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METHOD OF PREPARING SUBSTITUTED UREA-THICKENED GREASES

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24 Claims. (Cl. 252—51.5)

The present invention relates to an improved method of manufacturing lubricant greases. More particularly, it relates to a novel process for the manufacture of greases comprising a lubricant vehicle thickened with one or more alkyl or aryl-substituted ureas.

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° 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 higher 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.

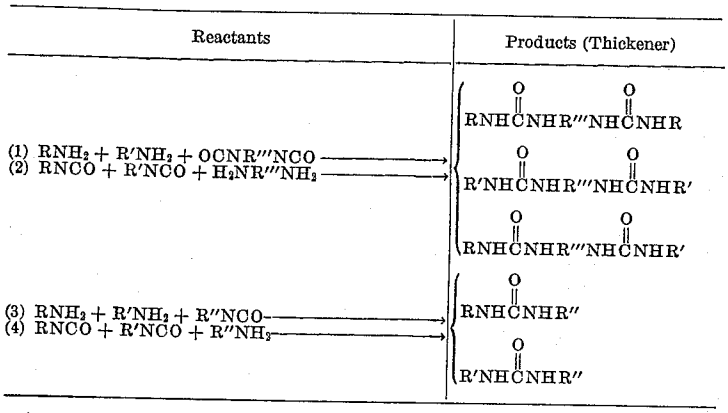
In our copending application for Letters Patent S. N. 318,321, filed November 1, 1952 (of which the present application is a continuation in part), it is disclosed that certain very high melting aromatic ureas, diureas, amides, and diamides, all of which contain at least one



radical wherein R is an aryl radical; and which are referred to broadly as aryl carbamyl 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 over a wide range of 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 over a wide range of temperatures.

In copending application for Letters Patent S. N. 393,010 filed November 18, 1953 (which is also a continuation in part of S. N. 318,321), greases prepared with thickeners comprising mixtures of at least two different aryl substituted ureas and/or diureas are described and claimed. Thus, in accordance with the invention described in said application, mixtures of aryl substituted ureas prepared by reacting (1) at least two different aryl isocyanates with at least one aryl amine (mono- or diamine) or (2) at least two different aryl monoamines with at least one aryl isocyanate (mono- or diisocyanate). Thus, greases are prepared in accordance with the later filed application which comprises an oleaginous lubricant 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 or substituted aryl radical which may be same as or different from R and R'. These 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, aryl, alkylaryl, arylalkyl, sulfonyl, carboxyl, hydroxyl, amido, sulfonamido, etc. or one may be monocyclic and the other polycyclic, e. g. phenyl, diphenyl, naphthyl, etc. 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 p-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 isocyanate, e. g. p-chlorophenyl isocyanate. Examples of other reactants and the products obtainable therefrom will be hereinafter set forth. R''' is a divalent arylene radical, 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''.

It has been discovered that improved, high consistency greases of the type claimed in the foregoing copending applications can be prepared with substantial savings in the amount of thickener employed by preparing the substituted urea thickeners by chemical reaction in the lubricating oil vehicle.

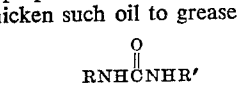
Furthermore, related greases embodying alkyl substituted urea thickeners can readily be prepared by this technique. And whereas, for purposes of illustration, the following detailed description will refer particularly

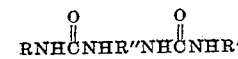
to the preparation of aryl substituted urea thickened greases, it should be understood that the invention is broadly concerned with an improved method of preparation of greases which comprise lubricant vehicles thickened by alkyl substituted ureas and/or ureas substituted by both aryl and alkyl radicals, as well. These latter thickeners will also be described in greater detail.

