

1

3,374,170

GREASE COMPOSITION

John F. Hedenburg, Cheswick, and Chester S. Tempalski, Pittsburgh, Pa., assignors to Gulf Research & Development Company, Pittsburgh, Pa., a corporation of Delaware

No Drawing. Filed Apr. 4, 1966, Ser. No. 539,745
10 Claims. (Cl. 252-28)

This invention relates to an improved lubricating composition and more particularly to a lubricant having the consistency of a grease suitable for high temperature lubrication.

The trend in design of modern aircraft has accentuated the need for a lubricant having the consistency of a grease which will lubricate anti-friction bearings operating at high rotational speeds and high temperatures. Considerable progress has been made in recent years in producing improved thickened lubricants for aircraft. For example, lubricating compositions having the consistency of a grease are now available for lubricating bearings operating at 10,000 to 20,000 revolutions per minute at temperatures up to about 400° F. However, great difficulty has been encountered in producing a lubricating composition having the consistency of a grease which will effectively lubricate bearings operating at speeds up to about 20,000 revolutions per minute and at temperatures up to about 600° F. for prolonged periods of time.

We have discovered that a lubricating composition having improved lubricating characteristics for an extended period of time when used to lubricate bearings operating at temperatures up to about 600° F. and speeds up to about 20,000 revolutions per minute can be obtained by incorporating into a synthetic lubricating oil in oil thickening proportions a polyaryl urea which prior to being incorporated into the oil has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent. Thus, the improved lubricating composition of our invention comprises a dispersion in a synthetic lubricating oil of a sufficient amount to thicken the lubricating oil to a grease consistency of a "heat-treated" polyaryl urea.

The polyaryl urea which is heat-treated prior to use in the composition of the invention is the reaction product of an aryl isocyanate having the formula:



where R is selected from the group consisting of arylene (e.g., phenylene, biphenylene and naphthylene), diphenylmethane and C₁ to C₄ alkyl substituted arylene radicals containing not more than 12 cyclic carbon atoms and n is an integer of 2 to 3 and an aryl amine having the formula:



where R₁ is selected from the group consisting of aryl, alkaryl, aminoaryl, hydroxyaryl, cyanoaryl, haloaryl, alkoxyaryl, aryloxyaryl and aminoaryloxyaryl radicals wherein the alkyl portions of said alkaryl and alkoxyaryl radicals contain from 1 to 4 carbon atoms and m is an integer of 1 to 3, and wherein said reaction product is prepared by reacting the aryl isocyanate and the aryl amine in amounts such that the ratio of the isocyanate groups to the amine groups is within the range of about 1:1 to about 1:2.

In accordance with the invention, the polyaryl urea can be prepared by reacting the aryl isocyanate with one aryl amine or with two or more different aryl amines. Likewise, two or more different aryl isocyanates can be reacted with one aryl amine or with two or more different aryl amines.

2

The polyaryl urea is readily prepared by intimately contacting the aryl isocyanate and the aryl amine, preferably in the presence of an organic solvent such as acetone, methanol, etc., at a temperature within the range of room temperature (about 70° F.) to about 350° F. The aryl isocyanate and the aryl amine are preferably employed in amounts so that the ratio of the isocyanate (—NCO) groups to the amine (—NH₂) groups is within the range of about 1:1 to about 1:2. Thus, if an aryl diisocyanate is reacted with an aryl monoamine, the mole ratio of the aryl diisocyanate to the aryl monoamine is within the range of about 1:2 to about 1:4. If an aryl diisocyanate is reacted with an aryl diamine, the mole ratio of the aryl diisocyanate to the aryl diamine is within the range of about 1:1 to about 1:2. Of course, if an aryl diisocyanate is reacted with a mixture comprising an aryl monoamine and an aryl diamine, the number of moles of the aryl diisocyanate can be equal to or greater than the number of moles of each aryl amine taken singly, provided that the total number of the amine groups is at least equal to, preferably greater than, the total number of the isocyanate groups.

Examples of suitable aryl isocyanates which can be employed in preparing polyaryl ureas for subsequent heat-treatment in accordance with the invention are 1,4-diisocyanato benzene; 1,3-diisocyanato benzene; 1,3,5-triisocyanato benzene; 2,4-tolylene diisocyanate; 2,6-tolylene diisocyanate; 3,5-diisocyanato-t-butyl-benzene; p,p'-diisocyanato biphenyl; 3,3'-dimethylbiphenylene-4,4'-diisocyanate; 3,3'-dibutylbiphenylene-4,4'-diisocyanate; naphthylene diisocyanate; diphenylmethane-4,4'-diisocyanate; 3,3'-dimethyldiphenylmethane-4,4'-diisocyanate; 3,3'-di-t-butylidiphenylmethane-5,5'-diisocyanate; mixtures thereof; etc.

