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POLYUREA THICKENED GREASE

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U.S. Cl. 252—51.5 A 13 Claims

ABSTRACT OF THE DISCLOSURE

Improved greases, having wide-temperature utility and good oxidation stability, are provided comprising a hydrogenated olefin polymer vehicle and a grease-forming quantity of a thickening agent comprising a polyurea.

BACKGROUND OF THE INVENTION

(1) Field of the invention

This invention relates to grease compositions and, in one of its aspects, relates to improved 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 grease compositions which contain a combination of certain hydrogenated olefin polymer vehicles and polyurea thickening agents, 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, the use of olefin polymers has heretofore been suggested as vehicles for grease formulations. It has been found, however, that while grease containing olefin polymer vehicles can perform satisfactorily at relatively high temperature ranges, while exhibiting a minimum effect with respect to deterioration of sealant materials, nevertheless such greases have not been found to exhibit a concomitant good oxidation stability. Thus, the ability to prepare a grease formulation in which each of the aforementioned characteristics is present, viz. reduced deterioration of sealant materials and good high temperature performance is highly desirable from a commercial standpoint. Insofar as thickening agents are concerned, most high temperature greases have been formulated with fatty acid salts. These salts have provided relatively high melting point compositions, e.g., lithium soaps of fatty acids. It has been found, however, that these fatty acid salts tend to catalyze the oxidation of the lubricant. At relatively higher 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 lubricants 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, reduced deterioration effect on sealants and relatively high dropping points, can be

produced by employing, as the lubricating vehicle, a hydrogenated olefin polymer in which the polymer has been prepared from olefins having from about 6 to about 12 carbon atoms per molecule, and by employing, as the thickening agent, a polyurea having the formula

$$R'-NH-\left(\begin{matrix}O\\ \|\\ C\end{matrix}NH-R'''NHCNH-R-NH-\right)_x\begin{matrix}O\\ \|\\ C\end{matrix}NH-R'''NH\begin{matrix}O\\ \|\\ C\end{matrix}NH-R''$$

wherein x is a number having a value from 1 to 3, R, R′ and R″ are hydrocarbon radicals containing from 1 to 30 carbon atoms, and R‴ is a hydrocarbon radical containing from 2 to 30 carbon atoms. In this respect, as also more fully hereinafter described, it has been found that if the hydrogenated olefin polymer is prepared from olefins having less than about 6 carbon atoms per molecule, the resulting grease composition will deteriorate rapidly at elevated temperatures due to loss of vehicle by volatilization. On the other hand, it is found that if the hydrogenated olefin polymer is prepared from olefins having more than 12 carbon atoms per molecule, the resulting grease composition will not possess suitable low torque values at relatively low temperatures. The presence of the above-described polyurea thickening agent makes possible the formulation of greases which, in general, exhibit dropping points in excess of 400° F. and more usually in excess of 450° F.

The preparation of the lubricating vehicles of the improved greases of the present invention can be carried out in accordance with the process described in U.S. Pat. 3,514,401. In one aspect of the invention, the preparation of the lubricating vehicle may be carried out, in general, by distilling a liquid polymerized normal alpha-monoolefin synthetic lubricant to obtain a fraction which contains dimer, and a residual fraction which is essentially free from dimer, and then completely saturating the residual fraction by hydrogenation under catalytic hydrogenation conditions. Thus, the thermally polymerized olefins that are utilizable in producing the synthetic lubricating vehicle in the improved greases of the present invention include, for example, 1-hexene, 1-heptene, 1-octene, 1-nonene, 1-decene, 1-undecene and 1-dodecene. The olefin reactant can be substantially pure normal alpha-monoolefins, mixtures of olefins and/or paraffins containing substantial amounts of normal alpha-monoolefins, having between about 6 and about 12 carbon atoms per molecule.

The aforementioned polymerization procedure can, in general, be carried out over a wide temperature range. More specifically, when catalytic polymerization is to be conducted, polymerization temperatures from about 0° F. to about 450° F. are preferably employed. When thermal polymerization is to be conducted, polymerization temperatures from about 500° F. to about 700° F. are preferably employed. The polymerization period may vary from about 1 hour to as high as about 20 hours, or longer. The above-indicated polymerization procedures are more fully described in U.S. Pat. 3,149,178.