For purposes of illustration, therefore, an aryl urea thickened grease is prepared in accordance herewith by first introducing the amine component or components dissolved in an organic solvent to a solution of the isocyanate or isocyanates in the lubricant vehicle, e. g. a silicone oil. Various solvents may be used. Their requirements are that they be chemically inert with respect to the vehicles and reactants, that they boil at a temperature permitting ready removal from the grease preferably substantially below 300° F., and that they dissolve substantially completely the reactants employed to produce the ureas. An immediate reaction occurs at room temperature to produce the arylurea thickener during rapid agitation of the mixture. Higher temperatures may be employed if desired. When reaction is complete, the solvent, e. g. dioxane, chloroform, benzene, ethyl acetate, 2-butanone, etc., is removed, preferably by heating at atmospheric pressure (vacuum may be employed if desired.) The solvent-free grease may then be milled to produce a smooth homogeneous product. But it is preferred, and especially with arylurea thickened silicone oils intended for use at very elevated temperatures, that the grease be heated after solvent removal and preferably before milling to the highest proposed operating temperature at which the grease is ultimately to be employed (this will depend particularly on the thermal stability of individual oil and thickener) and it is retained at such temperature for a period of time which may vary from about 30 minutes to about 72 hours. After the heating step is complete, the grease is cooled to room temperature and milled. The resulting greases are smooth and buttery in texture and have excellent thermal stability. Whereas it is preferred that the isocyanate be dissolved in the lubricant vehicle and the amine component be added thereto in a solvent, this procedure may be reversed with the amine being dissolved and/or melted in the oil and the isocyanate being added via the solvent.

It has been found that improved greases may be manufactured, in accordance herewith, by preparing (by chemical reaction) the thickener in situ in the lubricant vehicle in the absence of a solvent. But it is preferred to employ a solvent because the same contributes in large measure to the completeness of the reaction of isocyanate and amine and the dispersion of resulting thickener throughout the oil. In cases where one or more of the reactants is a solid, e. g. 4-biphenylyl isocyanate (p-xenyl isocyanate), it may be heated in the oil until melted or it may be dissolved in the solvent first and then added to the oil either before or simultaneously with the amine.

In accordance with the present invention, lubricating vehicles such as silicone polymer oils, mineral lubricating oils derived from petroleum, synthetic lubricating oils such as polyalkylene glycols and their derivatives, dicarboxylic esters, fluorocarbons, etc. and preferably the silicone polymer oils may be thickened to grease consistency by thickeners of the type described herein prepared by chemical reaction in the lubricating oil itself. Amounts of such thickeners of from 5 to 70% and preferably from about 10 to 50% may be employed. Thus, in accordance herewith, substituted urea thickeners comprising one or more of the following type compounds (designated by general formula) are prepared in lubricating oils in an amount sufficient to thicken such oil to grease consistency.





In the above formulae, R and R′ represent aryl or alkyl radicals which may be the same or different. These radicals may be substituted or unsubstituted, e. g. by substituent groups such as nitro-, halo-, alkyl-, aryl-, alkylaryl-, arylalkyl, sulfonyl-, carboxyl-, hydroxyl, amido, sulfonamido, etc.; where aryl they may be mono- or polycyclic, e. g. phenyl, diphenyl, naphthyl, etc. R″ is a divalent aryl or alkyl radical (i. e. an arylene or alkylene radical) such as phenylene, biphenylene, naphthylene, ethylene, propylene, nonylene, etc., which may be substituted by such hydrocarbon or other substituent groups as are above enumerated with respect to R and R′. Where alkyl or substituted alkyl radicals are employed, the number of carbon atoms therein may vary from 1 to about 30 and preferably from 2 to about 10 carbon atoms. R″, when alkyl, may have from 2 to about 20 carbon atoms and preferably from 2 to about 10.

Obviously, a wide variety of such ureas may be produced in accordance herewith and these are dependent upon the number and type of isocyanate and amine reactants selected. Thus, by way of illustration and not of limitation, a number of isocyanates which may be employed in accordance with the present invention to produce such greases are set forth below. And it should be understood, as indicated above, that the reactants may be selected so as to produce either mixtures of alkyl and/or aryl-substituted ureas or individual alkyl or aryl-substituted ureas and they may be mono- or poly-ureas.

Suitable aryl isocyanates which may be employed in accordance herewith are p-chlorophenyl isocyanate, p-tolyl isocyanate, tolylene 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.

