

1

3,766,071

DIURETHANE-DIUREA-THICKENED GREASE COMPOSITIONS

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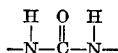
11 Claims

ABSTRACT OF THE DISCLOSURE

Grease compositions comprising an oleaginous base vehicle having incorporated therein a minor amount of a diurethane-diurea thickening agent have excellent high temperature dynamic lubricating properties. The diurethane-diurea thickeners are produced from dihydric alcohols, diisocyanates and monoamines.

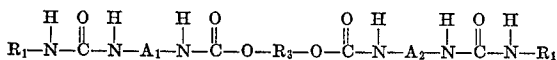
This invention relates to grease compositions and to thickening agents incorporated therein. More particularly, it relates to grease compositions comprising an oleaginous base vehicle gelled to grease consistency by the use of a class of novel diurethane-diurea thickening agents.

A continuing need exists in the art for the development of grease compositions capable of providing effective lubrication at high temperatures, e.g., temperatures of 300° F. to 400° F. and above. Numerous thickening agents have been proposed for use in such greases including soap base thickeners, inorganic clay thickeners and more recently, organic thickening agents. Examples of this latter category of thickeners include ureas, ureido compounds, aminoaryl diureas, triazines and the like. Such thickening agents are generally prepared by reacting one or more mono-, di-, or poly-amines with one or more mono-, di-, or poly-isocyanates which results in the formation of a compound having a plurality of urea linkages, (i.e.,



linkages). While thickeners of this type generally produce greases having dropping points significantly higher than metal soap-based greases, the urea-type organic thickening agents have frequently been found to have less than desirable properties in other important aspects, for example, shear stability, oxidation stability and high temperature bearing performance.

It has now been found that greases thickened with a minor amount of a diurethane-diurea compound do not exhibit the aforementioned deficiencies or at least to a considerably less degree, and therefore are eminently suitable for high temperature lubricating applications as well as for applications at lower temperatures. The diurethane-diurea thickening agents which impart the unique properties to the present compositions are those of the general formula:



wherein R₁ and R₂ are hydrocarbyl radicals having 4 to 30 carbon atoms, R₃ is an hydrocarbylene radical having from 2 to 12 carbon atoms, and A₁ and A₂ are aromatic hydrocarbylene radicals having from 6 to 18 carbon atoms.

The aforesaid thickening agents can be conveniently prepared by reacting separately, or in situ in the base vehicle, one or more diisocyanates with one or more dihydric alcohols and one or more monoamines as herein-after described.

The reaction of the alcohol component with the diiso-

2

cyanate component produces urethane linkages which are believed to be largely responsible for the unique characteristics of the present thickeners, not exhibited by previously proposed thickening agents.

Dihydric alcohol which can be used in the preparation of the diurethane-diurea thickeners of the invention include those having from 2 to 12, preferably from 2 to 6 carbon atoms. Examples of such alcohols include ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, include ethylene glycol, propylene glycol, 1,3-propanediol, 1,2-butanediol, 1,3-butanediol, 1,4-butanediol 1,5-pentanediol 1,6-hexanediol, 1,10-decanediol cyclohexane-1,4-dimethanol, diethylene glycol, triethylene glycol and aromatic dihydroxy compounds such as biphenyl, 4,4'-isopropylidene diphenyl and the like. Aliphatic dihydric alcohols are preferred, especially ethylene glycol and 1,3-propanediol, which have been found to form particularly advantageous thickeners.

Monoamines suitable for preparing the present thickening agents include primary or secondary amines having from 4 to 30 carbon atoms. Primary and secondary aliphatic amines having from 9 to 24 carbon atoms are especially preferred. Illustrative of suitable amines are butylamine, pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, octadecenylamine, eicosylamine, docosylamine tetracosylamine, benzylamine, cumylamine, naphthylamine and mixtures thereof. Greases gelled with thickening agents prepared with octadecylamine and octadecenylamine or mixtures thereof have been found to be particularly advantageous.

Diisocyanates which can be effectively reacted with the aforescribed dihydric alcohols and monoamines are preferably mono- or di-nuclear aromatic diisocyanates having a total of from 6 to 20 carbon atoms. Such diisocyanates include biphenylenediisocyanates, naphthylenediisocyanates and monphenylenediisocyanates including tolylenediisocyanate. Illustrative of such diisocyanates are 3,3-dimethylbiphenyl-4,4'-diisocyanate, diphenylmethane-4,4'-diisocyanate, 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate, 2,4-tolylenediisocyanate, 1,5-naphthylenediisocyanate and mixtures of 2,4- and 2,6-tolylenediisocyanates. 2,4-tolylenediisocyanate and mixtures of 2,4- and 2,6-tolylenediisocyanates are particularly preferred diisocyanate reactants.

