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ARYL UREA-THICKENED GREASES

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13 Claims. (Cl. 252—49.6)

The present invention relates to novel lubricant greases and to the method of preparing same. More particularly, it relates to novel greases comprising a lubricant vehicle thickened with certain high melting aromatic ureido compounds. Greases of this type, particularly those wherein the lubricant vehicle comprises a silicone polymer oil, have demonstrated exceptional stability and lubricity at elevated temperatures.

As lubricants are required to perform at higher and higher temperatures because of increased speeds of engines and machines, the advent of jet propulsion, atomic energy as a source of power, etc., it has become increasingly difficult to prepare greases fulfilling the requirements of such lubricants. In attempting to provide such greases, the art has progressed from the use of petroleum lubricant vehicles thickened with metal soaps of long chain fatty acids, e. g. lithium hydroxy-stearate, to more thermally stable synthetic lubricating oils such as the aliphatic diesters of dicarboxylic acids, silicone polymers, etc., thickened with such soaps or inorganic materials such as silica gels. The progress of thickener research has not in general, however, kept pace with the development of lubricant vehicles. And at temperatures as high as 400° to 450° F. there are few if any greases available which will retain their consistency and lubricity for any substantial period of time.

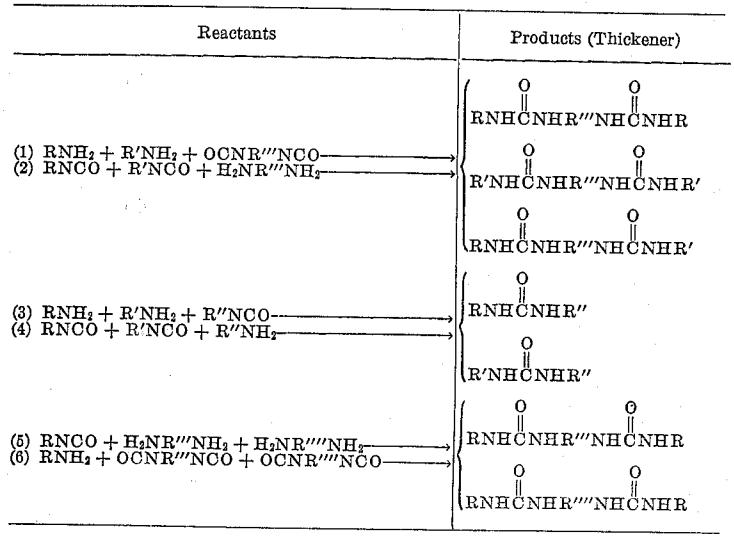
In recent years various synthetic lubricant vehicles, e. g. the silicones, fluorocarbons, etc., have been found to be potentially valuable for use in greases employed at very high temperatures because of their thermal stability and relatively low volatility. Unless, however, a thickener having substantially the same degree of thermal stability is available to produce a grease from such an oil, they are of little use.

In our co-pending application for Letters Patent Serial No. 318,321 filed November 1, 1952 (of which the present application is a Continuation in Part) it is disclosed that certain very high melting aromatic ureas, di-ureas, amides, and di-amides, all of which contain at least one



radical, wherein R is an aryl radical, and which are referred to broadly as arylcarbamyl compounds, may be employed to thicken silicone polymer oils, as well as other known lubricant vehicles, to produce greases which are stable and display excellent lubricant properties at high temperatures. Whereas silicone polymer oils are particularly preferred for use in greases employed at temperatures as high as about 450° F., other lubricant vehicles, either natural or synthetic, may also be thickened with these materials to produce greases of particular utility between about 250° F. and about 400° F.