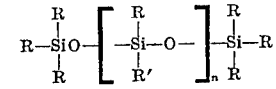
Examples of alkyl isocyanates which may be employed are hexyl isocyanate, chlorononyl isocyanate, 1,6-di-isocyanato hexane, 1,12-di-isocyanato dodecane, cyclohexyl isocyanate, octadecyl isocyanate, etc.

Examples of suitable aryl amines are p-aminobenzoic acid, p-aminobiphenyl, benzidine, dianisidine, o-tolidine, p-aminophenol, p-aminobenzonitrile, p-phenylene diamine, m-phenylene diamine, o-phenylene diamine, 2,5-dichloroaniline, aniline, p-toluidine, etc.

Typical of the alkyl amines which may be employed are hexylamine, dodecylamine, octylamine, nonylamine, cyclohexylamine, chlorodecylamine, 1,6-di-amino hexane, 1-10-diamino-decane, 1,3,diamino propane, diethylene triamine, triethylene tetramine, etc.

The above enumerated amines and isocyanates, as well as others not specifically referred to but which will be readily suggested to one skilled in the art as result of the examples given, may be reacted to produce a wide variety of mono- and/or diureas. Thus, if symmetrical monoureas or diureas are desired, either an amine and an isocyanate having the same hydrocarbon radical may be reacted or, for example, a single isocyanate may be reacted with a diamine. On the other hand, for example, if mixtures of aryl substituted ureas of the type claimed in S. N. 393,010 filed November 18, 1953 are desired, then at least one amine and at least two isocyanates or vice versa must be reacted. From such as this latter mixture of reactants, a thickener comprising a mixture of different ureas would necessarily result.

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 unsubstituted

alkyl, aryl, alkylaryl, arylalkyl, or cycloalkyl radicals. Such compounds may be produced by well-known method, 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, phenylmethylsilicone 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. Another is Dow Corning 510 Silicone Fluid, etc.

Other oleaginous lubricant 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 ureido 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. Thus, any lubricating oil, natural or synthetic, which when thickened in accordance herewith, will result in a useful lubricant grease, may be employed in accordance herewith. Mixtures of these various vehicles may be employed if desired. Thus, for example, a mixture of diester and fluorocarbon; of various silicone fluids; a diester and a hydrocarbon oil; etc. may be employed.

The following are detailed working examples illustrative of the present novel method of grease manufacture as applied to the preparation of aryl ureas. The characteristics and thermal stability of the greases so prepared, as well as others prepared in like manner, are compared in Table 1 with greases of the same general type, i. e. arylurea thickened greases prepared by milling a prepared arylurea thickener with an oil. The greater consistency obtained with substantially less thickener by the use of the present novel method is striking.

EXAMPLE 1

A five-gallon double-action scraper kettle was charged with 2000 grams of D. C. 550 Silicone Fluid (phenylmethylpolysiloxane product of Dow Corning more fully defined hereinabove), 160 grams of p-chlorophenyl isocyanate, and 204 grams of p-biphenylyl isocyanate. The mixture was heated to 150° F. to melt the p-biphenylyl isocyanate.

To the above stirred mixture, 184 grams of benzidine dissolved in about 2 liters of 2-butanone was added over a period of 20 minutes.

The remainder of the silicone oil, 1000 grams, was then added and the solvent was boiled off and the resulting grease was heated with stirring for 4 hours at 420° F. After the grease was cooled to room temperature, it was passed through a colloid mill to complete the preparation. The finished grease had an ASTM penetration of 318 (unworked) (Kaufmann micropenetration of 132), 338 after 60 strokes, and 354 after 100,000 strokes. An A. B. E. C.-N. L. G. I. bearing test (hereinafter described) employing this grease at 450° F. and 10,000 R. P. M. ran for 553 hours.

EXAMPLE 2

A mixture of 13.1 grams of p-biphenylyl isocyanate dissolved in 92 grams of solvent extracted SAE–20 petroleum lubricating oil was introduced to a beaker; 9.9 grams of 1,2-propylene diamine was added thereto with stirring. The resulting soft, grainy paste was heated overnight at a temperature of 250° F. and then milled to produce a grease having a micropenetration of 131. The heating and milling steps were repeated and the micropenetration at the conclusion thereof had gone up to 162.