The aforementioned normal alpha-monoolefins, employed for producing the polymer oil vehicles of the greases of the present invention, may be polymerized in the presence of ditertiary alkyl peroxide catalysts, such as are described in U.S. Pat. 2,937,129. Particularly preferred are the di-tertiary lower alkyl peroxides as catalysts. Of these, the most outstanding catalyst is di-tertiary butyl peroxide. The amount of peroxide catalyst employed is from about 0.01 to about 0.3 mole per mole of normal alpha-monoolefin reactant. The temperature employed is the activation temperature of the peroxide catalyst, and can vary from about 100° C. to about 200° C. In general the reaction time will vary from about one to about six hours.

The polymerized normal alpha-monoolefin oils uti-

lizable in obtaining the lubricating vehicles of the present invention can also be readily prepared in the presence of Friedel-Crafts catalysts under relatively mild conditions, as described in U.S. Pat. 3,149,178. To a great extent, the choice of catalyst and of reaction conditions can be made in order to produce polymer lubricants of desired viscosity.

The polymerization of 1-decene (or its equivalent), as a representative olefin within the aforementioned C_6–C_{12} olefin polymer range, with $AlCl_3$ catalyst at temperatures below about 70° C. will produce lubricating oils having a kinematic viscosity of 25–45 centistokes at 210° F. In general, such oils are produced by gradually mixing the olefin with 1–3 weight percent (based on total olefin charge) of $AlCl_3$ over a period of from about 2 to about 6 hours. A preferable procedure involves an incremental addition of olefin to a slurry of catalyst in an inert hydrocarbon, e.g., n-heptane. Polymerization of 1-decene (or its equivalent) in the presence of $AlCl_3$ at temperatures of 100–200° C. produces oils of about 12 centistokes kinematic viscosity, measured at 210° F. A feasible method of operations is to add $AlCl_3$ rapidly to the olefin, permitting the temperature to rise suddenly to 150° C. or higher. Under these conditions polymerization occurs readily to the extent that most of the olefin is consumed before the reaction mixture reaches the boiling point of decene.

In a preferred modification, when a BF_3-catalyzed polymerization procedure is carried out, pressure or a catalyst promoter is necessary in order to produce synthetic lubricants of high quality. Suitable promoters include BF_3-decanol complex, decanol, acetic acid, and acetic acid-BF_3 complex. In general, the polymerization is carried out at temperatures below about 60° C. for a total reaction time in the order of about 2 to about 4 hours. When BF_3 polymerization is carried out under pressure, a reaction time of 2 to 4 hours is employed. The pressure, measured in terms of BF_3 pressure, can vary between about 10 pounds per square inch gauge and about 500 pounds per square inch gauge, or higher. In both types of BF_3 catalyzed polymerization of 1-decene (or its equivalent), polymer oils are produced having kinematic viscosities of about 3–12 centistokes at 210° F.

It will be understood, that the term "polymerized normal alpha-monoolefin synthetic lubricant" as used herein, is intended to denote synthetic lubricants improved by polymerizing the aforementioned normal alpha-monoolefins, having from about 6 to about 12 carbon atoms per molecule, either thermally or catalytically, in the presence of a di-tertiary alkyl peroxide or in the presence of a Friedel-Crafts catalyst, which includes boron trifluoride and aluminum chloride under mild polymerization conditions, as previously indicated. In addition, as contemplated herein, the aforementioned term is intended to exclude polymers which are produced in the presence of other peroxides, such as diacyl peroxides, which polymers contain structural elements of the peroxy catalyst. It has been found, in this respect, that polymers produced in the presence of a di-tertiary alkyl peroxide do not contain structural elements of the peroxide catalyst. In this respect, the latter polymers are the substantial equivalent of thermally polymerized olefins. As previously indicated, when Friedel-Crafts catalysts are employed, the polymerization conditions must be relatively mild.

As previously indicated, the polymerized normal alpha-monoolefin synthetic lubricant, to be employed as a vehicle in the novel grease compositions of the present invention, is subjected to saturation by hydrogenation. A more detailed description for conducting such hydrogenation will be found in U.S. Pat. 3,149,178, the subject matter of which is incorporated, in its entirety, in this application, by reference. In general, the hydrogenation treatment, as previously indicated, is carried out under catalytic hydrogenation conditions, effective to produce the desired hydrogenated polymer wherein the polymer, as previously indicated, was prepared from an olefin having from about 6 to about 12 carbon atoms per molecule. Insofar as the aforementioned polymerization technique, itself, is concerned, these procedures are more fully described in U.S. Pat. 2,937,129 and U.S. Pat. 3,149,178, the subject matter of which is incorporated, in its entirety, in this application, by reference.

The preparation of the polyurea thickening agents of the improved greases of the present invention can be carried out in accordance with the process described in U.S. Pat. 3,243,372.

