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GREASE THICKENERS

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This invention relates to new thickening agents for greases and like compositions and to the compositions containing these agents. More particularly, it relates to aminoaryl diureas which impart extremely high dropping points to grease compositions in which they are employed.

It has become increasingly important that grease compositions be able to provide adequate lubrication at high temperatures, e.g., at temperatures in excess of 350° F. and particularly at ranges from 400° F. to considerably in excess of 500° F. The requirement for higher dropping points has resulted from the increased power in speeds of modern automotive and aircraft equipment. Contributing to the increased requirements is the expanded use of jet and turbine-type engines, which naturally operate at high temperatures, and the increased speed of ordinary engine and gear-train components. With the increase in speeds, there is a naturally concomitant rise in operating temperatures.

In the lubrication art, greases having relatively high dropping points have been produced from salts of certain fatty acids and other organic acids. For example, lithium salts of various fatty acids have been used to produce high dropping point greases. However, the metallic salts tend to contribute ions to the compositions that promote oxidation of the lubricants themselves and also promote corrosion of the metallic parts being bathed in the lubricant oils. Further, greases with dropping points higher than about 450° F. have been found to be quite difficult to produce with thickeners of this type.

More recently, ureido compounds, such as diureas, etc., have been employed to impart high temperature characteristics to grease compositions. Greases utilizing these types of thickeners have shown excellent high-temperature characteristics. However, it is desirable to provide lubricant compositions capable of providing adequate lubrication at even higher temperatures.

It has now been found that grease compositions displaying extremely high dropping points and thus capable of providing adequate lubrication at temperatures in excess of 450° F. can be produced by the incorporation in a lube oil of a minor amount of a monoamino-substituted aryl diurea. In accordance with this invention, the diureas are of the following general structure:

$$NH_2(R—NH)_xR—NHCONH—R_1—NHCONH—R_2$$

wherein R is a hydrocarbylene radical of from 1 to 15 carbon atoms, x is 0 to 6, the total number of carbon atoms in the R radicals is 2 to 15, R_1 is a divalent aromatic hydrocarbon radical of from 6 to 15 carbon atoms, and R_2 is a hydrocarbyl radical of from 1 to 32 carbon atoms.

The aminoaryl diureas of this invention can be prepared by reacting one mole of an aromatic diisocyanate with one mole of a primary or secondary monoamine and one mole of a polyamine.

Examples of primary amines which may be employed include methylamine, dimethylamine, isoamylamine, methyl-2-ethyl hexylamine, aniline, diphenylamine, octadecylamine, naphthylamine, cyclohexylmethylamine, piperidine, etc.

Examples of the aromatic radicals represented by R_1 in the general formula and derived from diisocyanates include ortho-phenylene, meta-phenylene, para-phenylene, tolylene, dimethylphenylene, naphthylene, methylene-bisphenyl, and biphenylene, etc.

Examples of the polyamines from which the radicals represented by R are derived include ethylene diamine, propylene diamine, trimethylene diamine; polyalkylene polyamines such as diethylene triamine, tetraethylene pentamine, etc.; heterocyclic amines, such as N-aminoethylpiperazine, etc.; and aromatic polyamines, such as benzidine, para-phenylene diamine, etc.

It is preferred that R be aromatic; for example, in a preferred species R is phenylene, X is O, R_1 is tolylene and R_2 is higher alkyl.

In the reaction, minor amounts of other polyureido compounds will be formed; however, the primary product will be the amino diurea.

The thickeners are preferably prepared in situ, that is, by mixing the amines and isocyanates together utilizing as a solvent a portion of the oil that is to serve as the lubricant base, and heating the mixture in a reaction vessel at temperatures from about 70° F. to 600° F. for a time sufficient to cause formation of the desired thickener. The mixture can then be immediately milled to the proper consistency.

The following examples illustrate the preparation of the amino diureas and the grease compositions of this invention. The examples are illustrative and are not intended to be limiting.

Example 1

12.0 g. (0.20 moles) of ethylene diamine, 60 g. (0.20 moles) of tallowamine (octadecylamine), and 10 g. of an aromatic amine oxidation inhibitor were heated together over a steam plate until the mixture became liquid. The mixture was then added to 34.8 g. of an 80:20 isomeric mixture of 2,4-, 2,6-, tolylene diisocyanate in 400 g. of paraffinic oil having a viscosity of 480 SUS at 100° F. The mixture was stirred in a high-speed blender and a grease formed immediately. This grease was further hand worked. Additional oil was added and the grease was milled in a high-pressure mill at about 8,000 p.s.i., yielding a smooth, buttery grease containing 11.8% by weight of the thickener, having an ASTM dropping point of 480° F. and an ASTM worked penetration of 304.

Example 2

The procedure of Example 1 was followed substituting 21.6 g. (0.20 moles) of meta-phenylene diamine for the ethylene diamine. A grease composition resulted which contained 10.8% by weight thickener, had an ASTM dropping point of 580° F. plus and a P_{60} of 285.

