stability; that is, the ASTM worked penetration values (P_{60}) of the grease at 77° F. do not change appreciably after the grease has been subjected to a high speed bearing test described hereinbelow.

As used herein, the term "condensation product" means the product obtained by reacting together an alkylphenol, a fatty acid, and formaldehyde. The order of the reaction is of no consequence herein, since the reactants are blended together in the formation of the condensation product.

The alkylphenols used as reactants may have one or more alkyl radicals, and the alkyl radicals may be saturated or unsaturated aliphatic groups having a total of from 1 to 36 carbon atoms. Each of the alkyl radicals

of the alkylphenols may contain from 1 to 24 carbon atoms. Because of the greater effectiveness of the resulting condensation product as a grease-thickening agent, it is preferred to use an alkylphenol having one alkyl radical substituted thereon, which alkyl group contains no more than 18 carbon atoms, preferably from 12 to 18 carbon atoms.

Examples of alkyl groups of the alkylphenols include methyl, ethyl, propyl, isopropyl, butyl, tertiarybutyl, amyl, tertiaryamyl, octyl, dodecyl, tetradecyl, hexadecyl, octadecyl, butenyl, octenyl, dodecenyl, tetradecenyl, octadecenyl, butenyl polymers containing from 12 to 16 carbon atoms, etc.

Examples of alkylphenols include methylphenol, dimethylphenol, trimethylphenol, isopropylphenol, ethylphenol, diethylphenol, diamylphenol, triamylphenol, octylphenol, methyloctylphenol, dodecylphenol, octadecylphenol, vinylphenol, butenylphenol, octadecenylphenol, polybutylenephenol, wherein the polybutylene groups contain from 12 to 16 carbon atoms, etc.

The aldehyde reactant is formaldehyde, and it may be used as such in the reaction, that is, as gaseous formaldehyde, or as the aqueous solution of formaldehyde. Also, compounds which yield formaldehyde, such as paraformaldehyde, may be used.

The fatty acids used herein are the aliphatic monocarboxylic acids having from 2 to 22 carbon atoms. Examples of fatty acids include acetic acid, propionic acid, butyric acid, valeric acid, hexanoic acid, octanoic acid, decanoic acid, undecanoic acid, dodecanoic acid (e.g., lauric acid), tetradecanoic acid (e.g., myristic acid), hexadecanoic acid (e.g., palmitic acid), octadecanoic acid (e.g., stearic acid), arachidic acid, behenic acid, etc.

The metals which can be used in the formation of the soaps of the alkylphenol-fatty acid-aldehyde condensation product include the metals of Groups I, II, III, and IV of Mendeléeff's Periodic Table. Particular metals include the alkali metals (e.g., lithium, sodium, and potassium), and the alkaline earth metals (e.g., calcium, strontium, and barium), zinc, and cadmium. Because of the increased work stability and improved texture, it is preferred to use sodium.

The metal salts used as grease thickening agents according to this invention are incorporated in lubricating oils in amounts sufficient to thicken the lubricating oils to the consistency of greases; that is, the metal salts are used in amounts of 5 to 50%, by weight, preferably from 10 to 20%, by weight.

Lubricating oils which are suitable base oils for the compositions of this invention include a wide variety of lubricating oils, such as napthenic base, paraffin base, and mixed base; other hydrocarbon lubricants, e.g., lubricanting 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 ethylene oxide polymers prepared by acetylating ethylene oxide polymers containing hydroxyl groups; polyethers prepared from ethylene glycols, e.g., ethylene glycol; etc.

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, furamic acid, maleic acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethyl hexyl alcohol, dodecyl alcohol, etc. Examples of dibasic (dicarboxylic acid) acid ester synthetic oils include dibutyl adipate, dihexyl adipate, and di-2-ethylhexyl sebacate.

Synthetic oils of the alkylbenzene type include those which are prepared by alkylating benzene (e.g., dodecylbenzene, tetradecylbenzene, etc.). Synthetic oils of the types of polymers of silicon include the liquid esters of silicon and the polysiloxanes, which include those exemplified by tetraethyl silicate, tetraisopropyl silicate, polymethylphenyl) siloxane, and poly(siloxy glycols), 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.

In the preparation of the condensation products, alkylphenols, fatty acids, and aldehydes are present in the reaction mixture in molecular ratios as follows: from 0.5 to 1.5 mols of fatty acids per mol of alkylphenol, and from 1 to 3 mols of aldehyde per mol of alkylphenol. That is, for each mol of alkylphenol in the reaction mixture, there can be from 0.5 to 1.5 mols of fatty acid, and from 1 to 3 mols of aldehyde. It is preferred that the mol ratios of alkylphenols to fatty acids be from about 0.5 to 2.

The condensation reaction is preferably carried out at temperatures ranging from 200° F. to 300° F.; however, temperatures from 120° F. to 500° F. may be used.

