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GREASE COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

Grease compositions are provided comprising a major proportion of an oil of lubricating viscosity, a minor proportion of a thickening agent and from about 0.5 to about 5 percent, by weight, based upon the grease, of a thiobis-(dichlorophenol) as an extreme pressure and antiwear agent.

This invention has to do with grease compositions. More specifically, the invention relates to grease compositions having excellent extreme pressure and wear properties.

There has been a demand for some years for grease compositions capable of providing satisfactory lubrication when subjected to rigorous operating conditions. Many grease lubrication operations are conducted at extreme pressures such that greases fail to perform as desired. The compositions become unstable with separation of the lubricating oil vehicle and thickening agent of which they are comprised. As a result, metal parts are inadequately lubricated by the compositions and become worn or otherwise damaged.

Numerous efforts have been made to improve the extreme pressure properties of grease compositions. Invariably, however, the compositions are worsened in one or more other properties. For example, sulfur- and chlorine-containing additives used to date have been found to cause softening or loss of shear stability of the compositions. While with some steel mill lubricant greases, such disadvantages can be tolerated, no such disadvantages can be tolerated with greases used in ball bearings. The same additives and others hitherto used increase the viscosity of the grease compositions, an undesirable characteristic for low temperature lubrication.

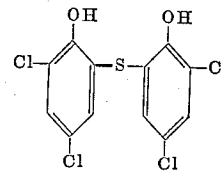
Not only should an additive impart extreme pressure and antiwear characteristics to grease compositions, but it should also be fluid or soluble in the lubricant vehicle of the compositions, or it should be microcrystalline in nature in order to avoid surface scratching of bearing race ways and plugging of small openings in bearing retainers and centralized lubricant pumping systems.

It has now been found that extreme pressure and antiwear properties can be imparted to grease compositions by incorporating therein a relatively small amount of a thiobis(dichlorophenol).

It is an object of this invention, therefore, to provide grease compositions having improved extreme pressure and antiwear properties. Another object is to provide such greases without worsening other desirable characteristics of grease compositions. A specific object is to provide such grease compositions in which the thickening agent is an inorganic thickener. Other objects of the invention will be apparent from the following description.

In accordance with the invention, there are provided grease compositions comprising a major proportion of an oil of lubricating viscosity, a minor proportion of a thickening agent and from about 0.2 to about 5 percent by weight (based upon the grease composition), of a thiobis-(dichlorophenol). Preferred of such phenols is 2,2'-thio-

bis(4,6-dichlorophenol), which is represented by the formula



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 carbon atoms per molecule. The metals 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 (Patent No. 2,197,263); barium stearate-acetate (Patent No. 2,564,561); calcium stearate-caprylate-acetate complexes (Patent No. 2,999,065); calcium caprylate-acetate (Patent No. 2,999,066); and calcium salts and soaps of low-, intermediate- and high-molecular weight acids and of nut oil acids.

Another group of thickening agents comprises substituted ureas, phthalocyanines, indanthrene, pigments such as perylimides (Patent No. 3,137,653), anthanthrones, naphthalic imidazoles and oxazoles.

The preferred thickening or 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 of the latter are dimethyl dibenzyl quaternary ammonium chloride and dimethyl dioctadecyl quaternary ammonium chloride. 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 generally regarded as metallic oxide radicals. 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. The thickening agent is employed in an amount from about 0.5 to about 30, and preferably from 5 percent to 15, percent by weight of the total grease composition.

The lubricating vehicles employed in the grease compositions can comprise any of the conventional oils of lubricating viscosity including mineral or synthetic lubricating oils, aliphatic phosphates, esters and diesters, silicates, siloxanes and oxyalkyl ethers and esters. Mineral lubricating oils can be of any suitable lubricating viscosity

ranging from about 45 SUS at 100° F., to about 3500 SUS at 100° F. and preferably from about 50 to about 250 SUS at 210° F. The oils may have viscosity indexes, varying from below 0 to about 130 or higher. Other hydrocarbon oils include synthetic hydrocarbon polymers having improved viscosity indices, which polymers are prepared by polymerizing an olefin, or mixtures of olefins, having from 5 to 18 carbon atoms per molecule in the presence of an aliphatic halide and a Ziegler-type catalyst. Such synthetic hydrocarbon oils are described by Armstrong et al. in application U.S. Ser. No. 314,575, filed Sept. 26, 1963, and now abandoned.