Lubricating oils which can be employed as base oils in the grease compositions of this invention include a wide variety of oils such as napthenic base, paraffin base, and mixed base mineral lubricating oils; synthetic oils, for example, polymers of propylene and butylene, etc.; propylene oxide polymers; dicarboxylic acid esters, for example, those prepared by the esterification of azelaic acid with 2-ethylhexyl alcohol; and silicon esters, such as tetraethyl silicate, hexa(4-methyl-2-pentoxy)-disiloxane, etc. The grease oils may also comprise mixtures of the aforementioned mineral and synthetic oils.

The grease compositions of this invention contain the amino diureas in amounts sufficient to thicken the oils to the consistency of greases. In general, amounts of from 5 to 50% by weight are sufficient; amounts from 10 to 30% by weight are preferred.

In order to demonstrate the superiority of grease compositions prepared using the amino diureas of this invention, grease compositions were prepared which contain non-substituted diureas corresponding to the amino diureas of Examples 1 and 2.

A comparison of the ASTM dropping points, ASTM Unworked Penetration (P_0), ASTM worked penetration (P_{60}), and the concentration of each thickener required

to thicken an oil to comparable consistency is listed in the following table.

The base oil employed in each case was a California paraffinic base lubricating oil having a viscosity of 480 SSU at 100° F.

	Thickener Type	Thickener 1:1:1 Mol Reaction Product of—			Thickener Weight Percent	P_0	P_{60}	ASTM Dropping Point, d.p. ° F.
		Diamine or Monamine	Monamine	Diisocyanate				
1	Amino diurea	Ethylene diamine	Tallowamine (C–18)	Tolylene diisocyanate 80:20 mixture as in Ex. 1.	11.8	262	304	480
2	Diruea	n-Propylamine	do	do	19.6	250	285	400
3	Amino diurea	Metaphenylenediamine	do	do	10.8	242	285	580+
4	Diurea	Aniline	do	do	17.5	278	310	540

It will be noted from the above table that the compositions containing the amino diureas require significantly less thickener at substantially the same consistency and yield a higher dropping point than the compositions containing the unsubstituted diureas. For example, a comparison of No. 1 and No. 2 shows that the amino diurea gives a d.p. of 480° F. and requires 11.8% thickener in contrast to a d.p. of 400° F. and 19.6% thickener for the corresponding diurea. Thus, due to the superior gelling action of the present thickeners, grease compositions having extremely high dropping points can be prepared using relatively less thickening agents than with the diurea compounds.

This invention thus describes grease compositions with high dropping points which are particularly suitable for use in applications wherein high temperatures are encountered. Typical applications are steel mill motors, transfer table bearings, paper mill roller bearings, etc. In heavy moving equipment and heavy-duty trucks, braking produces extremely high temperatures in wheel bearings and the compositions of this invention are especially suitable for lubricating these points.

In addition to the thickening agents heretofore described, the grease compositions may contain other grease thickening agents, oxidation inhibitors, viscosity-improving agents, dyes, etc.

While in the presentation of this invention numerous examples have been given and the invention described with respect to certain embodiments, it is not so limited; and it is to be understood that variations and modifications obvious to those skilled in the art may be made without departing from the scope or the spirit of the invention, which is only to be limited by the appended claims.

I claim:

1. A grease composition comprising an oil of lubricating viscosity and, in an amount sufficient to thicken said oil to the consistency of a grease, an amino aryl diurea of the general formula:

$$NH_2(R—NH)_xR—NHCONH—R_1—NHCONH—R_2$$

wherein R is a hydrocarbylene radical of 1 to 15 carbon atoms, x is 0 to 6, the total number of carbon atoms in the R radicals is from 2 to 15, R_1 is a divalent aromatic hydrocarbon radical of from 6 to 14 carbon atoms and R_2 is a hydrocarbyl radical of 1 to 32 carbon atoms.

2. The grease composition of claim **1** wherein R is an aromatic hydrocarbon radical of 6 to 15 carbon atoms.

3. The grease composition of claim **1**, wherein the amino diurea is present in the amount from 5% to 50% by weight.

4. The grease composition of claim **3** wherein the amino diurea is present in an amount from 10% to 30% by weight.

5. An amino aryl diurea of the general formula:

$$NH_2(R—NH)_xR—NHCONH—R_1—NHCONH—R_2$$

wherein R is a hydrocarbylene radical of 1 to 15 carbon atoms, x is 0 to 6, the total number of carbon atoms in the R radicals is from 2 to 15, R_1 is a divalent artomatic hydrocarbon radical of from 6 to 14 carbon atoms and R_2 is a hydrocarbyl radical of 1 to 32 carbon atoms.

6. The aminodiurea of claim **5** wherein R is an aromatic hydrocarbon radical of from 6 to 15 carbon atoms.

7. The aminodiurea of claim **6** wherein R is phenylene, R_1 is tolylene and R_2 is alkyl.

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