The thickeners employed in the present compositions are advantageously prepared in two steps, either separately and then added to the base vehicle, or in situ employing the base vehicle as solvent. In a preferred method of preparation, the dihydric alcohol and diisocyanate components are reacted separately and the resulting reaction product then further reacted with the monoamine component in situ in the base vehicle. This method of preparation is described in further detail in Example I.

The molar proportions of dihydric alcohol, diisocyanate and monoamine involved in the reaction are 1/2:1:1 respectively.

The afore-described diurethane-diurea thickeners are employed in the present compositions in an amount sufficient to gel the oleaginous base vehicle to a grease consistency. The amount can vary, for example, from about 5 to 50% by weight of the total composition. Normally, however, thickener concentrations of 8 to 25% by weight are sufficient to impart the desired consistency to the inventive compositions.

A wide variety of lubricating oils may be employed as the base vehicle in the present compositions. Suitable base oils include mineral lubricating oils such as naphthenic base, paraffin base or mixed base oil having a viscosity in the range of from 50 SSU at 100° F. to 300 SSU at 210° F.; synthetic hydrocarbon oils such as oligomerized alpha-olefins and oils derived from coal products;

synthetic oils such as alkylene polymers, alkylene oxide-type polymers, polyalkene glycols, silicon polymers, polyethers, phosphate esters, dicarboxylic acid esters and pentaerythritol esters. The above oils may be used individually or in mixtures thereof, wherever miscible or made so by the use of solvents. Of the aforementioned base oils, mineral lubricating oils having viscosities of from about 400 to 700 SSU at 100° F. are especially preferred.

In addition to the diurethane-diurea thickeners, the present compositions can also contain anticorrosion additives such as disodium sebacate, glyceryl monooleate, sodium sulfonates, sodium nitrite, amino- and benzo-triazoles, and isostearamides or imidazolines of tetraethylenepentamine; oxidation inhibitors such as phenyl- α -naphthylamine, phenyl- β -naphthylamine, diphenylamines, phenothiazine, dithiocarbamates and various alkylated derivatives thereof; viscosity index improvers such as methacrylate polymers and copolymers; extreme pressure agents, and any other additive recognized in the art to perform a particular function or functions.

The following examples illustrate the method of preparation of the present compositions and their unique properties. It is to be understood, however, that these examples are presented for illustrative purposes only and that the invention in its broader aspects should not be limited thereto.

EXAMPLE I

69.6 g. of 2,4-tolylenediisocyanate was dissolved in 100 ml. of dry alcohol-free chloroform. To this solution was added 6.2 g. of ethylene glycol and the resulting mixture stirred at room temperature for four hours. 100 ml. of dry hexane was then added to the mixture and the stirring continued for an additional three hours, after which the mixture was allowed to stand for five hours. The product which crystallized from the reaction mixture was collected by filtration and recrystallized from a mixture of chloroform and hexane to yield a product having a melting point of 137–139° C. 10.5 g. of the recrystallized product was mixed with 188 g. of a paraffinic-base mineral oil having a viscosity of 70 SSU at 210° F. 27.0 g. of octadecylamine was then added and the mixture heated to 150° C. with stirring. The mixture was diluted with additional oil to the desired consistency and milled in a three-roll paint mill. The resulting grease contained 13.0% by weight thickener, had an ASTM dropping point of 430° F., as ASTM unworked penetration (P_0) of 280, and an ASTM worked penetration (P_{60}) of 302.

EXAMPLE II

The procedure of Example I was repeated, but in this case a mixture of 45% by weight octadecenylamine and 55% by weight octadecylamine was employed in place of the octadecylamine reactant used in Example I. The resulting grease contained 11% by weight thickening agent, had an ASTM dropping point of 430° F., and an ASTM worked penetration (P_{60}) of 275.

EXAMPLE III

The procedure of Example I was repeated, but in this case 1,3-propanediol was employed in place of ethylene glycol and the amounts of reactants were varied as indicated below.

