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2,849,400

GREASES THICKENED WITH POLYAMIDO ACID SALTS

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No Drawing. Application December 31, 1953 Serial No. 401,696

7 Claims. (Cl. 252—33.6)

This invention pertains to grease compositions having improved resistance to oxidation and resistance to emulsification in water. The grease compositions embodied in this invention are thickened with agents which impart greater resistance to oxidation and emulsification in water than thickening agents which are presently used.

Metal soaps of fatty acids, such as calcium and lithium stearates, are examples of well-known agents which have been used and which are being used to thicken lubricating oils to the consistency of a grease. Because such metal soaps are pro-oxidative, that is, they increase the susceptibility of grease compositions to oxidation, it has been necessary to incorporate great amounts of oxidation inhibitors in these greases.

The grease compositions of this invention are more resistant to oxidation and have greater resistance to emulsification in water than those thickened with metal soaps of fatty acids. Furthermore, the grease compositions described in this invention are more resistant to heat than fatty acid soap thickened greases; that is, at increased temperatures, the thickening agents of the grease compositions of this invention do not lose their thickening action as rapidly as do the metal soaps of fatty acids.

The selection of greases for particular jobs involves more than the selection of a grease because of its general appearance at room temperature, its consistency at room temperature, its extreme pressure characteristics, its melting point, etc. The selection of greases must be accompanied by assurance that the grease will maintain its grease characteristics and perform its duties over wide ranges of temperature and wide variances in pressures at the surfaces being lubricated for long periods of time.

A detrimental result of the oxidation of grease compositions during the period of lubrication is the loss in thickening power of the thickening agent (e. g., the soap) used in the grease composition. When greases lubricate the desired surfaces, the greases normally become quite warm. When hot greases become oxidized, they lose their grease structure in the form of a melt. This melt then flows away from the surfaces being lubricated, thereby producing lubrication failure. In some greases, the melt, upon continued oxidation, becomes hard and brittle, thereby affording no lubrication of the surfaces. In some instances, the melt becomes oxidized to the degree where acids are formed, which acids may corrode the surfaces which are to be lubricated.

It is a tremendous advantage in lubricating systems which are not readily accessible to use grease compositions which withstand high temperatures and the effects of oxidations for long periods of time. Greases which are used to lubricate such parts as found in sealed bearings of electric motors, sealed bearings of compressors, rocker arms of airplane motors, numerous pieces of high speed equipment, such as high speed motors, must be resistant to oxidation while performing the specific task of lubricating, and at the same time have high temperature stability.

Some degree of satisfaction has been obtained in the preparation of greases containing lithium soaps of fatty

acids as thickening agents; however, such products are usually expensive for many of the uses, and also, lithium soap greases usually have less resistance to oxidation than is required in a number of phases of lubrication.

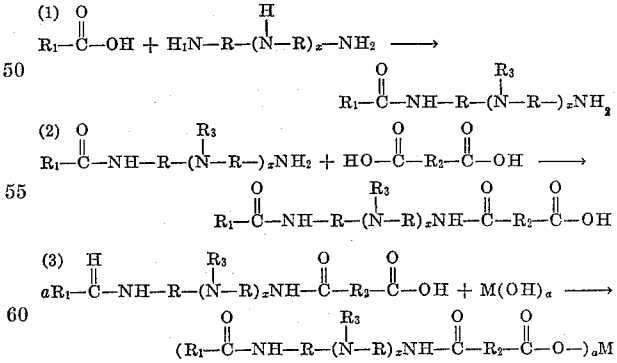
Numerous other grease thickeners which have been heretofore proposed are disadvantageous in that they may improve one property of a grease at the expense of other desirable properties, or are insufficiently effective to be commercially satisfactory or are too expensive. For example, certain greases suffer from hardening on aging and/or deteriorate in the presence of water. Still others become gelatinous in bearing tests.

Industry has long realized that it would be highly efficient and highly acceptable to obtain one grease composition embodying the combined characteristics of high water resistance and good resistance to oxidation. It is extremely advantageous to be able to use one grease composition which has these combined characteristics, eliminating the constant turmoil existing in supplying a great number of greases for all the numerous specified uses.