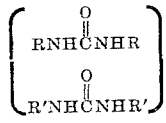
We have discovered that greases prepared with thickeners comprising certain mixtures of at least two different aryl substituted ureas and/or diureas may be prepared with substantially less thickener for a grease of given consistency. Thus, in accordance with the present invention, mixtures of aryl substituted ureas are prepared by reacting, preferably in the lubricant vehicle (in situ), (1) at least two different aryl isocyanates with at least one aryl amine (mono- or di-amine) or (2) at least two different aryl monoamines with at least one aryl isocyanate (mono- or diisocyanate). Thus, in accordance herewith, we may prepare novel greases comprising an oleaginous vehicle thickened with mixtures of aryl substituted ureas prepared, for example, as follows:



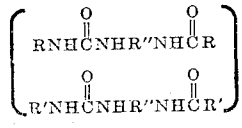
wherein R and R' are different aryl or substituted aryl radicals. R'' represents an aryl, alkylaryl, substituted aryl or substituted alkylaryl radical which may be the same as or different from R and/or R'. These radicals may differ in that one may be unsubstituted and the other substituted, or both may be substituted but by different functional groups, e. g. by groups such as nitro-, halo-, alkyl, sulfonyl, carboxyl, hydroxyl, amino, sulfonamido, etc. or one may be monocyclic and the other polycyclic, e. g. phenyl, diphenyl, naphthyl, etc. R''' and R'''' are different divalent arylene radicals, e. g. phenylene, biphenylene, naphthylene, etc. which may be substituted by such hydrocarbon or functional groups as are above enumerated with respect to R, R', and R''. Instead of the reactants being limited to two amines and one isocyanate or vice versa, as shown, the reactants may comprise a plurality of both amines and isocyanates and there may be

both mono- and di- substituted compounds of each class present in a given reaction. Thus, for example, an especially outstanding thickener may be prepared by reacting 4-biphenylyl isocyanate with p-phenylene diamine and benzidine, e. g. in a molar ratio of 4:1:1 respectively. To such a reaction mixture there may be added one or more additional isocyanates, e. g. p-chlorophenyl isocyanate. Examples of other reactants and the products obtainable therefrom will be hereinafter set forth.

The above six reactions demonstrate the manner in which mixtures of arylureas useful in accordance herewith are preferably prepared. And, as indicated, it is preferred that such reactions be carried out in the lubricant vehicle itself. However, mixtures of ureas may likewise be prepared by reacting an individual isocyanate with an individual amine and then combining the resulting aryl substituted urea with one or more differently substituted ureas individually prepared. The thus prepared mixture may then be milled with a lubricant vehicle to produce a grease in accordance herewith. Mixtures of ureas prepared in this manner may be as shown above or they may comprise compounds having the formula:



or



wherein R, R' and R'' represent hydrocarbon radicals of the type defined above.

It is a primary object of the present invention to provide lubricant greases which are stable and give excellent lubrication at elevated temperatures. A further object is to provide a readily producible series of greases embodying a novel class of thickening agents capable of yielding lubricants particularly suitable for use at temperatures of from about 250° F. to about 450° F. A particular object of the present invention is to provide greases which are effective lubricants at temperatures as high as about 450° F. for substantial periods of time. These and additional objects will be apparent from the following detailed description.

In accordance herewith, lubricating vehicles such as silicone polymer oils, mineral lubricating oils derived from petroleum, synthetic lubricating oils such as polyalkylene glycols and their derivatives, high molecular weight esters of dicarboxylic acids, etc. and preferably the silicone polymer oils may be thickened to grease consistency by the addition thereto of from 5 to 70% and preferably from about 10 to about 50% of such mixtures of aryl substituted ureas.

The possibilities of different compounds which may be produced by employing a reaction mixture of the type above set forth is very large and, of course, dependent upon the number and types of aryl and arylene groups in the reactants employed. For purposes of illustration, therefore, there are hereinafter set forth a few of the various products which may be obtained from the reaction of such compounds as for example (1) the reaction of phenyl isocyanate, p-tolyl isocyanate and p-aminobenzoic acid result in the formation of 1-(p-carboxyphenyl)-3-(p-tolyl)-urea and p-carboxy-s-diphenyl-urea. From the reaction of several amino compounds with an isocyanate,

for example, the reaction of aniline, p-toluidine and p-carboxyphenyl isocyanate would result in the same products as set forth above when employing two isocyanates and amino-benzoic acid. From the reaction of two isocyanates with a diamine compound, there are three expected products. For example, from the reaction of p-chlorophenyl isocyanate and p-tolyl isocyanate with benzidine, are produced 4,4'-bis-[3-(p-chlorophenyl)-ureido]-biphenyl, 4,4'-bis-[3-(p-tolyl)-ureido]-biphenyl, and 4-[3-(p-chlorophenyl)-ureido]-4'-[3 - (p - tolyl) - ureido]-biphenyl.