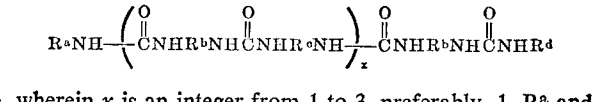
For many purposes polyureas having the following formula are particularly useful in the preparation of the greases of this invention.



wherein x is an integer of from 1 to 3, R and R''' may be the same or different and are hydrocarbylene of from 2 to 30 carbon atoms (hydrocarbylene is a divalent organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic or aromatic or combinations thereof, e.g., alkaryl, aralkyl, etc., having its two free valences on different carbon atoms); R' and R'' may be the same or different and are hydrocarbyl of from 1 to 30 carbon atoms (hydrocarbyl is a monovalent organic radical composed solely of carbon and hydrogen which may be aliphatic, aromatic, or alicyclic or combinations thereof, e.g., aralkyl alkaryl, etc.).

The polyureas of the above formula are readily prepared by mixing diisocyanates and diamines with monoisocyanates or monoamines in the proper proportions to form the desired polyurea. The greases thickened with the polyureas are useful at temperatures from about −100° F. to 500° F. and remain unctuous after long use, not, becoming hard or brittle. The grease compositions thus formed are extremely resistant to emulsification in water.

The preferred greases are thickened by compositions of the following formula:



wherein x is an integer from 1 to 3, preferably, 1, R^a and R^d are the same or different and are hydrocarbyl of from 5 to 28 carbon atoms, preferably of from 6 to 25 carbon atoms and R^b and R^c may be the same or different and will be hydrocarbylene of from 2 to 26 carbon atoms, more usually of from 2 to 18 carbon atoms. It is further preferred that in the tetraureas, the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30 and the sum of the carbon atoms of R^b and R^c is in the range of 12 to 40.

The monoamine or monoisocyanate used in the formation of the polyurea will form the terminal end group. As already indicated these terminal end groups will be of from 1 to 30 carbon atoms, but are preferably of from 5 to 28 carbon atoms and more desirably of from 6 to 25 carbon atoms. As already indicated, the substituent on the nitrogen is a hydrocarbon radical, which may be aliphatic, aromatic or alicyclic, may be aliphatically saturated or unsaturated, or may be combinations of the various types of hydrocarbon radicals.

Illustrative of various monoamines are pentylamine, hexylamine, heptylamine, octylamine, decylamine, dodecylamine, tetradecylamine, hexadecylamine, octadecylamine, eicosylamine, dodecenylamine, hexadecenylamine, octadecenylamine, octadecadienylamine, abietylamine, aniline, toluidine, naphthylamine, cumylamine, bornylamine, fenchylamine, tert.-butyl aniline, benzylamine, beta-phenethylamine, etc.

Illustrative of monoisocyanates are hexylisocyanate, decylisocyanate, dodecylisocyanate, tetradecylisocyanate, hexadecylisocyanate, phenylisocyanate, cyclohexyliso-

cyanate, tolueneisocyanate, xyleneisocyanate, cumeneisocyanate, abietylisocyanate, cyclooctylisocyanate, etc.

The preferred aromatic terminal end groups are those of from 6 to 12 carbon atoms. The preferred aliphatic terminal end groups are those of from 10 to 20 carbon atoms.

The diamines and diisocyanates which form the internal hydrocarbon bridges between the ureas are, as indicated, of from 2 to 30 carbon atoms, preferably from 2 to 26 carbon atoms and more desirably of from 2 to 18 carbon atoms.

Illustrative of various diamines are ethylenediamine, propanediamine, butanediamine, hexanediamine, dodecanediamine, octanediamine, hexadecanediamine, cyclohexanediamine, cyclooctanediamine, phenylenediamine, toluenediamine, xylenediamine, dianilinemethane, ditoluidinemethane, bisaniline, bistoluidine, etc.

Illustrative of diisocyanates are hexanediisocyanate, decanediisocyanate, octadecanediisocyanate, phenylenediisocyanate, toluenediisocyante, bis(diphenylisocyanate), methylene bis(phenylisocyanate), etc.

The aromatic hydrocarbylene or bridging groups will generally be of from about 6 to 18 carbon atoms. The aliphatic hydrocarbylene or bridging groups will generally be of from about 2 to 10 carbon atoms.

The polyurea grease thickeners have a polar/nonpolar balance. That is, there will be at least about 6 carbon atoms per urea group and more usually about 8 carbon atoms per urea group, but fewer than 20 carbon atoms per urea group and more usually fewer than 16 carbon atoms per urea group.

The tetraureas used in this invention have the following formula:



wherein R^a, R^b, R^c and R^d are as defined previously.

