

- [54] GREASE THICKENED WITH OXYGEN-
LINKED OR SULFUR-LINKED POLYUREAS
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252/403

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UNITED STATES PATENTS
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- [57] ABSTRACT
- Improved greases, having wide-temperature utility and good oxidation stability are provided comprising an oil of lubricating viscosity, as a vehicle, and a thickening quantity of a polyurea prepared by reacting a mono-amine, a diisocyanate and a diamine having one amino group attached to each of two hydrocarbyl groups and the hydrocarbyl groups being separated by an oxygen or sulfur atom.
- 11 Claims, No Drawings

GREASE THICKENED WITH OXYGEN-LINKED OR SULFUR-LINKED POLYUREAS

BACKGROUND OF THE INVENTION

1. Field of the Invention

This invention relates to grease compositions and, in one of its aspects, relates to grease compositions which are suitable for use over wide-temperature ranges and which exhibit good oxidation stability under varying operational conditions. More particularly, in this aspect, the invention relates to improved greases which contain a novel polyurea thickening agent, rendering these greases particularly effective in operations in which the aforementioned conditions are normally encountered.

2. Description of the Prior Art

Greases, heretofore prepared by the processes of the prior art, have generally comprised a vehicle, such as petroleum hydrocarbon lubricating oils, refined mineral oils or synthetic esters, in which various thickening agents, such as metal salts or soaps, are dispersed in grease-forming quantities in such degree as to impart to the resulting grease composition the desired consistency. In this respect, insofar as the thickening agents are concerned, most greases have been formulated with soaps. Some of the soaps have provided relatively high melting point compositions, e.g., lithium soaps of fatty acids. It has been found, however, that these soaps tend to catalyze the oxidation of the lubricant. At relatively high temperatures of operation, it is found that the rapid oxidative degradation of the lubricant increases the frequency with which the lubricant must be removed and new grease lubricant applied to the moving surface. It will therefore become evident that improved grease compositions which are thermally stable over wide-temperature ranges and which are not subject to the undesirable characteristics heretofore exhibited by greases of the prior art, are highly desirable.

SUMMARY OF THE INVENTION

In accordance with the present invention, as more fully hereinafter described, it has been found that improved grease compositions having wide-temperature utility, improved oxidation stability and relatively high dropping points, can be produced by employing, as the thickening agent, a polyurea prepared by reacting a monoamine, a diisocyanate and a diamine having one amino group attached to each of two hydrocarbyl groups and the hydrocarbyl groups being separated by an oxygen or sulfur atom. The term "hydrocarbyl" is intended to include alkyl, aryl, alkaryl and aralkyl.

In preparing the polyurea thickening agent, any monoamine may be employed. Representative of such amines are octadecenyl amine, phenyl alpha naphthylamine, pentylamine, hexylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, docosenylamine, hexadecenylamine, octadecadienylamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tert.-butyl aniline, benzylamine, betaphenethylamine, and cyclohexylamine.

Also, in preparing the polyurea, any diisocyanate may be employed. Representative of the diisocyanates are toluene diisocyanate, trimethylhexamethylenediisocyanate, octadecene diisocyanate, and phenylene diisocyanate.

As hereinbefore indicated, the diamine reactant may include any diamine having one amino group attached to each of two hydrocarbyl groups and in which the hydrocarbyl groups are separated by an oxygen or sulfur atom. Representative of these diamines are non-hydrocarbylene diamines including diamino diphenyl ethers, diamino diaryl oxides, diamino dialkyl oxides, diamino dihydrocarbyl oxides, diamino diaryl sulfides, diamino dialkyl sulfides, diamino dihydrocarbyl sulfides, 4,4'-diamino diphenyl ether, and 4,4'-diamino diphenyl sulfide.

The above-described monoamine, diisocyanate and diamine involved in the preparation of the polyurea thickening agent are, in general, stoichiometrically reacted at a temperature from about 45°F. to about 250°F. and, preferably from about 65°F. to about 150°F. In formulating the grease composition, the polyurea thickener is, in general, employed in any amount sufficient to provide a composition having the consistency of a grease, in combination with an oil of lubricating viscosity, as the vehicle. In general, in most applications, the thickener is employed in an amount from about 1 to about 40%, and preferably in an amount from about 2 to about 20%, by weight.