EXAMPLE 3

A solution of 9.8 grams of p-biphenylyl isocyanate in 50 milliliters of ethyl acetate was added with stirring to a mixture in a beaker comprising 12.8 grams of cetylamine, 60.8 grams of solvent extracted SAE–20 petroleum lubricating oil and a substantial amount of ethyl acetate. The resulting mixture was milled in a roller mill to produce a rather soft buttery grease.

EXAMPLE 4

A hot solution consisting of 276 grams of benzidine, 162 grams of p-phenylene diamine and two liters of ethyl acetate was poured rapidly into a solution of 10.8 pounds of D. C. 550 Silicone Fluid and 788 grams of p-tolyl isocyanate in the kettle referred to in Example 1. The mixture immediately thickened. After the solvent was removed by distillation, the mix was heated to about 420° F. and kept at this temperature for about four hours. The grease was then allowed to cool overnight without stirring and finally finished by milling. The resulting grease was smooth, opaque paste having an ASTM penetration of 300 (Kaufmann micropenetration –81).

EXAMPLE 5

The five-gallon, double-action scraper kettle was charged with 9.46 pounds of D. C. 550 Silicone Fluid and 780 grams of p-biphenylyl isocyanate. This mixture was heated to 160° F. in order to melt the isocyanate and make a homogeneous solution. A solution consisting of 184 grams of benzidine, 108 grams of p-phenylene diamine and 1500 grams of ethyl acetate was then poured very rapidly into the kettle. The mixture thickened immediately. The cover was then bolted in place and the kettle was heated by introducing 100 p. s. i. steam to the kettle jacket to raise the mixture to a temperature of about 320° F. The solvent was recovered by condensing it in a copper coil which was submerged in water bath. After the solvent was removed, the kettle was uncovered and heated electrically to 425° F. and kept at this temperature for one hour. The grease was allowed to cool overnight without stirring, and then milled. The resulting grease was a purple, smooth, opaque paste. Thickener concentration was 20%. ASTM Penetration: Unworked —318; worked—320.

The bearing test referred to in Example 1 above 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 1 the term "In situ" is employed to designate grease preparation by the method of the present invention as exemplified by illustrative examples 1, 2, and 3 above. The compound in parentheses following this term is the solvent employed. The term "solid milled" refers to grease preparation wherein the thickener is first prepared and then mixed and milled with the oil. The lubricant vehicle employed in the greases shown in Table 1 was D. C. 550 Silicone Fluid.

Table 1

Thickener		Method of Preparation	Micropenetration (Kaufmann)
Kind	Percent		
A	30	Solid milled	450+
A	10	In situ (benzene)	110
A	15	In situ (2-butanone)	47
A	30	Solid milled	212
B	20	In situ (chloroform)	77
B	30	Solid milled	450+
C	15	In situ (2-butanone)	75
C	15	In situ (dioxane)	82

A—product of the reaction of 1 equivalent of p-chlorophenyl isocyanate, 1 equivalent of p-biphenylyl isocyanate, and 1 equivanent of benzidine.
B—product of the reaction of 2 equivalents of p-biphenylyl isocyanate and 1 equivalent of benzidine.
C—product of the reaction of 2 equivalents p-chlorophenyl isocyanate and 1 equivalent of benzidine.

While the reasons are not fully understood, the particular solvent employed as well as the amount thereof and the time the grease is in contact therewith appear to have a definite effect on the quality of greases prepared in accordance herewith. Experiments were run to determine the effect of concentration of reactants and effect of prolonged contact of solvent with the grease. Particle size measurements were used to evaluate the techniques. It was found that the smaller the particle size, the higher the consistency of the grease, i. e. consistency is roughly determined by particle size when comparing greases of the same composition and thickener percentage. The data in Table 2 demonstrate this for certain greases prepared by the technique of the present invention embodying D. C. 550 Silicone Fluid lubricant vehicle.