696 g. of 2,4-tolylenediisocyanate was dissolved in 1 liter of chloroform to which was added 76 g. of 1,3-propanediol. 21.2 g. of the recrystallized reaction product was added to 190.9 g. of the same paraffinic-base mineral oil as employed in Example I. To this mixture was added 27.0 g. of the mixed octadecenylamine and octadecylamine reactant employed in Example II. Upon dilution and milling, a grease was obtained having a thickener concentration of 12% by weight, an ASTM unworked penetration (P_0) of 232, and a worked penetration (P_{60}) which was also 232.

EXAMPLE IV

A synthetic hydrocarbon based grease was prepared employing the present thickening agents by repeating the procedure of Example 1 using an oil comprising hydro-generated C_{16} to C_{70} oligomers of C_{2-10} normal alpha olefins in place of the mineral oil previously employed. The synthetic base oil used had a viscosity of 237 SSU at 100° F. and viscosity index of 128. The resulting grease contained 14.6% by weight thickener, had an ASTM unworked penetration (P_0) of 255, and ASTM worked penetration (P_{60}) of 280.

EXAMPLE V

In order to demonstrate the outstanding properties of the present compositions, a grease prepared in accordance with Example I containing 1.0% by weight of Irganox LO-6 (an antioxidant sold by Geigy Chemical Co.) was subjected to a series of tests as shown in Table I. For comparative purposes, a fully formulated, commercially available, tetra-urea thickened grease was also tested in accordance with the same procedures with the results as shown.

TABLE I

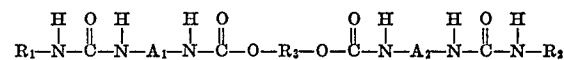
Test procedure	Grease 1	Commercial grease
Penetration (ASTMD 217):		
Unworked.....	280	275
60 strokes.....	302	305
100,000 strokes.....	382	430
Oxidation stability test (ASTMD 942 modif.):		
Pressure drop at 300° F., 48 hrs., p.s.i.....	13	37
ABEC bearing test (Fed. test mtd. No. 333):		
10,000 r.p.m., 350° F., hours to failure.....	508, 645	406
Wheel bearing test (ASTMD 1263): 275° F., percent loss.....	13.5	5.7

¹ Average of three runs. Samples for this test also contained 1% by weight sodium sebacate and 2% by weight glyceryl monooleate corrosion inhibitors.

The above data demonstrate the excellent shear stability, oxidation resistance and bearing performance properties of the present compositions. Grease 1 of the invention gelled with a diurethane-diurea thickening agent not only exhibited markedly superior resistance to oxidative degradation, but also surpassed the conventional urea-thickened grease in respect to bearing performance properties and shear stability. Thus, it is clearly evident that the diurethane-diurea structure of the thickening agents employed in the present compositions impart certain unique properties to the greases of the invention, not attainable by the use of previously proposed thickening agents.

I claim as my invention:

1. A grease composition consisting essentially of a major amount of an oleaginous base vehicle and in an amount sufficient to thicken the base vehicle to grease consistency, a diurethane-diurea compound having the formula:



wherein R_1 and R_2 are hydrocarbyl radicals having from 4 to 30 carbon atoms, R_3 is a hydrocarbylene radical having from 2 to 12 carbon atoms, and A_1 and A_2 are aromatic hydrocarbylene radicals having from 6 to 18 carbon atoms.

2. The composition of claim 1 wherein the diurethane-diurea compound is present in the amount of from 5 to 50% by weight.

3. The composition of claim 2 wherein R_3 is an alkylene radical having from 2 to 6 carbon atoms.

4. The composition of claim 3 wherein R_1 and R_2 are aliphatic hydrocarbyl radicals each having 9 to 24 carbon atoms.

5. The composition of claim 4 wherein the A_1 and A_2 radicals are derived from biphenylene, monophenylene or naphthylene diisocyanates.

5

6. The composition of claim 1 wherein the oleaginous base vehicle is a mineral lubricating oil having a viscosity of from 400 to 700 SSU at 100° F., and the diurethane-diurea compound is present in the amount of from 8 to 25%.

7. The composition of claim 6 wherein R₁ and R₂ are octadecyl, or octadecenyl groups.

8. The composition of claim 7 wherein R₃ is an ethylene group.

9. The composition of claim 7 wherein R₃ is a propylene group.

10. The composition of claim 8 wherein A₁ and A₂ are tolylene groups.

6

11. The composition of claim 6 wherein the oleaginous base vehicle is an oligomerized alpha-olefin lubricating oil.

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