By the use of the grease compositions of this invention, it is possible to eliminate a number of specific greases for the above exemplified uses. The grease composition of the present invention, having the combined characteristics of high water resistance and oxidation resistance, has a wide variety of applications, particularly where both water and high temperatures are encountered, such as in steel mill rollers and transfer table bearings, paper mill roller bearings, automotive wheel bearings under winter and flood conditions, including use in amphibious military vehicles, high temperature cannery equipment, exposed control surface bearings for aircraft, etc.

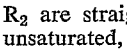
Thus, according to the present invention, it has been found that oxidation resistant and water resistant greases can be prepared by the use of the new compounds, metal salts of polyamido acids, as thickening agents in lubricating oils.

The polyamido acid salts set forth herein as thickening agents of this invention are prepared by first reacting an alkylene polyamine with a monobasic acid to form the corresponding fatty acid amide, which is then reacted with a dibasic acid to form the corresponding polyamido acid. This polyamido acid is then reacted with a metal basic substance to form the metal salt thereof. These reactions are illustrated by the following equations.

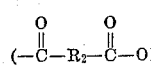


(Polyamido acid salt)

wherein R, R_1, and R_2 are straight-chain or branched-chain, saturated or unsaturated, hydrocarbon radicals, R_3 is hydrogen, or the fatty acid radical



or the radical



and M is a metal. When the polyamido acid salts herein are used as grease thickening agents, R is a straight-chain or branched-chain, saturated or unsaturated, hydrocarbon radical containing no more than 3 carbon atoms; R_1 is a saturated or unsaturated, straight-chain or branched-chain, hydrocarbon radical containing from 10 to 22 carbon atoms; R_2 is a saturated or unsaturated, straight-chain, branched-chain, or cyclic hydrocarbon radical containing from 1 to 8 carbon atoms; R_3 is hydrogen, or the fatty acid radical

$$(R_1\text{—}\overset{\overset{O}{\|}}{C}\text{—})$$

where R_1 represents the same as noted hereinabove; M is a metal; x is an integer having a value from 1 to 7; and a is an integer having a value equal to the valence of said metal.

For this purpose, it is particularly preferred that R is an ethylene radical; that R_1 is an aliphatic radical having from 12 to 18 carbon atoms; that R_2 is a hydrocarbon radical having from 2 to 6 carbon atoms; that R_3 is hydrogen; that M is an alkali metal; and that x is an integer having a value from 1 to 3.

As used herein, the terms "polyamido acid salts" and "salts of polyamido acids" mean the products represented by "polyamido acid salts" of Equation 3 hereinabove.

The metals which can be used in the formation of the soaps of this invention include the metals of Groups I, II, III, and IV of Mendeleef's Periodic Table. Particular metals include lithium, sodium, potassium, silver, magnesium, calcium, zinc, strontium, cadmium, barium, aluminum, and lead. Because of the increased melting points, improved texture and greater resistance to emulsification in water, it is preferred to use alkali metals, particularly sodium. Greater work stability, coupled with higher dropping points, are obtained with the sodium soap and the barium soap greases.

Examples of the R radicals include the following: methylene, ethylene, and propylene radicals; examples of the R_1 radicals include decyl, decenyl, dodecyl, dodecenyl, tetradecyl, tetradecenyl, hexadecyl, and octadecyl radicals derived from petroleum hydrocarbons, such as olefin polymers, e. g., polypropylene and polybutylene, etc.

Examples of R_2 radicals include methylene radicals, i. e., $(CH_2)_x$, wherein x is a number from 1 to 8 (2 to 6 preferred). Examples of dibasic acids from which the R_2 radical is obtained include the oxalic acid, malonic acid, methyl malonic acid, succinic acid, methyl succinic acid, adipic acid, pimelic acid, suberic acid, azelaic acid, sebacic acid, isophthalic acid, terephthalic acid, etc.

Examples of polyamines used in the preparation of the soaps used as thickening agents in grease compositions according to this invention include diethylene triamine, triethylene tetramine, tetraethylene pentamine, pentaethylene hexamine, hexaethyl heptamine, heptaethylene octamine, octaethylene nonamine; methylene diamine, dimethylene triamine; trimethylene tetramine, tetramethylene pentamine, pentamethylene hexamine, octamethylene nonamine; propylene diamine, dipropylene triamine, tripropylene tetramine, tetrapropylene pentamine, octapropylene nonamine, etc.