The quantity of polyurea employed is in such amount as is sufficient to thicken the hydrogenated olefin polymer to the desired grease consistency. In general, the amount of thickener may, for most practical purposes, range from about 1 to about 50% and preferably from about 5 to about 25%, by weight.

As indicated when preparing the polyureas, the monoamines or isocyanates are merely brought together with the diisocyanates and diamines in the proper proportion, preferably in the presence of an inert diluent. Usually, the vehicle to be thickened or gelled will be the preferred diluent. It is not necessary that the diluent be a solvent for all the reactants. With a heterogeneous system, efficient stirring helps to insure smooth reaction between the various reactants.

The temperature of the reaction will generally vary from about 20° C. to about 100° C., more usually from about 20° C. to 75° C. The reaction itself is exothermic and by starting at room temperature, elevated temperatures are obtained. However, external heating or cooling may be desirable. The concentration of polyurea in the final product may vary as hereinbefore indicated from about 1 to 50 weight percent, depending on the various reactants, the particular product desired, etc.

DESCRIPTION OF SPECIFIC EMBODIMENTS

The following data and examples will serve to illustrate the improved grease compositions of the present invention and their properties, with the parts recorded by weight. In order to illustrate the markedly improved results obtained by employing, as the vehicle of the novel grease compositions, a hydrogenated olefin polymer, prepared from olefins having from about 6 to about 12 carbon atoms per molecule, a series of grease compositions were prepared for comparative purposes. In each of these grease compositions tetraurea was employed as the thickening agent. This thickening agent was prepared in accordance with the following procedure:

A mixture of 3.6 grams of ethylenediamine, 30 grams of Armeen T (a commercial octadecenyl amine) and 7 grams of an antioxidant was heated at a temperature of 140° F. for a period of 10 minutes, to form a homogeneous solution. This solution was then added to the hereinafter specified hydrogenated olefin polymer oil vehicles and containing 17.4 grams of an isocyanate (an 80/20 mixture of 2,4-toluenediisocyanate and 2,6-toluenediisocyanate) with vigorous agitation in a blender. A gel was formed and the resulting grease composition was heated to 300° F. and then removed from the blender, hand mixed, and milled.

In the following table polyurea thickeners were employed in the respective indicated oil vehicles in Examples 1, 2 and 3. In Examples 4 and 5 lithium soaps and a non-soap thickener, respectively, were employed. The respective grease compositions as shown in the table were formulated with hydrogenated olefin oils including C_5, C_{10} and C_{12} monomers. The preparation of these olefin polymer vehicles is more fully set forth in the aforementioned U.S. Pat. 3,514,401. The individual finished grease formulations were then subjected to standard evaluation tests, as indicated.

TABLE

Example number	1	2	3	4	5
Formulation, percent by weight:					
Polyurea thickener	13	13	13		
Lithium soaps				11	
Non-soap thickener (Baragel clay and stabilizer)					10.03
Hydrogenated olefin polymer oil, percent by weight:					
Prepared form C_5 monomer [a]	87				
Prepared from C_{10} monomer [b]		87		89	89.7
Prepared from C_{12} monomer [c]			87		
Grease properties:					
(1) ASTM D1478—Low temperature starting torque at −40° F., gm. cm	1,327	649	4,720		
(2) ASTM D972—High temperature evaporaton loss at 350° F., 22 hrs., percent weight	39.2	5.6	4.4		
(3) Fed. std. 791, Method 331—High temp. performance endurance life at 350° F., hrs		500		<200	<200

[a] K.v. at 100° F.=29.5 cs.
[b] K.v. at 100° F.=31.9 cs.
[c] K.v. at 100° F.=49.3 cs.

As will be seen from the foregoing table, the grease of Example 2, employing the C_{10} hydrogenated olefin polymer vehicle, exhibited the lowest starting torque at −40° F. and also a very satisfactory evaporation loss of 5.6% at 350° F. These values are compared with maximum readings for an acceptable wide temperature range grease of 2000 gm. cm. maximum torque at −40° F. and 10% maximum evaporation loss at 350° F. On a comparative basis, it will be noted that the grease of Example 1, employing the C_5 hydrogenated olefin polymer vehicle, was found to exhibit an unacceptably high temperature range reading. The grease of Example 3, employing the C_{12} hydrogenated olefin polymer vehicle, exhibited an unsatisfactory reading at low temperature, although the amount of evaporation loss was satisfactory.