Table 2

Thickener		Micropenetration (Kaufmann)	Average Particle Length (μ)
	Percent		
A	20	55	0.16
A	20	113	0.57
B	15	139	0.44
B	15	249	0.60
C	15	132	0.66
C	15	203	0.75

A—2 moles p-tolyl isocyanate + 1 mole benzidine prepared with dioxane solvent.
B—2 moles p-chlorophenyl isocyanate + 1 mole benzidine prepared with 2-butanone solvent.
C—1 mole p-chlorophenyl isocyanate + 1 mole p-biphenylyl isocyanate + 1 mole benzidine prepared with 2-butanone solvent.

To further illustrate this point, p-chlorophenyl isocyanate, p-biphenylyl isocyanate, and benzidine were reacted in the presence of D. C. 550 in (1) the least amount of 2-butanone and (2) ten times the least amount of solvent which it previously had been determined would dissolve the reactants. Samples were withdrawn at intervals, viz. (1) immediately after mixing, (2) after 10 minutes, and (3) after refluxing for 24 hours. The particle sizes were strikingly different. In all cases, the particles were much larger after the greases had been refluxed for 24 hours and slightly larger 10 minutes after mixing. Furthermore, the particles as initially formed were smaller in the reaction using the least amount of solvent. These experiments were repeated using benzene as the solvent. The same increase in size was observed. In this case, the particles as initially formed were smaller than those formed initially in 2-butanone.

Accordingly, it is preferred to employ substantially no more solvent than the minimum amount required to dissolve the reactants employed in the production of substituted ureas in accordance herewith. And it is important that the solvent be removed from the thickener-oil mixture as soon as reaction is complete. The time of reaction cannot be known for all cases, but since the ureido compounds are usually formed substantially at once under adequate mixing conditions and the use of sufficient solvent, the solvent should be removed within about one-half hour and preferably within about 15 minutes from the time all the reactants had been admixed in the reaction medium.

As indicated above, the present method for preparing substituted urea greases is applicable to a variety of lubricant vehicles. In Table 3 are listed grease prepared by the present technique in vehicles other than silicone polymer oils. An ethyl acetate solvent was employed in each preparation.

Certain greases of the type set forth in Table 3 are stable at relatively high temperatures, e. g. 300 to 350°

Table 3

	Thickener	Percent	Oil	Viscosity at 100° F. Cstks.	Grease, Micropenetration
1	1,4-Bis-(3-phenylureido)-benzene 4,4'-Bis-(3-phenylureido)-biphenyl	20	Di-2-ethylhexyl sebacate [1]	22.2	89
2	1,4-Bis-(3-phenylureido)-benzene 4,4'-Bis-(3-phenylureido)-biphenyl	20	Solvent extracted SAE 20 petroleum lubracting oil.	70.7	117
3	1,4-Bis-(3-phenylureido)-benzene 4,4'-Bis-(3-phenylureido)-biphenyl	15	Solvent extracted SAE 40 petroleum lubricating oil.	174.9	243
4	1,4-Bis-(3-phenylureido)-benzene 4,4'-Bis-(3-phenylureido)-biphenyl	15	Orthosilicate ester [2]	6.9	203
5	1,4-Bis-(3-phenylureido)-benzene 4,4'-Bis-(3-phenylureido)-biphenyl	10	Fluorocarbon [3]	195.6	64
6	4,4'-Bis-(3-phenylureido)-biphenyl	20	Di-2-ethylhexyl sebacate	12.7	148
7	1,2-Bis-[3-(4-biphenylyl)-ureido]-propane	20	Solvent extracted SAE 20 petroleum lubricating oil.	70.7	162
8	4,4'-Bis-(3-phenylureido)-biphenyl	12	Fluorocarbon [4]	2,000	95

[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 anti-foam, 0.001%.
[2] "Orsil BF-1-S" (product of Oronite Chemical Corp.).
[3] A mixture comprising 41% "Fluorolube" (CP-320-52) D-8433 (an experimental product of Hooker Chemical Co.) and 59% of "Kel-F-40" (product of The M. W. Kellogg Co.).
[4] "Kel-F-40"—Product of The M. W. Kellogg Co.