Lubricating oils which are suitable base oils for the 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 thereof, 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 the alkylene glycols, e. g., ethylene glycol; etc.

The polymeric products prepared from the various alkylene oxides and alkylene glycols may be polyoxyalkylene or polyalkylene-glycol derivatives; that is, the terminal hydroxy group can remain as such, or one or both of the terminal hydroxyl 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, valeric acid, etc., with alcohols such as butyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, dodecyl alcohol, etc. Examples of dicarboxylic acid esters synthetic oils include dibutyladipate, dihexyladipate, di-2-ethylhexylsebacate, di-n-hexylfumaric polymer.

Synthetic oils of the alkylbenzene type include those which are prepared by alkylating benzene (e. g., dodecyl benzene, tetradecyl benzene, 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 tetraethylsilicate, tetraisopropylsilicate, 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(methylphenylsiloxane), 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 grease compositions of this invention, dicarboxylic acids can be used which are known as dimer acids, which are obtained from Emery Industries, Inc., Cincinnati, Ohio. These dicarboxylic acid preparations contain a small amount of tricarboxylic acids (approximately 12%), which also form grease thickening agents when reacted according to the present invention.

As previously stated, the thickening agents of this invention were prepared by reacting monobasic acids with alkylene polyamines to form the corresponding carboxylic amides, which carboxylic amides were then reacted with dibasic acids to form the corresponding polyamidocarboxylic acids, which in turn were reacted with metal base substances to form the salts of the polyamido acids.

More particularly, the thickening agents of this invention were prepared by reacting one mol of a monobasic acid with one mol of an alkylene polyamine to form the corresponding carboxyamide. One mol of the carboxyamide was then reacted with one mol of a dibasic acid to form the corresponding polyamido acid. The resulting polyamido acid was then reacted with one mol of a metal base to form the desired metal salt of the polyamido acid. The following examples illustrate the preparation of the thickening agents of this invention.

Example I.—Preparation of sodium salt grease

A mixture of 284 grams (1.0 mol) of stearic acid and 206 grams (2 mols) of diethylene triamine was heated with agitation at 390° F. for a period sufficient to allow the theoretical quantity of water to be removed. To this cooled mixture was then added 500 grams (3 mols) of adipic acid, and the mixture was heated at 390° F. for about 2 hours to remove substantially all of the water of reaction.

A mixture of 30 grams of the above acid and 170 grams of a California solvent-refined naphthenic base oil having a viscosity of 450 SSU at 100° F. was heated at

460° F. until solution was complete. The mixture was cooled, and 3.7 grams of sodium hydroxide in 10 ml. of water was added. The whole mixture was heated to 460° F., then cooled, and milled through an 80 mesh screen. The resulting grease had an ASTM dropping point of 336° F. In the boiling water test, the grease was still completely intact after 60 minutes.

In testing the water resistance property of this grease, a 5-gram ball of grease was immersed in boiling distilled water. At the end of 60 minutes, the grease ball was still intact.

Example II.—Preparation of sodium salt grease

A mixture of 284 grams (1 mol) of stearic acid and 115 grams (1 mol) of diethylene triamine was charged to a reaction vessel and heated with agitation at 390° F. for a period to allow the theoretical quantity of water to be removed from the reaction mixture. To this reaction mixture (cooled) was added 146 grams (1 mol) of adipic acid, and the mixture was heated at 390° F. for about two hours to remove water of reaction. The resulting product was a tan, brittle solid.

A mixture of 30 grams of the above tan polyamido acid and 170 grams of a California solvent-refined naphthenic base mineral oil having a viscosity of 51 SSU at 210° F. and 450 SSU at 100° F. was placed in a reaction vessel and heated, with agitation, at 300° F. until solution was complete. The mixture was then cooled to 200° F., after which 1.45 grams of sodium hydroxide in 10 ml. of water was added. The whole mixture was then slowly heated with agitation to a temperature of 500° F. The liquid product was poured into a pan to cool. The resulting grease had an ASTM dropping point of 250° F.

Example III.—Preparation of sodium salt grease

A mixture of 284 grams (1 mol) of stearic acid and 51.5 grams (0.5 mol) of diethylene triamine was heated at 390° F. until amidation was complete. 73 grams (0.5 mol) of adipic acid was then added to the mixture and the heating was continued at about 200° C. for an additional two hours.