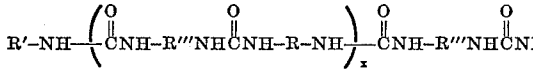
On a further comparative basis, the improved oxidation stability of the polyurea thickener, i.e., the above-described prepared tetraurea, at relatively high temperatures is demonstrated by the High Temperature Performance (Fed. Std. 791, Method 331) Endurance Life at 350° F. Example 2, having the polyurea thickener in the preferred C_{10} hydrogenated olefin polymer oil, is compared with this same oil vehicle, employing a lithium soap thickener in Example 4 and also compared with a non-soap thickener (Baragel clay and stabilizer) in Example 5. Thus it will be noted that the C_{10} hydrogenated polymer oil in combination with the above-described polyurea thickener exhibits an Endurance Life at 350° F. of 500 hours as compared with an Endurance Life of less than 200 hours with the lithium soap and clay thickeners of Examples 4 and 5.

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 which comprise an effective combination of the specified hydrogenated olefin polymer vehicles and polyurea thickening agents, over conventional-type greases, which do not employ the aforementioned combination of vehicles and thickeners, has been established. If so desired, other illustrative polyurea thickeners of the present invention may be formulated to include hexaurea and octaurea, for example, which can also be prepared in accordance with the disclosure of the aforementioned U.S. Pat. 3,243,372. 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 for the purpose of imparting anti-wear, anti-rust 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 purposes 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.

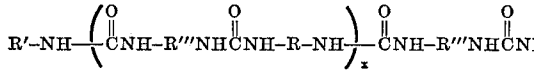
I claim:

1. A grease composition comprising a hydrogenated olefin polymer vehicle, said polymer having been prepared from an olefin having from about 6 to about 12 carbon atoms per molecule, and a grease-forming quantity of a thickening agent comprising a polyurea having the following formula:



wherein x is a number having a value from 1 to 3, R, R′ and R″ are hydrocarbon radicals containing from 1 to 30 carbon atoms, and R‴ is a hydrocarbon radical containing from 2 to 30 carbon atoms.

2. A grease composition as defined in claim **1** wherein the polyurea thickener has the following formula:



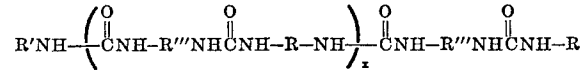
wherein x is a number having a value from 1 to 3, R′ and R″ are hydrocarbon radicals containing from 1 to 30 carbon atoms, and R and R‴ are hydrocarbon radicals containing from 2 to 30 carbon atoms.

3. A grease composition as defined in claim **1** wherein the polyurea thickener is present in an amount from about 1 to about 50 percent, by weight.

4. A grease composition as defined in claim **1** wherein the polyurea thickener is present in an amount from about 5 to about 25 percent, by weight.

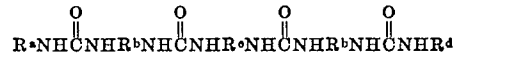
5. A grease composition as defined in claim **1** wherein the ratio of carbon atoms in the number of urea groups in the thickener is at least 6:1.

6. A grease composition as defined in claim **1** wherein the polyurea thickener has the following formula:



wherein x is a number having a value of from 1 to 3, R′ and R″ are hydrocarbon radicals of from 5 to 28 carbon atoms, and R‴ and R are hydrocarbon radicals of from 2 to 26 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least about 6:1.

7. A grease composition as defined in claim **1** wherein the polyurea thickener has the following formula:



wherein R^a and R^d are hydrocarbyl of from 5 to 28 carbon atoms, and R^b and R^c are hydrocarbylene of from 2 to 26 carbon atoms, wherein the ratio of carbon atoms to the number of urea groups is at least about 6:1.

8. A grease composition as defined in claim **7** wherein R^a and R^d are from 6 to 25 carbon atoms and R^b and R^c are from 2 to 18 carbon atoms.

9. A grease composition as defined in claim **7** wherein R^2 and R^d are aliphatic of from 10 to 20 carbon atoms.

10. A grease composition as defined in claim **7** wherein R^a is an aliphatic radical of from 10 to 20 carbon atoms and R^d is an aryl radical of from 6 to 12 carbon atoms.

11. A grease composition as defined in claim **7** wherein the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30.

12. A grease composition as defined in claim **7** wherein the sum of the carbon atoms of R^a and R^d is in the range of 10 to 30 and the sum of the carbon atoms of all of the R^b and R^c groups is in the range of 12 to 40.

13. A grease composition as defined in claim **1** wherein the vehicle comprises hydrogenated polydecene and the thickening agent comprises polytetraurea.

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3,514,401	5/1970	Armstrong et al.	252—28
3,243,372	3/1966	Dreher et al.	252—51.5

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