Examples of suitable aryl amines which can be employed in preparing polyaryl ureas for subsequent heat-treatment in accordance with the invention are p-biphenylamine; benzidine; p-anisidine; o-tolidine; p-aminophenol; p-amino-benzonitrile; p-phenylenediamine; m-phenylenediamine; o-phenylenediamine; aniline; p-chloroaniline; p-fluoroaniline; diaminodurene; p-toluidine; o-toluidine; 1,2,4-benzenetriamine; 2,5-dichloroaniline; p,p'-oxydianiline; mixtures thereof; etc.

An especially outstanding polyaryl urea for subsequent heat-treatment in accordance with the invention is obtained by reacting 3,3'-dimethylbiphenylene-4,4'-diisocyanate with a mixture of p,p'-oxydianiline and p-chloroaniline in a mole of about 4:4:1.

In order to stabilize the polyaryl urea for use in compositions of the invention, the polyaryl urea, prior to being incorporated in the oil, is heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce its weight by about 20 to about 40 percent. The heat-treated product thus obtained has a melting point above the polyaryl urea prior to being heat-treated, the melting point of the heat-treated product being above about 400° C. The heat-treated product is a dark brown powder. While we do not wish to be limited to any theory with respect to what happens while heat-treating the polyaryl urea, we believe that some polymerization may take place and/or that some of the lower molecular weight materials are driven off. Regardless of the theory with respect to what happens during the heat-treating step, we have found that a grease composition prepared from a heat-treated polyaryl urea has excellent lubricating characteristics when used to lubricate a bearing operating at a temperature of 600° F. at a speed of 20,000 revolutions per minute.

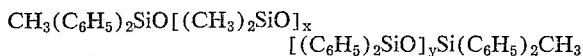
The polyaryl urea used in the composition of our invention is preferably heated at a temperature of about 450° F. until no more vapors are evolved. When no more vapors are formed at 450° F., the temperature of the polyaryl

urea is gradually increased to 600° F. The temperature is then maintained at 600° F. until no further vapors are evolved. The time required to effect a 20 to 40 percent reduction in the weight of the polyaryl urea may vary from less than an hour to one hundred hours or more depending upon the efficiency of the heating method, the amount of polyaryl urea being treated and the degree of agitation during the heating. In any event, we prefer to employ an initial temperature of about 450° and a subsequent temperature of about 600° F. with agitation to effect a 20 to 40 percent reduction in weight in a minimum amount of time.

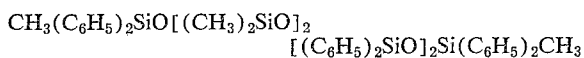
The amount of heat-treated polyaryl urea which we use may vary depending upon the particular lubricating base employed and upon the characteristics desired in the ultimate composition. In any event, the amount of heat-treated polyaryl urea used is an amount sufficient to thicken the lubricating oil to a grease consistency. In general this amount comprises about 10 to about 25 percent by weight of the total composition.

Many of the lubricating characteristics of a thickened lubricant are imparted to the lubricant by the lubricating oil used in preparing the lubricant. Thus, a lubricating oil is required which is thermally stable at temperatures in the order of 600° F. While some lubricating compositions having the consistency of a grease have been prepared by thickening mineral lubricating oils, especially hydrotreated mineral lubricating oils, the volatility of mineral lubricating oils is such that as a general rule they do not give adequate lubrication at temperatures in the order of 600° F. over prolonged periods of time. Synthetic oils are substantially more resistant to thermal degradation than mineral oils. Synthetic oils, particularly the polyorgano siloxanes known as the silicone oils in addition to being more resistant to thermal degradation than mineral oils also have high viscosity indices making their use at high and ambient temperatures especially desirable. Thus, the lubricating oil employed in the composition of this invention is a synthetic lubricating oil.

The synthetic lubricating oil which is employed in the composition of the invention is a liquid polyorgano siloxane having a high phenyl content and diphenylmethylsilyl end groups. The polyorgano siloxanes can be obtained by hydrolyzing and polymerizing a mixture of diphenylmethylchlorosilane, dimethyldichlorosilane and diphenyldichlorosilane preferably in a ratio of 1:1:1, respectively, according to procedures known to those familiar with the art. While the polyorgano siloxanes are generally a mixture of polymers, a general formula representing the polymer mixture by an ideal molecule is as follows:



where x and y can be from 1 to 10 or more. An ideal molecule of a polyorgano siloxane having diphenylmethylsilyl end groups and a molecular weight of 954 is represented by the formula



The polyorgano siloxane content of the compositions prepared according to this invention comprises about 60 to about 90 percent by weight to the total composition.