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 6,000 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, corrosion inhibitors, extreme pressure agents, anti-wear agents, viscosity index improvers, supplementary thickeners, 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; 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 grease kettle, colloid mill, Stratco Con-

tactor, 3-roll ink mill, Manton-Gaulin homogenizer and the like.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following data and examples will serve to illustrate the improved grease compositions of the present invention and their preparation with the parts recorded by weight.

EXAMPLE I

A mixture comprising 12 grams oxydianiline, 30 grams octadecenyl amine and 7 grams of phenyl alpha naphthylamine (Mixture A) was heated to a temperature of 140°F. with stirring for a period of 10 minutes to form a uniform mixture. A second mixture (Mixture B) was prepared comprising 223 grams petroleum oil, 500 SUS at 100°F., and 17.4 grams toluene diisocyanate. This latter Mixture B was then placed in a blender and stirred for a period of 2 minutes. The above-described Mixture A was then added to the second Mixture B in the blender, with constant stirring for a period of 1 hour. The resulting combined mixtures were then heated with constant stirring to a temperature of 350°F. The final resulting thick mixture was then cooled to room temperature, mixed with additional oil, and worked until smooth on a 3-roll mill. With a thickener content of 12.7%, the worked penetration was found to be 279, with a dropping point of 543°F.

Pope Elevated Temperature Bearing Test results showed a bearing life of 841 hours for this grease versus 409 hours for a similar tetraurea type grease made according to U.S. Pat. No. 3,243,372 when tested under the following conditions:

Bearing type — Fafnir 204 K Cl

Loading, radial — 5 pounds

Loading, axial — 5 pounds

Temperature, °F. — 350

R.P.M. — 3,500

The test procedure was conducted by cycling for a period of 20 hours on and 4 hours off.

EXAMPLE II

The procedure followed in Example I was repeated except that 50 ml of acetone was added to Mixture A to facilitate solution, and the resulting mixture was stirred for an additional 10 minutes. The resulting cooled, firm product was mixed with additional oil and worked until smooth on a 3-roll mill. With a thickener content of 12.6%, the worked penetration was found to be 285, with a dropping point of 516°F.

EXAMPLE III

The procedure followed in Example I was repeated except that 50 ml of toluene was added to Mixture B in the blender. This batch thickened in about 5 minutes. After cooling, the resulting firm product was mixed with additional oil and worked until smooth on a 3-roll mill. With a thickener content of 12.1%, the worked penetration was found to be 278, with a dropping point of 556°F.

EXAMPLE IV

A mixture comprising 12.9 grams 4, 4' - diamino diphenyl sulfide, 30 grams octadecenyl amine and 7 grams phenyl alpha naphthylamine (Mixture A) was heated to a temperature of 200°F. with stirring for a pe-

riod of 15 minutes to form a uniform mixture. A second mixture (Mixture B) was prepared comprising 223 grams petroleum oil, 500 SUS at 100°F., and 17.4 grams toluene diisocyanate. This latter Mixture B was then placed in a blender and stirred for a period of two minutes or until a uniform blend had been formed. The above-described Mixture A was then added to the second Mixture B in the blender, with constant stirring for a period of 20 minutes. The resulting product thickened to a high viscosity. The final thickened mixture was then cooled to room temperature, mixed with additional oil, and worked until smooth on a 3-roll mill. With a thickener content of 12.9%, the worked penetration was found to be 275, with a dropping point of 550°F.

EXAMPLE V

A mixture comprising a silicone fluid, 12 grams oxydianiline, 30 grams octadecenyl amine and 7 grams of phenyl alpha naphthylamine (Mixture A) was heated to a temperature of 140°F. with stirring for a period of 10 minutes to form a uniform mixture. A second mixture (Mixture B) was prepared comprising 223 grams of a silicone fluid and 17.4 grams toluene diisocyanate. The latter Mixture B was then placed in a blender and stirred for a period of 2 minutes. The above-described Mixture A was then added to the second Mixture B in the blender with constant stirring for a period of one hour. The resulting thick mixture was grease-like in consistency with an unworked penetration of 300 and a dropping point > 500°F.