30 grams of the above amido acid was added to 170 grams of a California solvent-refined naphthenic base oil and heated at 300° F. until solution was complete. After cooling, 2.3 grams of sodium hydroxide in 10 ml. of water was added. The mixture was then heated to 500° F., and the product was poured into pans to cool. The resulting solid gel was milled through an 80-mesh screen to yield a very smooth homogenous grease. The worked penetration (ASTM penetration at 77° F. after 60 strokes) was 280, and the ASTM dropping point was 200° F.

Example IV.—Preparation of sodium salt grease

A mixture of 426 grams (1.5 mols) of stearic acid and 94.5 grams (0.5 mol) of tetraethylene pentamine was heated with agitation at 390° F. until substantially all of the water of reaction had been removed. To this reaction mixture was added 146 grams (1.0 mol) of adipic acid, and the mixture was heated at 390° F. for about 2 hours.

A mixture of 30 grams of the above polyamido acid and 170 grams of a California solvent-refined naphthenic base oil having a viscosity of 450 SSU at 100° F. was heated at 300° F. until solution was complete. The mixture was then cooled to 200° F., after which 3.1 grams of sodium hydroxide in 10 ml. of water was added. The whole mixture was then heated to 500° F., and the product was cooled. The ASTM dropping point was 230° F., and the ASTM penetration at 77° F. after 60 strokes was 315.

The ASTM worked penetration is obtained from the ASTM Test No. D-217, which is described in the Petroleum Division of the ASTM Manual of Test Procedures. In this test, a perforated disk was plunged through a grease sample for the designated number of strokes (e. g., 60 strokes) at 77° F., after which the penetration value was obtained.

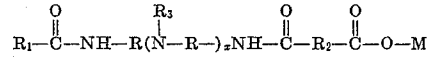
As thickening agents, the polyamido acid salts of this invention may be used in lubricating oils in amounts sufficient to thicken the lubricating oil to the consistency of a grease. For this purpose, from about 5% to about 50% may be used; however, from about 10% to about 20% are the preferred amounts for the preparation of grease compositions. In the preparation of more fluid grease compositions which are useful as air filter oils, only about 2.5% of the thickening agents of this invention are necessary for use in lubricating oils. On the other hand, in the preparation of brick-type greases, approximately 40% of the thickening agents of this invention will be required. All of the percentages are by weight.

Besides being excellent thickening agents for greases, the polyamido acid soaps of this invention are suitable as improving agents in lubricating oils, in pigment manufacture, in dusting powders; for imparting greater waterproofness in such materials as leather, textiles, wood and other fibrous or porous materials; etc.

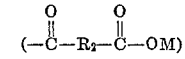
In addition to the components noted hereinabove, the grease composition may include such other additives as various corrosion inhibitors, extreme pressure agents, antiwear agents, stabilizers, V. I. improvers, and the like.

I claim:

1. A grease composition comprising at least 50%, by weight, of a mineral oil of lubricating viscosity, and, in an amount sufficient to thicken said lubricating oil to the consistency of a grease, a polyamido acid salt of the formula:

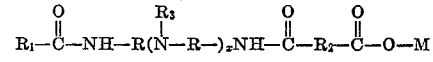


wherein R is an alkylene radical containing no more than 3 carbon atoms; R_1 is a hydrocarbon radical of the acyl group derived from a fatty acid, said hydrocarbon radical containing from 10 to 22 carbon atoms; R_2 is an alkylene radical containing from 1 to 8 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals containing from 10 to 22 carbon atoms, and the radical

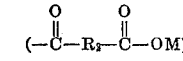


M is an alkali metal; x is a number having a value from 1 to 7.

2. A grease composition comprising at least 50%, by weight, of a mineral lubricating oil, and, from 5% to 50%, by weight, of a polyamido acid salt of the formula:

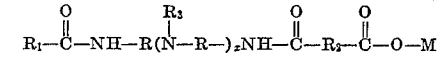


wherein R is an alkylene radical containing no more than 3 carbon atoms; R_1 is a hydrocarbon radical of the acyl group derived from a fatty acid, said hydrocarbon radical containing from 10 to 22 carbon atoms; R_2 is an alkylene radical containing from 1 to 8 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals containing from 10 to 22 carbon atoms, and the radical



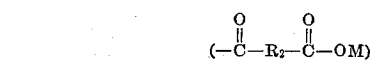
M is an alkali metal.