F. and higher, but are generally useful at temperatures somewhat below those at which greases embodying a silicone oil as the lubricant vehicle, may be employed. Greases of the type herein described, particularly embodying a petroleum lubricating oil, are useful at temperatures encountered in normal automotive or industrial uses and admirably fulfill the requirements of a multipurpose grease.

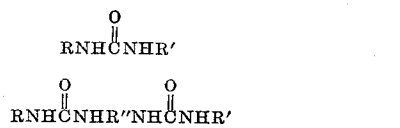
Whereas the substituted urea thickeners employed in accordance herewith have been prepared in each instance by the reaction of an amine with an isocyanate, such materials may be prepared by other reactions and it should be understood that this invention is not limited to the preferred described chemical reaction (i. e. amine-isocyanate) for producing such thickeners. Thus, for example, ureido compounds 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 whereas 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 present in situ method of producing greases. And accordingly, its use, generally, is not recommended. The azide-amine reaction, however, will produce a suitable grease thickener with nitrogen evolution and since nitrogen is inert, such a reaction may readily be employed in accordance herewith.

Percentages given herein and in the appended claims are by weight unless otherwise specified.

The greases of the present invention may contain added constituents such as 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 as follows:

1. The method of manufacturing a lubricant grease comprising a substituted urea-thickened lubricant vehicle which comprises producing in situ in a reaction medium comprising the lubricant vehicle of the grease substituted urea selected from the group consisting of



and mixtures thereof wherein R and R′ represent hydrocarbon radicals selected from the class consisting of aryl, alkyl, and substituted aryl, said aryl radicals having no more than 12 cyclic carbon atoms and said alkyl radicals having from 1 to 30 carbon atoms, and R″ represents a hydrocarbon radical selected from the class consisting of alkylene, arylene, substituted alkylene, and substituted arylene radicals, said alkylene radicals having from 2 to about 20 carbon atoms and said arylene radicals having no more than 12 cyclic carbon atoms, said substituted urea being prepared in an amount sufficient to thicken the amount of lubricant vehicle in which it is prepared.

2. The method of claim 1 wherein the ultimate mixture of substituted urea and lubricant vehicle is milled.

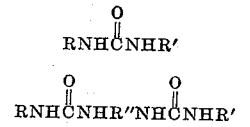
3. The method of claim 1 wherein said substituted urea is formed in situ in said lubricant vehicle by chemical reaction in said lubricant vehicle of a mixture comprising a compound selected from the group consisting of RNCO, OCNR′NCO and mixtures thereof and a compound selected from the group consisting of $R''NH_2$ and $H_2NR'''NH_2$ in which R and R″ are hydrocarbon radicals selected from the group consisting of alkyl radicals having from 1 to about 30 carbon atoms and aryl and substituted aryl radicals having no more than 12 cyclic carbon atoms, and R′ and R‴ are hydrocarbon radicals selected from the group consisting of alkylene and substituted alkylene radicals having from 2 to about 20 carbon atoms and arylene and substituted arylene radicals having no more than 12 cyclic carbon atoms.

4. The method of claim 3 wherein the reactants from which the aryl-substituted urea is produced comprise p-chlorophenyl isocyanate, p-biphenylyl isocyanate and benzidine.

5. The method of claim 3 wherein the reactants from which the aryl-substituted urea is produced comprise p-tolyl isocyanate, p-phenylene diamine and benzidine.

6. The method of claim 3 wherein the reactants from which the aryl-substituted urea is produced comprise p-biphenylyl isocyanate, p-chlorophenyl isocyanate, p-phenylene diamine, and benzidine.