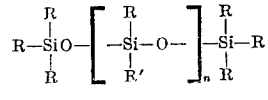
From the above empirical formulae, reaction equations, and the specific examples set forth, it will be apparent to one skilled in the art that the products obtainable from a given set of reactants may readily be determined. Thus, without any intention of limiting the present invention to the following specific examples, there will be set forth typical aryl isocyanates and amines as well as bifunctional isocyanates and amines containing a bivalent aryl radical, which may be employed in accordance herewith.

Examples of suitable aryl isocyanates which may be employed in accordance herewith are p-chlorophenyl isocyanate, p-tolyl isocyanate, toluene diisocyanate, p-biphenylyl isocyanate (p-xenyl isocyanate), phenyl isocyanate, p-carboxyphenyl isocyanate, α-naphthyl isocyanate, p-p'-diisocyanato-biphenyl, 1,4-diisocyanato-benzene, 2-5-dichlorophenyl isocyanate, o-biphenylyl isocyanate (o-xenyl isocyanate), o-chlorophenyl isocyanate, p,p'-diisocyanatodiphenylmethane, etc.

Example of suitable amines are p-aminobenzoic acid, p-amino-biphenyl, benzidine, dianisidine, o-tolidine, p-aminophenol, p-amino-benzonitrile, p-phenylene diamine, m-phenylene diamine, o-phenylene diamine, 2,5-dichloro-aniline, aniline, p-toluidine, etc.

As indicated above, these isocyanates and amines may be reacted in various combinations and as long as at least two isocyanates and at least one amine or vice versa are present, the thickener resulting from the reaction of these compounds will comprise a mixture of arylureas. It is preferred to have present during the reaction a bifunctional reactant, e. g. a diamine or a diisocyanate, but it is not necessary. On the other hand, more than one bifunctional material may be employed with a resulting increase in the number of possible products obtained.

The silicone polymer oils which may be employed in accordance with the present invention are those falling substantially within the lubricating oil viscosity range. In general, such oils have the following unit structure:



wherein R and R' represent substituted or unsubstitued alkyl, aryl, alkylaryl, arylalkyl or cycloalkyl radicals. Such compounds may be produced by well-known methods, e. g. the hydrolysis of dialkyldichlorosilanes or dialkyldiethoxysilanes with a suitable chain stopper, e. g. a tri-substituted mono-chlorosilane. For purposes of the present invention, those polymers which are high boiling liquids within the lubricating oil viscosity range are suitable, these generally possessing a viscosity at 100° F. which is within the range of from about 25 to about 3500 S. S. U. It is preferred, for purposes hereof, to employ such oils as have a viscosity at 100° F. of from about 100 S. S. U. to about 1250 S. S. U. Such products are generally colorless and inert, have a very low volatility and undergo relatively slight change in viscosity for a given change in temperature. Relatively common oils of this type are dimethylsilicone polymer, phenylmethyl-silicone polymer, chlorophenylmethylsilicone polymer,

etc., it being preferred to employ the phenylmethylsilicone polymer in accordance herewith. Methods of preparing such compounds are taught in numerous patents, e. g. U. S. 2,410,346, U. S. 2,456,496, and in the literature such as "Chemistry of the Silicones" by Rochow, page 61, et seq. A particularly desirable phenylmethylsilicone polymer for use in accordance with the present invention is Dow-Corning 550 Silicone Fluid, a product of Dow-Corning, Inc., which has a viscosity at 100° F. of about 300 to about 400 S. S. U.