Synthetic vehicles suitable herein include: polypropylene, polypropylene glycol, trimethylol propane esters, neopentyl and pentaerythritol esters, di-(2-ethylhexyl) sebacate, di-(2-ethylhexyl) adipate and related adipates, dibutyl phthalate, polyethylene glycol di-(2-ethyl hexoate), and polysiloxanes (silicones).

Outstanding in conjunction with the inorganic clay-type thickeners identified above are synthetic ester lubricants, particularly esters of adipic acid and isooctyl and isodecyl alcohols.

When inorganic clay-type thickeners are used, it is generally advantageous to include a stabilizing agent such as pentaerythritol or anhydroenneaheptitol.

Other improving agents can also be included in the grease compositions of this invention, in order to obtain the benefit of their known characterizing features. Antioxidants can be used such as amines and mixtures of amines, such as a mixture of dioctyl phenyl amine and 4,4'-methylenebis(2,6-dietertiarybutylphenol). Phenyl alpha naphthylamine (PAN) is preferred. Lubricity improving agents such as free fat, free fatty acids, sulfurized fats, lead soaps and esters of alkyl and/or aryl acids can be used. Rust inhibitors such as sodium nitrite are also suitable in the new compositions.

The greases of this invention can be prepared in accordance with conventional grease manufacturing procedures. The extreme pressure and antiwear agent—a thiobis (dichlorophenol)—can be incorporated in a base grease when the latter is heated at a temperature about 100° F. to about 300° F., and thoroughly mixing of the resulting grease composition. If the grease composition is subjected to homogenization, as in a Manton-Gaulin homogenizer, the agent can be incorporated before or after homogenization.

The concentration of the extreme pressure and antiwear agent is from about 0.2 to about 5, and preferably 0.5 to 2, percent by weight of the finished grease.

The greases of this invention are illustrated in the several following examples. A base grease was prepared from approximately 9 parts by weight of sodium montmorillonite clay treated with dimethyl dibenzyl quaternary ammonium chloride (identified hereinafter as Clay 1), about 1 part by weight of pentaerythritol and about 90 parts by weight of a mixture of synthetic neutral esters comprising a mixture of isooctyl and isodecyl adipates (Ester 1 hereinafter). The mixed esters have a viscosity of 62 SUS at 100° F. and 36 SUS at 210° F. The several components are mixed and heated together in a grease kettle to a temperature of about 300° F. during a time interval of approximately 1–3 hours. The resulting mixture is then cooled to about 200° F., and an extreme pressure, antiwear agent—2,2'-thiobis(4,6-dichlorophenol)—is incorporated. The material is then homogenized in a Manton-Gaulin homogenizer at about 2000–3000 pounds per square inch (p.s.i.)

The illustrative greases were evaluated on the 4-ball extreme pressure tester according to U.S. Federal Method 6503.1, which provides an index of load-carrying ability. This shows the maximum load which can be imposed directly upon the grease. From the data measured in this test mean Hertz load values are determined. An extreme pressure lubricant is considered to be one having a mean Hertz load value above about 30.

Example 1

	Parts by wt.
Clay 1	9
Pentaerythritol	1
Ester 1	89
PAN	1

The grease composition formed from the foregoing components has a mean Hertz load value of 28.

A grease composition formed from 99 parts by weight of the composition identified above and 1 part by weight of 2,2'-thiobis(4,6-dichlorophenol), has a mean Hertz load value of 36.7. This is an improvement of more than 30 percent.

Example 2

	Parts by wt.
Clay 1	10
Pentaerythritol	1.67
Mineral oil	88.33

Viscosity at:
210° F., 44.94 SUS.
100° F., 149.3 SUS.
—40° F., —7226 centistokes.

The grease composition formed of the three components identified above has a mean Hertz load value of 28.

When 99 parts by weight of this composition and 1 part by weight of the thiobis compound of Example 1 are mixed together, the grease product obtained thereby has a mean Hertz load value of 36. This is an improvement of approximately 30 percent.

Example 3

	Parts by wt.
Clay 1	10
Pentaerythritol	1
Sodium nitrite	1.5
PAN	1.0
Ester 1	85.5

A grease formed from the foregoing components has a mean Hertz load value of 28.

Addition of 0.5 part by weight of the thiobis compound of Example 1 to 99.5 parts by weight of the base grease, increased the mean Hertz load value to 35.

Properties characterizing the final grease composition of Example 3 are given below:

ASTM penetration (D217–60T), unworked/worked	288/288.
ASTM bomb at 210° F. (D942–50)	2 lb. drop/100 hours.
4-ball mean Hertz load (Federal 6503.1)	35 or greater.
Bearing performance at 250° F., 10,000 r.p.m. (Federal 331)	1000 hours.