The alkylphenol-fatty acid-aldehyde condensation products herein are prepared preferably by forming an admixture of an alkylphenol and a fatty acid, heating said admixture to temperatures ranging from 120° F., to 300° F., followed by the addition of the aldehyde. The whole mixture is then heated for a period of 1 to 4 hours at temperatures from 300° F. to 500° F., followed by cooling and subsequent neutralization by a metal oxide or hydroxide of the metals noted hereinabove.

A grease composition is obtained from the soap thus formed by heating the soap in an oil of lubricating viscosity until a continuous phase is formed, after which the oil-soap blend is cooled to form a grease structure. It is preferred to form the soap of the condensation product in the oil; that is, the alkylphenol-fatty acid-aldehyde condensation product may be blended in the oil, after which the metal oxide (or hydroxide) is added to the oil blend.

The examples presented hereinbelow illustrate the preparation of the alkylphenol-fatty acid-aldehyde condensation products and the metal salts thereof, and the formation of grease compositions by the use of such metal salts.

Example 1

A mixture of 108 grams (1 mol) of p-cresol and 284 grams (1 mol) stearic acid was heated with constant agitation in a 1-liter glass reaction flask to 212° F., forming a homogeneous solution. 60 grams (2 mols) of paraformaldehyde was added to this mixture, and the resulting composition was heated for 2 hours at temperatures ranging from 212° F. to 257° F., followed by heating for an additional 2 hours at 320° F. to 355° F. When the condensation reaction had been completed, as indicated by the water of reaction obtained, the admixture was cooled to room temperature. 30 grams of the resulting product was added to 179 grams of a California solvent-refined paraffin base oil having a viscosity of 450 SSU at 100° F. and the mixture was heated to 350° F., followed by cooling to 200° F., at which temperature 3 grams of sodium hydroxide in about 10 ml. of water were added. The resulting mixture was heated with stirring to 400° F., followed by pan cooling, and subsequent milling through an 80-mesh screen.

The resulting grease had an ASTM unworked penetration of 189 at 77° F., and an ASTM worked penetration of 248, after 60 strokes in the ASTM worker at 77° F. The ASTM dropping point was 342° F.

Example 2

A mixture of 284 grams (1 mol) of stearic acid and 150 grams (1 mol) of p-tertiarybutylphenol was heated with agitation in a 1-liter glass reaction flask to 100° C., forming a homogeneous solution. 30 grams (1 mol) of of paraformaldehyde was added to the mixture, which was then heated for 2 hours at temperatures ranging from 100° C. to 125° C., followed by heating for an additional 2 hours at temperatures ranging from 160° C. to 180° C. After completion of the reaction, the mixture was cooled to room temperature.

30 grams of the above product, which was a brown, semi-crystalline solid having a neutralization number of 153 (that is, milligrams of KOH per gram of sample) was incorporated in 191 grams of a California solvent-refined paraffin base oil having a viscosity of 450 SSU at 100° F., and the whole mixture was heated to 300° F. until a homogeneous solution resulted, followed by cooling to 200° F. 3.28 grams of sodium hydroxide in 10 ml. of water were added to the lubricating oil-condensation product blend at 200° F., and the whole mixture was heated with agitation to 400° F., followed by pan cooling, and subsequent milling through an 80-mesh screen.

The resulting grease had an ASTM unworked penetration of 397 at 77° F., and an ASTM dropping point of 282° F.

Example 3

A mixture of 284 grams (1 mol) of stearic acid and 150 grams (1 mol) of p-tertiarybutylphenol was heated with agitation in a 1-liter glass reaction flask to a temperature of 100° C., forming a homogeneous solution, after which 60 grams (2 mols) of paraformaldehyde was added. This mixture was heated for 2 hours at temperatures ranging from 100° C. to 125° C., followed by heating for an additional 2 hours at temperatures ranging from 160° C. to 180° C. When the reaction had been completed, the whole mixture was cooled to room temperature.

30 grams of the above product, which was a brown, hard cake having a neutralization number of 124, was blended with 180 grams of a California solvent-refined paraffin base oil having a viscosity of 450 SSU at 100° F. by heating the mixture to 300° F. with agitation. The mixture was cooled to 200° F., at which temperature 2.66 grams of sodium hydroxide in 10 ml. of water was added. The whole mixture was heated with agitation to 400° F., followed by pan cooling, and subsequent milling through an 80-mesh screen.

The resulting grease had an ASTM unworked penetration of 193 at 77° F., and an ASTM worked penetration of 260 after 60 strokes in an ASTM worker at 77° F. The ASTM dropping point was 378° F.

Example 4

A mixture of 108 grams of p-cresol (1 mol) and 284 grams (1 mol) of stearic acid was heated with agitation in a 1-liter glass reaction flask to 100° C., forming a homogeneous solution. To this mixture was added 60 grams (2 mols) of paraformaldehyde. The mixture was heated for 2 hours at 100° C. to 125° C., followed by further heating for another period of 2 hours at 160° C. to 180° C. When the reaction had been completed, the whole mixture was cooled to room temperature.