Other oleaginous vehicles which may be employed herewith are, for example, mineral oils in the lubricating oil viscosity range, i. e. from about 50 S. S. U. at 100° F. to about 300 S. S. U. at 210° F. These mineral oils are preferably solvent extracted, to substantially remove the low V. I. constituents, e. g. aromatics, with phenol, furfural, B,B'-dichlorodiethylether (Chlorex), liquid SO_2, nitrobenzene, etc. Synthetic lubricating oils resulting from polymerization of unsaturated hydrocarbons or other oleaginous materials within the lubricating oil viscosity range such as high molecular weight polyoxyalkylene compounds such as polyalkylene glycols and esters thereof, aliphatic diesters of dicarboxylic acids such as the butyl, hexyl, 2-ethylhexyl, decyl, lauryl, etc. esters of sebacic acid, adipic acid, azeleic acid, etc., may be thickened by the mixed aryl ureas of the present invention to produce excellent greases. Polyfluoro derivatives of organic compounds, particularly hydrocarbons, in the lubricating oil viscosity range have shown excellent promise when thickened with compounds of the present invention.

Greases of the present invention may be produced by one of the following methods:

(1) The thickener may be prepared apart from and then admixed with the lubricant vehicle and milled in a colloid mill, 3-roll mill, etc.

(2) The thickener may be formed in situ in the oil by introducing the reactants and the desired amount of lubricant vehicle, heating for a relatively short time, e. g. from about five minutes to an hour to drive off volatile by-products, and then cooling and milling the mixture.

(3) As a slight modification of method 2 above, a solvent such as chloroform, ethyl acetate, dioxane, 2-butanone, benzene, etc. may be employed as a diluent and mutual solvent for the reactants. The solvent is then evaporated and the grease is milled, etc. substantially as set forth. Both this method and that of (2) are exceptionally useful, and result in a saving of from 20 to 50% in thickener cost over method (1) above. Co-pending application for Letters Patent Serial Number 392,996, filed November 18, 1953, is directed to the preparation of substituted urea thickened greases generally by the in situ technique. It is preferred to employ this method (3) of preparation in accordance herewith.

(4) As a step in any of the above three methods, it has been found that improved properties may be imparted to the grease by "heat-treating" the grease mixture, i. e. subjecting the same to an elevated temperature for at least about half an hour and preferably longer, e. g. from about 1 to 20 hours. Prolonged heating at such temperature may evaporate a portion of the lubricant vehicle; this loss should be replaced and then the mixture should be milled. If desired, the heating and readdition of vehicle may be repeated before milling. The temperature to which the mixture may be heated will, of course, depend upon the particular lubricant vehicle employed. Thus, a silicone polymer oil may be heated to a temperature of about 450° F. but mineral oils may only be heated from about 200° to 225°; diesters and other synthetic oils may be heated somewhat higher.

In Table 1 are set forth the data obtained on certain greases comprising DC 550 Silicone Fluid (phenylmethyl silicone polymer oil product of Dow Corning, Inc. having a methyl-phenyl ratio of about 0.6 and viscosity of about 300 to 400 S. S. U. at 100° F.) thickened in accordance herewith. The bearing test referred to in the table is a tentative one adopted by the Coordinating Research Council during the last war and is generally referred to as the A. B. E. C.-N. L. G. I. test. It is conducted as follows:

3 grams of grease are placed in each of two bearings disposed on the test spindle. One bearing, a special heat treated precision 204 K Norma-Hoffman (or Marlin-Rockwell) bearing, is subjected to a temperature of 450° F. in an oven, the other bearing, a standard New Departure 204 K bearing, is at a sufficiently low temperature to avoid any failure due to thermal stability of the grease. Temperature is determined by a thermocouple inserted in the grease between the races of the bearing in the oven. Failure is adjudged to occur when (1) the temperature in the test bearing reaches 470° F. or higher, (2) wattage in excess of 300% of normal wattage is required, or (3) the bearing does not turn over at the beginning of a test cycle (the test is conducted in cycles of 20 hours operating and 4 hours at rest).

In Table 2 is set forth a series of greases prepared from certain aryl-substituted urea mixtures and lubricant vehicles other than silicone oil. Each of these greases was prepared by the above described "in situ" technique, i. e. the thickeners listed were prepared in the lubricant vehicle indicated. An ethyl acetate solvent (as per method (3) supra) was employed in each case.