Example 4

	Parts by wt.
Lithium-calcium stearates	10
PAN	0.3
Mineral oil, 750 SUS at 100° F.	89.7

A mean Hertz load value of 26.3 was obtained for a grease formed of the foregoing components.

When 1 part by weight of the thiobis compound of Example 1 was incorporated with 99 parts by weight of the base grease, the mean Hertz load was only increased to 27.9. However, a concentration of 2 percent by weight of the additive, increased the load value to 30.6, thereby bringing the grease into the range of extreme pressure lubricants.

Example 5

	Parts by wt.
Calcium tallow soap	11
Mineral oil, 750 SUS at 100° F.	89

The mean Hertz load value was only 21.8 for the grease formed from the foregoing components.

Here again, incorporation of one percent of the thiobis

compound of Example 1 increased the load value to an unsatisfactory value of 27.9. A 2.5 percent concentration increased the load value to 34.2.

Example 6

	Parts by wt.
Lime flour	6.2
Acetic acid	7.1
C_{14-18} fatty acids	7.5
PAN	1
Mineral oil, 400 SUS at 100° F.	78

A grease was formed from the foregoing components by following the procedure described in U.S. Patent No. 2,197,263. The mean Hertz load of the grease was 42.8. Incorporation of one percent of the thiobis compound of Example 1 into the grease, increased the load value to 47.1.

Example 7

	Parts by wt.
Sodium soaps of stearic acid and castor oil fatty acids	16
PAN	0.5
Mineral oil, 150 SUS at 100° F.	83.5

A grease formed of the named components has a mean Hertz load of 22.3. One percent concentration of the thiobis compound of Example 1 increased the load value slightly to 24.2; however, a value of 35.2 was obtained with a 2 percent concentration of the same additive.

Example 8

	Parts by wt.
Cab-O-Sil	10
Mineral oil, 80 SUS at 100° F.	82

Cab-O-Sil is a silica aerogel having a particle size of about 0.015 micron; it is marketed by the Cabot Corporation.

A grease formed of Cab-O-Sil and the mineral oil has a mean Hertz load of 20.4. One percent of the thiobis compound increased the load value to 29.4. In view of this substantial increase with a one percent concentration of the additive, larger concentrations would further increase the load value to well over 30.

Example 9

	Parts by wt.
p-Methoxyphenyl perylimid	18
Silicone fluid, 400 SUS at 100° F.	82

A grease formed of the foregoing components following the procedure of U.S. Patent No. 3,108,962, has a mean Hertz load value of 20.1. While a one percent concentration of the thiobis compound of Example 1 increased the load value only to 23.7, a five percent concentration provided a value of 38.7.

The silicone fluid is comprised of phenylmethyl siloxanes having a ratio of approximately 20 methyl groups to one phenyl group, and contains a small amount of iron octoate.

The greases of this invention are suitable for a wide range of industrial applications. Some, for example, are suitable for use as multi-purpose automotive and aviation greases, serving as chassis, wheel-bearing, grease lubricants. Others are multi-purpose industrial greases serving as plain-bearing and anti-friction greases for heavily loaded equipment.

We claim:

1. A grease comprising
a major proportion of an oil of lubricating viscosity,
a grease forming amount of a thickening agent, and
from about 0.2 to about 5 percent by weight, based upon the grease, of a thiobis(dichlorophenol).

2. A grease defined by claim 1 wherein the phenol is 2,2'-thiobis(4,6-dichlorophenol).

3. A grease defined by claim 1 wherein the oil is a synthetic ester.

4. A grease defined by claim 1 wherein the oil is a mineral oil.

5. A grease defined by claim 1 wherein the oil is a synthetic hydrocarbon polymer having a viscosity index of at least about 110 and prepared from an olefin having from about 5 to about 18 carbon atoms per molecule.

6. A grease defined by claim 1 wherein the thickening agent is an essentially hydrophobic clay.

7. A grease defined by claim 1 wherein the thickening agent is a reaction product of sodium montmorillonite clay and a dimethyl dibenzyl quaternary ammonium halide.

References Cited

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UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,349,034 October 24, 1967

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

Column 2, lines 3 to 10, for that portion of the formula reading " ——C" read -- ——Cl --; column 3, line 31, for "dietertiarybutylphenol" read -- ditertiarybutylphenol --.

Signed and sealed this 17th day of December 1968.

SEAL)
ttest:

dward M. Fletcher, Jr.
ttesting Officer

EDWARD J. BRENNER
Commissioner of Patents