30 grams of the above product was incorporated in 173 grams of a California solvent refined paraffin base oil having a viscosity of 450 SSU at 100° F., and heated to 300° F. to form a homogeneous mixture, followed by cooling to 200° F., at which temperature 3.15 grams of lithium hydroxide monohydrate in about 10 ml. of water was added to the lubricating oil solution. The whole mixture was heated with agitation to about 400° F., fol-

lowed by pan cooling, and subsequent milling through an 80-mesh screen.

The resulting grease composition had an ASTM unworked penetration of 193 at 77° F., and an ASTM worked penetration of 260 after 60 strokes in the ASTM worker at 77° F. The ASTM dropping point was 378° F.

The resistance of the grease to emulsibility in water was tested by placing a sample of the grease in boiling water for a period of 60 minutes. The grease sample at this time was still intact, showing that the grease was highly resistant to emulsification in water.

The work stability of this grease was obtained by packing a No. 205 shielded ball bearing with the grease, then rotating the packed bearing at 3450 r.p.m. for 30 minutes at room temperature, after which the ASTM penetration value after 60 strokes in the ASTM worker at 77° F. was obtained. The ΔP_{60} was +35, representing a change in ASTM worked penetration values (i.e., after 60 strokes in the ASTM worker at 77° F.) of only 35 points.

In addition to the grease thickening agents of this invention, the grease composition may include other agents which will further enhance resistance to oxidation, extreme pressure characteristics, resistance to wear, agents which serve as color correctors, rust inhibitors, other thickening agents, etc.

I claim:

1. 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 product obtained by reacting, for a period of 1–4 hours, at temperatures ranging from 120° F. to 500° F., an alkylphenol containing from 1 to 36 carbon atoms in the alkyl radical and, for each mol of said alkylphenol, from 0.5 to 1.0 mol of a fatty acid containing from 2 to 22 carbon atoms, and from 1 to 3 mols of an aldehyde selected from the group consisting of formaldehyde and formaldehyde producing compounds.

2. The composition of claim 1, wherein said aldehyde is formaldehyde.

3. The composition of claim 1, wherein the alkyl radical of said phenol contains from 1 to 24 carbon atoms, said fatty acid is an alphatic monocarboxylic acid having from 2 to 22 carbon atoms, and said aldehyde is formaldehyde.

4. The composition of claim 1, wherein said metal is an alkali metal.

5. The composition of claim 1, wherein said metal is sodium.

6. 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 product obtained by reacting, at temperatures ranging from 200° F. to 300° F., an alkylphenol containing a total of from 1 to 36 carbon atoms in the alkyl radicals, and, for each mol of said alkylphenol, 0.5 to 1.5 mols of an aliphatic monocarboxylic acid containing from 2 to 22 carbon atoms, and 1 to 3 mols of an aldehyde selected from the group consisting of formaldehyde and formaldehyde producing compounds, wherein the reaction time is from 1 to 4 hours.

7. A grease composition comprising a major proportion of an oil of lubricating viscosity and from 5% to 50%, by weight, of a metal salt of a product obtained by reacting, at temperatures ranging from 200° F. to 300° F., an alkylphenol containing a total of from 1 to 36 carbon atoms in the alkyl radicals, and for each mol of said alkylphenol, 0.5 to 1.5 mols of an aliphatic monocarboxylic acid containing from 2 to 22 carbon atoms, and 1 to 3 mols of an aldehyde selected from the group consisting of formaldehyde and formaldehyde producing compounds, wherein the reaction time is from 1 to 4 hours.

8. The grease composition of claim 7, wherein said metal is selected from the metals of Groups I, II, III, and IV of Mendeléeff's Periodic Table.

9. The grease composition of claim 7, wherein said metals are selected from the group consisting of the alkali metals and the alkaline earth metals.

10. A grease composition comprising a major proportion of an oil of lubricating viscosity and from 10% to 20%, by weight, of a metal salt of a product obtained by reacting, at temperatures ranging from 200° F. to 300° F., an alkylphenol containing a total of from 1 to 36 carbon atoms in the alkyl radicals, and, for each mol of said alkylphenol, 0.5 to 1.5 mols of an aliphatic monocarboxylic acid containing from 2 to 22 carbon atoms, and 1 to 3 mols of an aldehyde selected from the group consisting of formaldehyde and formaldehyde producing compounds, wherein the reaction time is from 1 to 4 hours.

11. 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 sodium salt of a product obtained by reacting p-cresol, and, for each mol of said cresol, 1 mol of stearic acid and 2 mols of paraformaldehyde, at temperatures ranging from 200° F. to 300° F.

12. The grease composition of claim 11, wherein said oil is a petroleum lubricating oil.

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