Table I

Thickener			Oil	Grease			
Reactants		Proportions (Mole)		Percent Thickener	Penetration*	Hours in Bearing** Before Failure	Method of Prep.
Amine	Isocyanate						
(1) Benzidine	p-chlorophenyl isocyanate + p-xenyl isocyanate	1:1:1	DC550	15	132	(a) 1,171; (b) 716	(3). 2-Butanone.
(2) Benzidine	p-chlorophenyl isocyanate + p-xenyl isocyanate	1:1:1	DC550	15	203	553	(3). 2-Butanone.
(3) Benzidine	p-chlorophenyl isocyanate + p-tolyl isocyanate + p-xenyl isocyanate	3:2:2:2	DC550	11	178	484	(3). Dioxane.
(4) Benzidine	p-chlorophenyl isocyanate + p-tolyl isocyanate	1:1:1	DC550	20	147	420	(1).
(5) p-aminobenzoic acid	phenyl isocyanate + p-tolyl isocyanate	2:1:1	DC550	19	203	----------	(3). Dioxane.
(6) Benzidine p-phenylene diamine	p-xenyl isocyanate	1:1:4	DC550	14	165	797	Ethyl Acetate.
(7) Benzidine	p-xenyl isocyanate + p-chlorophenyl isocyanate	1:1:1	DC550	12	162	632	(3). (3). Dioxane.

*Kaufmann Micropenetration.
**A. B. E. C.-N. L. G. I. Test—the two numbers given in Example 1, i. e. (a) and (b) are the results of two runs employing the same grease.

Table 2

Thickener	Percent	Oil	Viscosity at 100° F., Cstks.	Grease, Micro-penetration
1,4-Bis-(3-phenylureido)-benzene	20	Di-2-ethylhexyl sebacate [1]	22.2	89
4,4'-Bis-(3-phenylureido)-biphenyl				
1,4-Bis-(3-phenylureido)-benzene	15	Solvent extracted SAE 20 petroleum lubricating oil.	70.7	117
4,4'-Bis-(3-phenylureido)-biphenyl				
1,4-Bis-(3-phenylureido)-benzene	15	Solvent extracted SAE 40 petroleum lubricating oil.	174.9	243
4,4'-Bis-(3-phenylureido)-biphenyl				
1,4-Bis-(3-phenylureido)-benzene	15	Orthosilicate [2] ester	6.9	203
4,4'-Bis-(3-phenylureido)-biphenyl				
1,4-Bis-(3-phenylureido)-benzene	10	Fluorocarbon [3]	195.6	64
4,4'-Bis-(3-phenylureido)-biphenyl				

[1] In addition to the di-(2-ethylhexyl) sebacate, which comprises 90.6% of the vehicle, there is present Acryloid HF-825, 3.9%; phenothiazine, 0.5%; tricresyl phosphate, 5.0%; silicone antifoam, 0.001%.
[2] "Orsil BF-1-S" (product of Oronite Chemical Corp.).
[3] A mixture comprising 41% "Fluorolube" trifluorovinyl chloride polymer (CP-320-52) D-8433 (an experimental product of Hooker Chemical Co.) and 59% of "Kel-F-40" trifluorochloroethylene polymer (product of The M. W. Kellogg Co.).

Greases of the type set forth in Table 2 are stable at high temperatures although generally somewhat less stable than those prepared with silicone oil as the lubricant vehicle. Accordingly, they are more suitably employed at temperatures up to about 250° F. and perhaps somewhat higher for certain individual greases, e. g. those prepared from fluorocarbon oils, diesters, etc. It should be understood, in any event, that while the greases of the present invention are particularly suitable for use at temperatures of about 250° F. and above, they are also extremely useful at lower temperatures. Thus, a mineral lubricating oil derived from petroleum thickened with mixtures of aryl ureas may be employed as multipurpose grease for automotive and industrial uses.

Whereas the mixtures of aryl-substituted ureas employed as thickeners for lubricating vehicles in accordance herewith have been prepared in each instance by the reaction of an amine with an isocyanate, such materials may be prepared by other techniques and should be understood that this invention is not limited to the described method of preparing the thickener. Thus, for example, substituted ureas of the type herein described may be prepared by the reaction of an amine with an acid azide or a substituted carbamyl chloride rather than an isocyanate as herein described. From the reaction of an acid azide with an amine, nitrogen is evolved while from the reaction of a carbamyl chloride with an amine, hydrogen chloride is a by-product. The evolution of hydrogen chloride has certain disadvantages in the "in situ" method of producing greases and accordingly is not recommended for use in lubricants generally. The azide-amine reaction, however, will produce a suitable grease thickener whether prepared in situ or apart from the lubricant vehicle and later milled therewith.