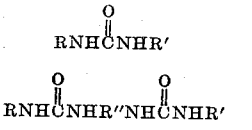
7. The method of manufacturing a lubricant grease comprising a substituted urea-thickened lubricant vehicle which comprises producing in situ in a reaction medium comprising the lubricant vehicle of the grease substituted urea selected from the group consisting of



and mixtures thereof wherein R and R′ represent hydrocarbon radicals selected from the class consisting of aryl, alkyl, and substituted aryl, said aryl radicals having no more than 12 cyclic carbon atoms and said alkyl radicals having from 1 to 30 carbon atoms, and R″ represents a hydrocarbon radical selected from the class consisting of alkylene, arylene, substituted alkylene, and substituted arylene radicals, said alkylene radicals having from 2 to about 20 carbon atoms and said arylene radicals having no more than 12 cyclic carbon atoms, said substituted urea being prepared in an amount sufficient to thicken the amount of lubricant vehicle in which it is prepared, and heating the mixture of substituted urea and lubricant vehicle to a temperature within the range of from about 150° F. to about 450° F. for a period of from about ½ hour to a period of 72 hours.

8. The method of claim 7 wherein the ultimate mixture of substituted urea and lubricant vehicle is milled.

9. The method of manufacturing a lubricant grease comprising a substituted urea-thickened lubricant vehicle which comprises producing in situ in a reaction medium comprising the lubricant vehicle of said lubricant grease and an organic solvent having a boiling point below about 300° F. in which solvent the reactants from which the substituted urea is produced are substantially completely soluble, substituted urea selected from the group consisting of

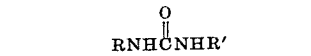


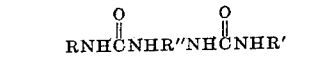
and mixtures thereof where R and R′ represent hydrocarbon radicals selected from the class consisting of aryl, alkyl, and substituted aryl, said aryl radicals having no more than 12 cyclic carbon atoms and said alkyl radicals having from 1 to 30 carbon atoms, and R″ represents a hydrocarbon radical selected from the class consisting of alkylene, arylene, substituted alkylene, and substituted arylene radicals, said alkylene radicals having from 2 to about 20 carbon atoms and said arylene radicals having no more than 12 cyclic carbon atoms, said substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared, and then removing said solvent.

10. The method of claim 9 wherein the ultimate mixture of substituted urea and lubricant vehicle is milled.

11. The method of manufacturing a lubricant grease comprising a substituted urea-thickened lubricant vehicle which comprises producing in situ in a reaction medium comprising the lubricant vehicle of said lubricant grease

and an organic solvent having a boiling point below about 300° F. in which solvent the reactants from which the substituted urea is produced are substantially completely soluble, substituted urea selected from the group consisting of





and mixtures thereof wherein R and R′ represent hydrocarbon radicals selected from the class consisting of aryl, alkyl, and substituted aryl, said aryl radicals having no more than 12 cyclic carbon atoms and said alkyl radicals having from 1 to 30 carbon atoms, and R″ represents a hydrocarbon radical selected from the class consisting of alkylene, arylene, substituted alkylene, and substituted arylene radicals, said alkylene radicals having from 2 to 20 carbon atoms and said arylene radicals having no more than 12 cyclic carbon atoms, said substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared, removing said solvent, and heating the remaining mixture of substituted urea and lubricant vehicle to a temperature within the range of from about 150° F. to about 450° F. for a period of from about ½ hour to a period of 72 hours.

12. The method of claim 11 wherein the ultimate mixture of substituted urea and lubricant vehicle is milled.

13. The method of claim 11 wherein the organic solvent comprises dioxane.

14. The method of claim 11 wherein the solvent comprises 2-butanone.

15. The method of claim 11 wherein the solvent comprises benzene.

16. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises forming in situ, in a reaction medium comprising the lubricant vehicle of said lubricant grease, aryl substituted urea having the general formula



in which R and R′ are aryl radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals, said aryl substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared.

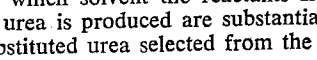
17. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises forming in situ, in a reaction medium comprising the lubricant vehicle of said lubricant grease, aryl substituted urea having the general formula



in which R and R′ are aryl radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals, said aryl substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared, adding additional lubricant vehicle to said urea-thickened lubricant vehicle and heating said resultant mixture to a temperature in the range of from 150° F. to about 450° F. for a period of from ½ hour to about 72 hours.

