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GREASE COMPOSITIONS

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U.S. Cl. 252—36 15 Claims

ABSTRACT OF THE DISCLOSURE

Grease compositions are provided comprising a lubricating vehicle, a grease-forming quantity of a thickening agent and a minor amount of an improving agent comprising an ethylene-vinyl ester-organic acid terpolymer.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to grease compositions and relates more particularly to grease compositions having improved resistance to water wash-out and resistance to softening at high temperature conditions.

(2) Description of the prior art

The prior art has, heretofore, proposed the incorporation of ethylene-vinyl acetate copolymers for improving water wash-out resistance of greases. The use of such copolymers has, however, not been effective in certain greases such as calcium-lead complex thickened formulations in which no significant water wash-out resistance was exhibited. Furthermore, it has also been found that such greases, as well as other grease formulations, in addition to exhibiting poor resistance to water wash-out, also tended to soften in high temperature environments.

SUMMARY OF THE INVENTION

In accordane with the present invention, there are provided grease compositions having improved resistance to water wash-out and resistance to softening at high temperature conditions, containing, as an improving agent, a minor amount sufficient to incorporate the aforementioned resistance, of an ethylene-vinyl ester-organic acid terpolymer, as more fully hereinafter described.

More specifically the terpolymers of the grease formulations of the present invention has a melt index of 0.5 to 200 and contain: (1) at least 65%, by weight, of ethylene, (2) at least 5%, by weight, of a second ethylenically unsaturated monomer which is an ester of the group consisting of the vinyl esters of the lower (1–6 carbon) saturated aliphatic carboxylic acids; the alkyl acrylates, the alkyl methacrylates, the dialkyl maleates and the dialkyl fumarates of the lower (1–6 carbon) aliphatic alcohols; and (3) 0.01 to 3%, by weight, of a third ethylenically unsaturated monomer of the group consisting of acrylic, methacrylic, itaconic, maleic and fumaric acids; the anhydrides of itaconic, maleic and fumaric acids; the alkyl hydrogen maleates and the alkyl hydrogen fumarates; the monoacrylates and monomethacrylates of glycols; 2-hydroxy-3-aminopropyl allyl ether, allyl glycerol ether, divinyl glycol, 2-dimethylaminoethyl acrylate, 2-dimethylaminoethyl methacrylate and N-vinyl pyrrolidone. The preparation of the above-described terpolymer improving agents is more fully disclosed in U.S. Pat 3,215,657, issued Nov. 2, 1965.

A wide variety of thickening agents can be used in the greases of this invention. Included among the thickening agents are alkali and alkaline earth metal soaps of fatty acids and fatty materials having from about 12 to about 30 carbons atoms per molecule. The meals are typified by sodium, lithium, calcium and barium. Fatty materials are illustrated by stearic acid, hydroxystearic acid, stearin, cottonseed oil acids, oleic acid, palmitic acid, myristic acid and hydrogenated fish oils.

Other thickening agents include salt and salt-soap complexes as: calcium stearate-acetate (Pat. No. 2,197,263); barium stearate-acetate (Pat. No. 2,564,561); calcium stearate-caprylate-acetate complexes (Pat. No. 2,999,065); calcium caprylate-acetate (Pat. No. 2,999,066); and calcium salts and soaps of low-, intermediate- and high molecular weight acids and of nut oil acids; and aluminum-complexes.

Another group of thickening agents comprise substituted ureas, phthalocyanines, indanthrene, pigments such as perylimides, pyromellitdiimides, ammeline, and carbon black.

Other thickening gelling agents employed in the new grease compositions are essentially hydrophobic clays. Such thickening agents can be prepared from clays which are initially hydrophilic in character, but which have been converted into a hydrophobic condition by the introduction of long chain hydrocarbon radicals into the surface of the clay particles, prior to their use as a component of a grease composition, as, for example, by being subjected to a preliminary treatment with an organic cationic surface active agent, such as an onium compound. Typical onium compounds are tetra alkyl ammonium chlorides, such as dimethyl dioctadecyl ammonium chloride, dimethyl dibenzyl ammonium chloride and mixtures thereof. This method of conversion, being well known to those skilled in the art, is believed to require no further discussion, and does not form a part of the present invention. More specifically, the clays which are useful as starting materials in forming the thickening agents to be employed in the grease compositions, can comprise the naturally occurring chemically unmodified clays. These clays are crystalline complex silicates, the exact composition of which is not subject to precise description, since they vary widely from one natural source to another. These clays can be described as complex inorganic silicates such as aluminum silicates, magnesium silicates, barium silicates, and the like, containing, in addition to the silicate lattice, varying amounts of cation-exchangeable groups such as sodium. Hydrophilic clays which are particularly useful for conversion to desired thickening agents include montmorillonite clays, such as bentonite, attapulgite, hectorite, illite, saponite, sepiolite, biotite, vermiculite, zeolite, clays and the like. Preferred thickening agents are calcium lead-acetate complexes employed in grease formulations as described in U.S. Pat. 2,898,297, issued Aug. 4, 1959. Such thickening agents comprise a mixture of (A) alkaline earth metal soaps and salts therewith, the alkaline earth metals being selected from the group consisting of calcium and a mixture (B) of calcium and barium, not more than about 15% of barium on a chemical equivalent basis being associated in said mixture (B) with calcium in said soaps and salts, the mixture (A) of said soaps and salts being present in a grease-forming quantity, and the metal salts of said mixture (A) being salts of a low molecular weight unsubstituted saturated monocarboxylic acid (I) having from 1 to 6 carbon atoms per molecule, and the metal soaps of