Greases of the present invention may have added thereto antioxidants, oiliness agents, extreme pressure additives, etc. without in any way departing from the scope of the present invention.

Having thus described our invention, what we claim as novel and desire to protect by Letters Patent is defined by the following claims:

1. A lubricant grease comprising an oleaginous lubricant vehicle thickened to grease consistency with a mixture of arylureas selected from the group consisting of

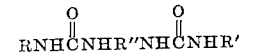


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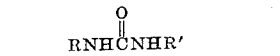


and mixtures thereof wherein R and R' represent hydrocarbon radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals and R" is a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals.

2. A lubricant grease comprising an oleaginous vehicle thickened with an amount of from about 5% to about 70% by weight of a mixture of arylureas selected from the group consisting of



and



and mixtures thereof wherein R and R' represent different hydrocarbon radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals and R" is a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals.

3. The lubricant grease of claim 2 wherein the oleaginous lubricant vehicle comprises a silicone polymer oil in the lubricating oil viscosity range.

4. The lubricant grease of claim 2 wherein the oleaginous lubricant vehicle comprises an acyclic ester of an aliphatic dicarboxylic acid in the lubricating oil viscosity range.

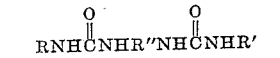
5. The lubricant grease of claim 2 wherein the oleaginous lubricant vehicle comprises a mineral lubricating oil derived from petroleum.

6. The lubricant grease of claim 2 wherein the oleaginous lubricant vehicle comprises a polyfluoro-product in the lubricating oil viscosity range, said polyfluoro product being a mixture of 41% trifluorovinylchloride polymer and 59% trifluorochloroethylene polymer.

7. A lubricant grease comprising a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70% by weight of a mixture of arylureas comprising 4-[3-(p-chlorophenyl)-ureido-]-4'-[3-(p-tolyl)-ureido]-biphenyl, 4,4'-bis-[3-(p-chlorophenyl)-ureido]-biphenyl, and 4,4'-bis-[3-(p-tolyl)-ureido]-biphenyl.

8. The lubricant grease comprising a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70% by weight of a mixture of arylureas comprising 1-(p-carboxyphenyl)-3-(p-tolyl)-urea, and p-carboxy-s-diphenyl-urea.

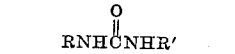
9. A lubricant grease comprising an oleaginous vehicle thickened with an amount of from about 5% to 70% by weight of a mixture of arylureas melting above about 250° F. comprising arylureas having the general formula



wherein R and R' represent hydrocarbon radicals con-

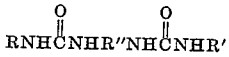
taining no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals and R'' is a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals.

10. A lubricant grease comprising an oleaginous vehicle thickened with an amount of from about 5% to about 70% by weight of a mixture of arylureas melting above about 250° F. comprising arylureas having the general formula

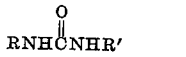


wherein R and R' represent hydrocarbon radicals selected from the group consisting of aryl and substituted aryl radicals containing no more than 12 cyclic carbon atoms.

11. The method of preparing a lubricant grease which comprises milling a lubricant vehicle and from about 5% to about 70% by weight of a mixture of arylureas selected from the group consisting of



and



and mixtures thereof wherein R and R' represent different hydrocarbon radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals and R'' is a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals.

12. The method of claim 11 wherein the lubricant vehicle is a silicone polymer oil in the lubricating oil viscosity range and said silicone polymer oil and said aryl compound are heated to a temperature between about 400° F. and 450° F. for a period of from about ½ hour to about 72 hours.

13. A lubricant grease comprising a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70% by weight of a mixture of arylureas comprising a 4-[3-(p-chlorophenyl)-ureido]-4'-[3-(4-biphenylyl)-ureido]-biphenyl, 4,4'-bis-[3-p-chlorophenyl)-ureido]-biphenyl, and 4,4'-bis-[3-(4-biphenylyl)-ureido]-biphenyl.

No references cited.