EXAMPLE VI

A mixture comprising a synthetic hydrocarbon fluid, 12 grams oxydianiline, 30 grams octadecenyl amine and 7 grams of phenyl alpha naphthylamine (Mixture A) was heated to a temperature of 140°F. with stirring for a period of 10 minutes to form a uniform mixture. A second mixture (Mixture B) was prepared comprising 223 grams of a synthetic hydrocarbon fluid 1,200-1,500 SUS at 100°F. and 17.4 grams toluene diisocyanate. The latter Mixture B was then placed in a blender and stirred for a period of 2 minutes. The above-described Mixture A was then added to the second Mixture B in the blender with constant stirring for a period of one hour. The resulting thick mixture was grease-like in consistency with a worked penetration of 290 and a dropping point of 496°F.

EXAMPLE VII

A mixture comprising 12 grams oxydianiline and 40 grams octadecenyl amine (Mixture A) was heated to a temperature of 170°F. with stirring for a period of 10 minutes to form a uniform mixture. A second mixture (Mixture B) was prepared comprising 223 grams petroleum oil, 500 SUS at 100°F., and 17 grams toluene diisocyanate. This latter Mixture B was then placed in a blender and stirred for a period of 2 minutes. The above Mixture A was then added to the second Mixture B in the blender, with constant stirring for a period of one hour. The resulting combined mixtures formed a grease with a melting point > 500°F. which was equal in oxidation inhibition to the grease illustrated in Example I containing phenyl alpha naphthylamine as tested by ASTM D-942 method.

Each of the above-described grease formulations was found to exhibit satisfactory consistency to temperatures of at least 500°F.

From a comparison of the examples and data hereinbefore set forth, it will be apparent that the superiority of the properties of the greases of the present invention, over conventional-type greases, resides in the specific polyurea thickener employed. It will also be noted that, if so desired, it is possible to blend these improved greases with conventional-type greases for the purpose of upgrading the quality level of the latter. Furthermore, it is also within the scope of the invention to incorporate in these greases additional additives, as hereinbefore indicated, for the purpose of imparting antiwear, antirust and extreme pressure properties, if so desired.

While preferred embodiments of the novel grease compositions of the present invention, and the method for their preparation, have been described for the purpose of illustration, it will be understood that various modifications and adaptations thereof, which will be obvious to those skilled in the art, may be made without departing from the spirit of the invention.

I claim:

1. A grease composition comprising an oil of lubricating viscosity, as a vehicle, and a thickening amount of a polyurea, said polyurea having been prepared by reacting stoichiometrically at a temperature of from about 45° to about 250°F a monoamine, a diisocyanate

and a diamine having one amino group attached to each of two hydrocarbyl groups and said hydrocarbyl groups being separated by an oxygen or sulfur atom.

2. A grease composition as defined by claim 1 wherein said thickener is present in an amount from about 1 to about 40%, by weight.

3. A grease composition as defined by claim 1 wherein said thickener is present in an amount from about 2 to about 20%, by weight.

4. A grease composition as defined by claim 1 wherein said monoamine is octadecenyl amine.

5. A grease composition as defined by claim 1 wherein said monoamine is phenyl alpha naphthylamine.

6. A grease composition as defined by claim 1 wherein said diisocyanate is toluene diisocyanate.

7. A grease composition as defined by claim 1 wherein said diamine is a diamino diphenyl ether.

8. A grease composition as defined by claim 1 wherein said diamine is a diamino diphenyl sulfide.

9. A grease composition as defined by claim 1 wherein said diamine is 4, 4' - diamino diphenyl ether.

10. A grease composition as defined by claim 1 wherein said diamine is 4, 4' - diamino diphenyl sulfide.

11. A grease composition as defined by claim 1 wherein said reaction is conducted at a temperature from about 65°F. to about 150°F.

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