said mixture (A) being soaps of different acids with said acid (I) as shown in the following tabulation:

Acid		Number of carbon atoms	Weight percent of total acids
(I)	Low molecular weight	1–6	10–50
(II)	Intermediate molecular weight	7–12	5–50
(III)	High molecular weight	(1)	5–40
(IV)	Oil acids	8–18	25–60

[1] At least 13.

said acid (II) being selected from unsubstituted, monohydroxy–substituted and methyl-substituted saturated aliphatic monocarboxylic acids, and acids (III) being selected from unsubstituted and monohydroxy-substituted saturated aliphatic monocarboxylic acids and monounsaturated aliphatic monocarboxylic acids; and said oil acids being nut oil acids comprising mixtures of acids containing from about 8 to 18 carbon atoms per molecule and predominating in C_{12}–C_{14} acids; and from about 0.5 to about 5%, by weight (expressed as PbO) of at least one lead compound of at least one of said acids (I) through (IV).

Oils used in the greases of this invention can be mineral or synthetic oils of lubricating viscosity. Suitable mineral oils have a viscosity (SUS) of at least 40 seconds at 100° F., and particularly those within the range of about 60 seconds to about 6000 seconds at 100° F.

Synthetic vehicles can be used, instead of mineral oils, or in combination therewith. Typical synthetic vehicles are: polypropylene, polypropylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di-(2-ethyl hexyl) sebacate, di(2-ethyl hexyl) adipate, dibutyl phthalate, polyethylene glycol di(2-ethyl hexoate), fluorocarbons perfluoro-alkyl-polyethers, silicate esters, silanes, esters of phosphorus-containing acids, liquid ureas, ferrocene derivatives, hydrogenated mineral oils, chain type polyphenyls, siloxanes, and silicones (polysiloxanes) fluorosilicones, alkyl-substituted diphenyl ethers typified by a butyl-substituted bis-(p-phenoxy phenyl) ether, and phenoxy phenyl ethers.

Other hydrocarbon oils include synthetic hydrocarbon polymers having improved viscosity indices, which polymers are prepared by polymerizing an olefin, or mixture of olefins, having from 5 to 18 carbon atoms per molecule in the presence of an aliphatic halide and a Ziegler-type catalyst.

It is to be understood, however, that the compositions contemplated herein can also contain other characterizing materials. For example, antioxidants such as phenyl alphanaphthylamine (PAN), corrosion inhibitors, extreme pressure agents, viscosity index agents, and fillers can be used. Among such materials are colloidal silica, calcium acetate, calcium carbonate and molybdenum disulfide. Such characterizing materials do not detract from the lubricating value of the compositions of this invention, nor do they detract from the beneficial character of the terpolymers; rather, the characterizing materials serve to impart their customary properties to the particular compositions in which they are incorporated.

The greases of this invention can be prepared in accordance with conventional grease manufacturing procedures, as by any mixing technique wherein solid particles are wetted by a fluid. Typical equipment for such use includes a colloid mill, 3-roll ink mill, Manton-Gaulin homogenizer and the like.

With reference to the terpolymer improving agents of the present invention, preferred terpolymers contain from about 20 to about 30%, by weight, of the aforementioned group (2) component, i.e. the second ethylenically unsaturated monomer component; and from about 0.1 to about 1%, by weight, of the aforementioned group (3) component, i.e. the third ethylenically unsaturated monomer component. Representative preferred terpolymer comprise, in addition to ethylene, from about 20 to about 30%, by weight, vinyl acetate and from about 0.1 to about 1%, by weight, acrylic acid; from about 20 to about 30%, by weight, vinyl acetate and from about 0.1 to about 1%, by weight, methacrylic acid; from about 20 to about 30%, by weight, ethyl acrylate and from about 0.1 to about 1%, by weight, acrylic acid; from about 20 to about 30%, by weight, ethyl acrylate and from about 0.1 to about 1%, by weight, methacrylic acid; from about 20 to about 30%, by weight, methyl methacrylate and from about 0.1 to about 1%, by weight acrylic acid; and from about 20 to about 30%, by weight, methyl methacrylate and from about 0.1 to about 1%, by weight methacrylic acid.