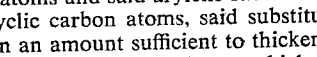
18. The method of claim 17 wherein the ultimate mixture of substituted urea and lubricant vehicle is milled.

19. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises forming in situ, in a reaction medium comprising the lubricant vehicle of said lubricant grease, aryl substituted urea having the general formula

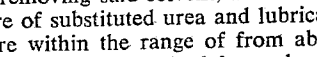


in which R and R′ are aryl radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals, and R″ is a divalent radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals, said aryl substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared.

20. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises forming in situ in a reaction medium comprising the lubricant vehicle of said lubricant grease a mixture of aryl substituted urea having the general formula

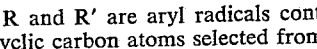


and aryl substituted urea having the general formula



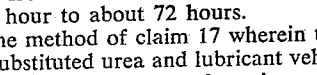
in which R and R′ are aryl radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals and R″ is a divalent radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals, said mixture of substituted ureas being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared.

21. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises producing in situ in a reaction medium comprising the lubricant vehicle of said lubricant grease and an organic solvent having a boiling point below about 300° F. in which solvent the reactants from which the aryl substituted urea is produced is substantially completely soluble, aryl substituted urea having the general formula



in which R and R′ are aryl radicals containing no more than 12 cyclic carbon atoms selected from the group consisting of aryl and substituted aryl radicals, said substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared, heating the mixture of arylurea, lubricant vehicle, and organic solvent to substantially completely remove said solvent, further heating the solvent-free mixture of arylurea and lubricant vehicle to a temperature within the range of from 150° F. to about 450° F. for a period of from ½ hour to about 72 hours, cooling said mixture, and milling said cooled mixture.

22. The method of manufacturing a lubricant grease comprising an aryl substituted urea-thickened lubricant vehicle, which method comprises producing in situ in a reaction medium comprising the lubricant vehicle of said lubricant grease and an organic solvent having a boiling point below about 300° F. in which solvent the reactants from which the aryl substituted urea is produced is substantially completely soluble, aryl substituted urea having the general formula



in which R and R′ are aryl 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 radical containing no more than 12 cyclic carbon atoms selected from the group consisting of arylene and substituted arylene radicals, said substituted urea being prepared in an amount sufficient to thicken to grease consistency the amount of lubricant vehicle in which it is prepared, heating the mixture of arylurea, lubricant vehicle, and organic solvent to substantially completely remove said solvent, further heating the solvent-free mixture of arylurea and lubricant vehicle to a temperature within the range of from 150° F. to about 450° F. for a period of from ½ hour to about 72 hours, cooling said mixture, and milling said cooled mixture.

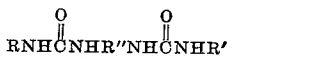
23. The method of manufacturing a lubricant grease comprising an alkyl substituted urea-thickened lubricant vehicle, which method comprises forming in situ, in a reaction medium comprising the lubricant vehicle of said lubricant grease, alkyl substituted urea having the general formula



in which R and R′ are alkyl radicals having from 1 to about 30 carbon atoms, said alkyl substituted urea being

prepared in an amount sufficient to thicken to grease consistency the lubricant vehicle in which it is prepared.

24. The method of manufacturing a lubricant grease comprising an alkyl substituted urea-thickened lubricant vehicle, which method comprises forming in situ, in a reaction medium comprising the lubricant vehicle which of said lubricant grease, alkyl substituted urea having the general formula



in which R and R′ are alkyl radicals having from 1 to about 30 carbon atoms and R″ is selected from the group consisting of alkylene and substituted alkylene radicals having from 2 to about 20 carbon atoms, said alkyl substituted urea being prepared in an amount sufficient to thicken to grease consistency the lubricant vehicle in which it is prepared.

References Cited in the file of this patent

UNITED STATES PATENTS

2,698,300 Hotten ---------- Dec. 28, 1954