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 and amido compounds. Grease 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 hydroxystearate, 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°F. 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. It has now been found that certain very high melting aromatic ureas, di-ureas, amides, and di-amides, all of which contain at least one

\[ R-NH- \]

radical, wherein R is an aryl radical, and which may hereinafter be referred to broadly as ary carbamamyl 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.

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.

We have found that 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 an arylcarbamyl compound selected from the group consisting of aromatic ureas, di-ureas, amides, and di-amides. Thus, in accordance herewith, arylcarbamyl compounds having the following empirical structure are contemplated as thickening agents in the art of grease manufacture:

\[ R-NH-C=O \]

In the above formulae, R, R' and R'' represent aryl or alkyl aryl radicals. With the exception that R' is necessarily a divalent radical, e.g. phenylene, biphenylene, naphthylene, etc., these radicals may be the same or different, e.g. phenyl, biphenyl, naphthyl, etc. in each compound. The aryl or alkyl aryl radicals may be substituted radicals containing various reactive substituents such as hydroxy, carboxy, halo, nitro, etc.

Examples of amides and di-amides which have been found to yield excellent greases when employed as thickeners are N-benzoyl-4-aminobiphenyl, N,N'-dibenzoyl-benzidine, N,N'-dibenzoyl-p-phenylene-diamine and N,N'-bis-(p-nitrobenzoyl)-benzidine. Such compounds may be readily prepared by techniques well known to the art, e.g. by reaction of an aromatic amine or diamine such as phenylene-diamine, aniline, benzidine, etc., with an aryl halide, e.g. benzoyl chloride. Diamides such as may be prepared by reacting an aromatic monoamine, e.g. aniline, with an aryl halide such as a phenyl halide, may likewise be employed in accordance herewith. These compounds may be employed alone or in combination to thicken oleaginous vehicles to grease consistency.

Examples of various ureas and di-ureas which have been found useful as thickeners in accordance herewith are p-carboxy-1,3-diphenylurea; p-chloro-1,3-diphenylurea; 1,3-di-(1-naphthyl)-urea; 4,4'-bis-(3-p-carboxyl-ureido)-biphenyl; 1-(p-carboxyphenyl)-3-(p-carboxyl-ureido)-urea; 1-(p-carboxyphenyl)-3-(3-carboxyl-ureido)-urea; 1,3-di-(p-biphenyl-ureido); 1,3-di-(o-biphenyl-ureido)-urea; 4,4'-bis-(3-phenylureido)-3,3'-dimethoxy-biphenyl; p-phenylurethan-1,3-diphenyl-urea; p-cyaano-1,3-diphenyl-urea; 1-(2,5-dichlorophenyl)-3-phenyl-urea; 4,4'-bis-(3-(2,5-dichlorophenyl)-ureido)-biphenyl; 1,4 - bis-(3-(2-chlorophenyl)-ureido)-benzene; 1,4 - bis -(3-(3-chlorophenyl)-ureido)-benzene; 1,3-bis -(3-(3-chlorophenyl)-ureido)-benzene, and 1,3-bis-(3-(2-chlorophenyl)-ureido)-benzene. Compounds of this type may readily be prepared by reacting an amine or diamine such as aniline, benzidine, phenylene-
diamine, etc. with an isocyanate of benzene, diphenyl, etc. It should be understood that the specific aryI carbamyl compounds set forth above are enumerated for purposes of illustration and not of limitation. Compounds of this class may be employed alone or in combination with other such compounds to thicken oleaginous vehicles in accordance herewith. Greases prepared with thickeners of the type described above, particularly those prepared from silicone oil, are exceptionally stable at elevated temperatures with those prepared from urido compounds being slightly superior to those prepared from amide type thickeners.

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:

\[
\begin{array}{c}
R & -O- & R' \\
R & -O- & R'
\end{array}
\]

wherein \( R \) and \( R' \) represent substituted or unsubstituted alkyl, aryl, alkyaryl, arylalkyl or cycloaliphatic radicals. Such compounds may be produced by well-known methods, e.g. the hydrolysis of dialkylchlorosilanes or dialkylalkoxy silanes 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 300 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 dimethyl silicone polymer, phenylmethyl silicone polymer, chlorophenylmethyl silicone polymer, etc., it being preferred to employ the phenylmethyl silicone 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. Particularly desirable phenylmethylsilicones 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 hereewith 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'-dichlorodimethyl ether (Chlorox), 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, alphatic diesters of dicarbonyl acids such as the butyI, hexyl, 2-ethylhexyl, decyl, lauryl, etc. esters of sebatic acid, adipic acid, azelaic acid, etc., may be thickened by the aryI carbamyl compounds 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 to about 450°F. 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 dioxane 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.

4. As a step in any of the above three methods, it has been found, when employing a silicone vehicle, that improved properties may be imparted to the grease by "heat-treating" the grease mixture, i.e. subjecting same to a temperature of about 450°F. 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 redilution of vehicle may be repeated before milling.