Insofar as the quantity of terpolymer improving agent is concerned, the latter, as previously indicated, is employed in a minor amount sufficient to incorporate in the grease formulation the desired resistance to water washout and resistance to softening at high temperature conditions. Particularly preferred are greases in which the terpolymer is present in an amount of at least about 0.01%, by weight, and for most purposes, the presence of the terpolymer in an amount from about 0.1 to about 5%, by weight, produces highly satisfactory improved grease compositions.

DESCRIPTION OF SPECIFIC EMBODIMENTS

In order to demonstrate the improvement of water washout resistance and resistance to softening at elevated temperatures, employing the above-described terpolymers, a typical calcium-lead complex grease was prepared comprising, by weight, 16% thickener, 80% vehicle and 4% additives.

The thickener was formed by the reaction of a slight stoichiometric excess of metal base consisting of 4.5 parts of lime to 1 part litharge, with fatty acids comprising 27.5%, by weight, of a low molecular weight acid, viz acetic acid; 58%, by weight, of an intermediate molecular weight fatty acid, viz caprylic acid; and 14.5%, by weight of high molecular weight acids, viz coconut oil acids (C_{12}–C_{18}). The vehicle comprised a naphthenic solvent-refined mineral oil stock of a viscosity of 800 SUS at 100° F. and 70 SUS at 210° F. The additives comprised 2%, by weight, of chlorinated wax as an extreme pressure agent; 0.8%, by weight, of antioxidants, viz hindered phenol and aromatic amine; and 1.2%, by weight, of corrosion inhibitors.

As is shown in the examples of the following Table I, varying quantities of a typical representative terpolymer were incorporated in the above-prepared grease for evaluation. This terpolymer comprised an ethylene-vinyl acetate-methacrylic acid terpolymer, having a melt index of 13 and containing 27.5%, by weight, vinyl acetate, 0.7%, by weight, methacrylic acid, and 71.8%, by weight, ethylene.

The respective grease formulations, containing the indicated amounts of the above-prepared terpolymer, by weight, were subjected to the standard Water Wash-out Test, ASTM D1264, employing a wider annular shield to facilitate passage of water into the grease-packed bearing.

TABLE I.—INFLUENCE OF TERPOLYMER ON WASH-OUT RESISTANCE

Ex.	Grease	Consistency ASTM D217 (UW/60W) [1]	Water Wash-out Test ASTM D1264 (percent wash-out) [2]
1	Base grease	312/328	25
2	Base grease plus 0.3% terpolymer	298/318	13
3	Base grease plus 0.5% terpolymer	272/272	7
4	Base grease plus 1.0% terpolymer	218/255	4

[1] UW/60W = Unworked/60 strokes worked.
[2] Employing a wider annular shield.

As will be apparent from the examples of the foregoing Table I, the terpolymers of the present invention are highly effective in imparting resistance to water wash-out of grease compositions.

As is shown in the examples of the following Table II, varying quantities of the above-described representative terpolymer were incorporated in the above-described grease

for evaluation with respect to resistance to softening effect at elevated temperatures.

TABLE II.—INFLUENCE OF TERPOLYMER ON SOFTENING EFFECT

Ex.	Grease	Consistency ASTM D217 (UW/60W) [1]	Softening effect (percent) 150° F.	200° F.	250° F.	320° F.	Wheel bearing leakage test ASTM D1263 modified (260° F.—130 g.), leakage (g.).
1	Base grease	301/318	21	35	[2] >50	[2] >50	12.1
2	Base grease plus 0.3% terpolymer	256/286	13	20	33	40	4.6

[1] UW/60W = Unworked/60 strokes worked.
[2] Too soft for penetration to be measured.

As will be apparent from the examples of the foregoing Table II, the terpolymers of the present invention are highly effective in imparting resistance of the grease to softening at elevated temperatures.

While this invention has been described with reference to preferred compositions and components therefor, it will be understood, by those skilled in the art, that departures from the preferred embodiments can be effectively made and are within the scope of the specification.