3. A grease composition comprising at least 50%, by weight, of a mineral lubricating oil, and, in an amount sufficient to thicken said oil to the consistency of a grease, a polyamido acid salt of the formula:



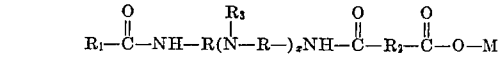
wherein R is a divalent ethylene radical; R_1 is hydrocarbon radical of the acyl group derived from a fatty acid,

said hydrocarbon radical having from 12 to 18 carbon atoms; R_2 is an alkylene radical having from 2 to 6 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals having from 12 to 18 carbon atoms, and the radical

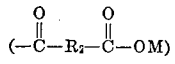


M is an alkali metal.

4. A grease composition comprising at least 50%, by weight, of a mineral lubricating oil, and, in an amount sufficient to thicken said lubricating oil to the consistency of a grease, a monovalent metal salt of a polyamido acid of the formula:

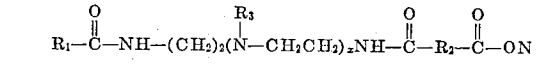


wherein R is an alkylene radical containing no more than 3 carbon atoms; R_1 is a hydrocarbon radical of the acyl group derived from a fatty acid, said hydrocarbon radical having from 12 to 18 carbon atoms; R_2 is an alkylene radical having from 2 to 6 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals having from 12 to 18 carbon atoms, and the radical

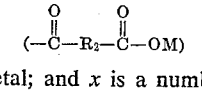


M is an alkali metal; and x is a number having a value from 1 to 3.

5. A grease composition comprising at least 50%, by weight, of a mineral lubricating oil, and from 10% to 20%, by weight, of a monovalent metal salt of a polyamido acid of the formula:

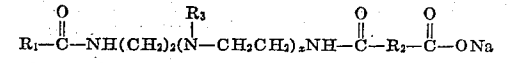


wherein R_1 is an aliphatic radical containing from 12 to 18 carbon atoms; R_2 is an alkylene radical containing from 1 to 8 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals having from 12 to 18 carbon atoms, and the radical

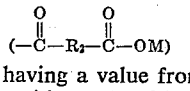


M is an alkali metal; and x is a number having a value from 1 to 3.

6. A grease composition comprising a major proportion of a mineral lubricating oil, and from 5% to 50%, by weight, of a sodium salt of a polyamido acid of the formula:

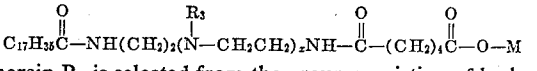


wherein R_1 is an aliphatic radical containing from 12 to 18 carbon atoms; R_2 is an alkylene radical containing from 1 to 8 carbon atoms; R_3 is selected from the group consisting of hydrogen, fatty acid radicals containing from 12 to 18 carbon atoms, and the radical

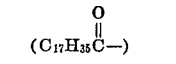


and x is a number having a value from 1 to 3.

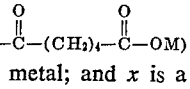
7. A grease composition comprising at least 50%, by weight, of a lubricating oil, and from 10% to 20%, by weight, of a polyamido acid salt of the formula:



wherein R_3 is selected from the group consisting of hydrogen, the radical



and the radical



M is a monovalent metal; and x is a number having a value from 1 to 7.

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,849,400 August 26, 1958

Bruce W. Hotten

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 2, Formula (1), for "H_1N" read -- H_2N --; Formula (3), for



read



column 6, line 66, after "metal", and before the period, insert -- ; x is a number having a value from 1 to 7 --; column 6, line 74, after "is", second occurrence, insert -- a --; column 7, line 9, after "metal", and before the period, insert -- ; x is a number having a value from 1 to 3 --; column 7, line 35, extreme right-hand portion of the formula, for "-ON" read -- -OM --.

Signed and sealed this 6th day of January 1959.

(SEAL)

Attest:

KARL H. AXLINE

Attesting Officer

ROBERT C. WATSON
Commissioner of Patents