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**Table 1**

<table>
<thead>
<tr>
<th>Thickener</th>
<th>Class</th>
<th>Percent (By Wt.)</th>
<th>Method of Preparation</th>
<th>Hours Before Failure in Bearing Test</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>N-Benzoyl-p-aminobenzenoic acid</td>
<td>[ \text{R'NHR} ] &amp; 38 &amp; (3) (4) &amp; 337 &amp; #1 or #2 grade* grease of excellent texture.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>N,N-Dibenzoylbenzidine</td>
<td>[ \text{R'NHR'NHR} ] &amp; 29 &amp; (2) &amp; 188 &amp; Smooth #1 grade* grease—very low evaporation loss and low leakage.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-bis(3-biphenylylureido)-biphenyl</td>
<td>[ \text{R'NHCONHR} ] &amp; 29 &amp; (3) (4) &amp; 437 &amp; Good appearing #2 grade* grease—highly stable.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do</td>
<td>[ \text{R'NHCONC} ] &amp; 18 &amp; (2) &amp; 446 &amp; Do.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-bis-(2,5-dichlorophenyl)-ureido)-biphenyl</td>
<td>[ \text{R'NHCONHR} ] &amp; 25 &amp; (3) (4) &amp; 456 &amp; Smooth buttery #1 or #2 grade* grease.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>p-carboxy-3,3-diphenylene</td>
<td>[ \text{R'NHONHR} ] &amp; 29 &amp; (3) (4) &amp; 603 &amp; Good appearance—#2 grade* grease.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Do</td>
<td>[ \text{R'NHCONHR} ] &amp; 23 &amp; (3) (4) &amp; 446 &amp; Do.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4,4'-bis(3-p-tolylureido)-biphenyl</td>
<td>[ \text{R'NHCONHR} ] &amp; 20 &amp; (3) (4) &amp; 418 &amp; Smooth buttery #2 grade.</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* N. L. G. I. consistency grade.
Table 2

<table>
<thead>
<tr>
<th>Lubricant Vehicle</th>
<th>Percent (By Wt.)</th>
<th>Consistency (Kuottman Micropenetration)</th>
<th>Method of Prep.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ucon BIS</td>
<td>33</td>
<td>104</td>
<td>(1)</td>
</tr>
<tr>
<td>Ds-2-ethylhexyl/alkanes</td>
<td>40</td>
<td>158</td>
<td>(3)</td>
</tr>
<tr>
<td>Tricresyl phosphate</td>
<td>41.5</td>
<td>147-148</td>
<td>(5)</td>
</tr>
</tbody>
</table>


2. Petroleum oil of high aromatic content.

3. Ket-P Polymer No. 46 (product of The M. W. Kellogg Co.).

4. The composition of this vehicle was as follows: 65.0% di-2-ethylhexyl sebacate, 25.0% synthetic acrylic base V, 0.0% stearates, 0.6% tricresyl phosphate, 0.0% U of silicone anti-foam, and 0.6% phenolactic.

5. Kantoian micropenetration.

6. Petroleum oil of high aromatic content.

7. Ket-P Polymer No. 46 (product of The M. W. Kellogg Co.).

8. The composition of this vehicle was as follows: 65.0% di-2-ethylhexyl sebacate, 25.0% synthetic acrylic base V, 0.0% stearates, 0.6% tricresyl phosphate, 0.0% U of silicone anti-foam, and 0.6% phenolactic.


10. Petroleum oil of high aromatic content.

11. Ket-P Polymer No. 46 (product of The M. W. Kellogg Co.).

12. The composition of this vehicle was as follows: 65.0% di-2-ethylhexyl sebacate, 25.0% synthetic acrylic base V, 0.0% stearates, 0.6% tricresyl phosphate, 0.0% U of silicone anti-foam, and 0.6% phenolactic.


14. Petroleum oil of high aromatic content.

15. Ket-P Polymer No. 46 (product of The M. W. Kellogg Co.).

16. The composition of this vehicle was as follows: 65.0% di-2-ethylhexyl sebacate, 25.0% synthetic acrylic base V, 0.0% stearates, 0.6% tricresyl phosphate, 0.0% U of silicone anti-foam, and 0.6% phenolactic.
6. The lubricant grease of claim 1 wherein the lubricant vehicle comprises a polyfluoro-compound in the lubricating oil viscosity range.

7. A lubricant grease comprising a lubricant vehicle thickened with from 5 to 70% by weight of at least one aryl carbamyl compound melting above about 400° F. which compound is selected from the group consisting of 

\[ \text{O} \text{R} \text{N}=\text{NHR}' \text{ and } \text{O} \text{R} \text{N}=\text{NHR}' \text{NHR}'' \] 

wherein R and R' represent hydrocarbon radicals containing no more than 12 cyclic carbon atoms, which radicals are selected from the group consisting of aryl, alkyl aryl, substituted aryl, and substituted alkyl aryl radicals, and R'' represents a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms, which radical is selected from the group consisting of arylene, alkyl arylene, substituted arylene, and substituted alkyl arylene radicals.

8. A lubricant grease comprising essentially a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70% by weight of 4,4'-bis-[3-(2,5-dichlorophenyl)-ureido]-biphenyl.

9. A lubricant grease comprising essentially a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70% by weight of N-benzoyl-p-aminobenzoic acid.

10. A lubricant grease comprising essentially a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to 70% by weight of N,N'-dibenzoyl-benzidine.

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

12. A lubricant grease comprising essentially a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to 70% by weight of 4,4'-bis-[3-(2,5-dichlorophenyl)-ureido]-biphenyl.

13. The method of preparing a lubricant grease which comprises milling a mixture comprising essentially a lubricant vehicle and from about 5% to about 70% by weight of an aryl carbamyl compound melting above about 250° F. selected from the group consisting of 

\[ \text{O} \text{R} \text{N}=\text{NHR}' \text{ and } \text{O} \text{R} \text{N}=\text{NHR}' \text{NHR}'' \] 

wherein R and R' represent hydrocarbon radicals containing no more than 12 cyclic carbon atoms, which radicals are selected from the group consisting of aryl, alkyl aryl, substituted aryl, and substituted alkyl aryl radicals, and R'' represents a divalent hydrocarbon radical containing no more than 12 cyclic carbon atoms, which radical is selected from the group consisting of arylene, alkyl arylene, substituted arylene, and substituted alkyl arylene radicals.