We claim:

1. A grease composition comprising a lubricating vehicle, a grease-forming quantity of a thickening agent and a minor effective amount of an improving agent comprising a terpolymer having a melt index of 0.5 to 200 and containing: (1) at least 65%, by weight, of ethylene, (2) at least 5%, by weight, of a second ethylenically unsaturated monomer which is an ester of the group consisting of: the vinyl esters of saturated aliphatic carboxylic acids having 1–6 carbons; the alkyl acrylates, the alkyl methacrylates, the dialkyl maleates and the dialkyl fumarates of aliphatic alcohols having 1–6 carbons; and (3) 0.01 to 3.0%, by weight, of a third ethylenically unsaturated monomer of the group consisting of: acrylic, methacrylic, itaconic, maleic and fumaric acids; the anhydrides of itaconic, maleic and fumaric acids; the alkyl hydrogen maleates and the alkyl hydrogen fumarates; the monoacrylates and monomethacrylates of glycols; 2-hydroxy-3-aminopropyl allyl ether, allyl glycerol ether, divinyl glycol, 2-dimethylaminomethyl acrylate, 2-dimethylaminoethyl methacrylate and N-vinyl pyrrolidone.

2. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, of the group (2) component.

3. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, of the group (2) component and from about 0.1 to about 1%, by weight, of the group (3) monomer component.

4. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, vinyl acetate and from about 0.1 to about 1%, by weight, acrylic acid.

5. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, vinyl acetate and from about 0.1 to about 1%, by weight, methacrylic acid.

6. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, ethyl acrylate and from about 0.1 to about 1%, by weight, acrylic acid.

7. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, ethyl acrylate and from about 0.1 to about 1%, by weight, methacrylic acid.

8. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, methyl methacrylate and from about 0.1 to about 1%, by weight, acrylic acid.

9. A grease composition as defined in claim 1 wherein the terpolymer contains from about 20 to about 30%, by weight, methyl methacrylate and from about 0.1 to about 1%, by weight, methacrylic acid.

10. A grease composition as defined in claim 1 wherein the vehicle comprises a mineral lubricating oil.

11. A grease composition as defined in claim 1 wherein the vehicle comprises a synthetic lubricating oil.

12. A grease composition as defined in claim 1 wherein said terpolymer is present in an amount of at least 0.01%, by weight.

13. A grease composition as defined in claim 1 wherein said terpolymer is present in an amount from about 0.1 to about 5%, by weight.

14. A grease composition as defined in claim 1 wherein the thickening agent comprises a mixture of (A) alkaline earth metal soaps and salts therewith, the alkaline earth metals being selected from the group consisting of calcium and a mixture (B) of calcium and barium, not more than about 15% of barium on a chemical equivalent basis being associated in said mixture (B) with calcium in said soaps and salts, the mixture (A) of said soaps and salts being present in a grease-forming quantity, and the metal salts of said mixture (A) being salts of a low molecular weight unsubstituted saturated monocarboxylic acid (I) having from 1 to 6 carbon atoms per molecule, and the metal soaps of said mixture (A) being soaps of different acids with said acid (I) as shown in the following tabulation:

Acid		Number of carbon atoms	Weight percent of total acids
(I)	Low molecular weight	1–6	10–50
(II)	Intermediate molecular weight	7–12	5–50
(III)	High molecular weight	[1]	5–40
(IV)	Oil acids	8–18	25–60

[1] At least 13.

said acid (II) being selected from unsubstituted, monohydroxy-substituted and methyl-substituted saturated aliphatic monocarboxylic acids, said acids (III) being selected from unsubstituted and monohydroxy-substituted saturated aliphatic monocarboxylic acids and monounsaturated aliphatic monocarboxylic acids; and said oil acids being nut oil acids comprising mixtures of acids containing from about 8 to 18 carbon atoms per molecule and predominating in C_{12}–C_{14} acids; and from about 0.5 to about 5%, by weight, expressed as PbO, of at least one lead compound of at least one of said acids (I) through (IV).

15. A grease composition as defined in claim 1 wherein said terpolymer has a melt index of about 13 and contains about 71.8%, by weight, ethylene, about 27.5%, by weight, vinyl acetate and about 0.7%, by weight, methacrylic acid.

References Cited

UNITED STATES PATENTS

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252—51.5 R, 51.5 A, 56 R

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,705,853 Dated December 12, 1972

Inventor(s) PAUL FAU and RICHARD J. PETRUCCO

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, Line 46 "has" should read --have--.

Column 2, Line 5 "meals" should read --metals--.

Column 3, Line 13 "and" should read --said--.

Column 3, Line 72 "terpolymer" should read --terpolymers--.

Column 5, Line 43 "dimethylaminomethyl" should read --dimethylaminoethyl--.

Signed and sealed this 22nd day of May 1973.

(SEAL)
Attest:

EDWARD M.FLETCHER,JR.
Attesting Officer

ROBERT GOTTSCHALK
Commissioner of Patents