The lubricating composition of this invention can contain conventional lubricant additives, if desired, to improve other specific properties of the lubricant without departing from the scope of the invention. Thus, the lubricating composition can contain an auxiliary thickening agent, a filler, a corrosion and rust inhibitor, an extreme pressure agent, an antioxidant, a metal deactivator, a dye and the like. Whether or not such additives are employed and the amounts thereof depend to a large extent upon the severity of the conditions to which the composition is subjected and upon the stability of the synthetic lubricating oil base in the first instance. Since the polyorgano

siloxanes, for example, are in general more stable than mineral oils, they require the addition of very little, if any, oxidation inhibitor. When such conventional additives are used they are generally added in amounts between about 0.01 and about 5 percent by weight based on the weight of the total composition.

In those instances when an auxiliary thickening agent such as finely-divided amorphous silica, p-polyphenyl, or a 1,3,5-triazine compound, e.g., ammeline is employed, it is added in amounts of about 0.5 to about 5 percent by weight.

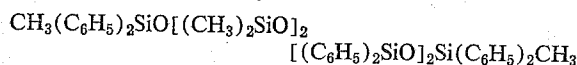
In compounding a composition of the present invention, various mixing and blending procedures may be used. According to one embodiment of the invention, the synthetic lubricating oil, the heat-treated polyaryl urea together with conventional lubricant additives, if desired, are mixed together at room temperature for a period of about 10 to 30 minutes to form a slurry. During this initial mixing period some thickening is evidenced. Some lumps may be formed. The slurry thus formed is then subjected to a conventional milling operation in a ball mill, a colloid mill, homogenizer or similar device used in compounding greases to give the desired degree of dispersion.

In order to illustrate the lubricating characteristics of a grease composition of the invention when used to lubricate bearings operating at 600° F. and at rotational speeds of 20,000 revolutions per minute, Pope spindles were used in a test procedure similar to that outlined by the Coordinating Research Council Tentative Draft (July 1954), "Research Technique for the Determination of Performance Characteristics of Lubricating Grease in Antifriction Bearings at Elevated Temperatures," CRC Designation L-35. According to the CRC L-35 test method, the test bearings are packed with 3.5 cc. (or equivalent weight) of grease. Because of the extremely short life of bearings packed with 3.5 cc. of grease, the present evaluations were made by packing the bearings completely full with about 6 to 8 grams of grease and using either a standard end cap with no additional grease or a special end cap holding a reservoir of about 10 grams of additional grease. The bearing assembly containing an eight-ball SAE No. 204 ball bearing is mounted on a horizontal spindle and is subjected to a radial load of 5 pounds. The portion of the spindle upon which the test bearing assembly is located is encased in a thermostatically controlled oven. By this means the temperature of the bearing can be maintained at a desired elevated temperature which in the tests reported hereinafter was 600° F. The spindle is driven by a constant belt-tension motor drive assembly, capable of giving spindle speeds of 20,000 revolutions per minute. The spindle is operated on a cycling schedule consisting of a series of periods, each period consisting of 20 hours running time and 4 hours shutdown time. The test continues until the lubricant fails. The lubricant is considered to have failed when any one of the following conditions occurs, (1) spindle input power increases to a value approximately 300 percent above the steady state condition at the test temperature; (2) an increase in temperature at the test bearing of 20° F. over the test temperature during any portion of a cycle; or (3) the test bearing locks or the drive belt slips at the start or during the test cycle.

The lubricating oil used in preparing the lubricating composition shown in Table I is a synthetic oil known as QF-6-7024 Fluid which is marketed by Dow-Corning Corporation. QF-6-7024 Fluid is considered to be a methylphenylsiloxane polymer wherein the "end" silicon atoms are substituted to a high degree by two phenyl groups and one methyl group. The material is highly resistant to radiation. QF-6-7024 Fluid has a typical characteristics a viscosity at 100° F. of about 930 to 1030 SUS, a viscosity at 210° F. of about 90 to 100 SUS, a viscosity index of about 108 to 110 and a pour point of +10° to +20° F. It is believed that the types of side chains present

5

and their approximate molar percentages (in brackets) in QF-6-7024 are phenyl (65), methyl attached through silicon to methyl (25) and methyl attached through silicon to phenyl (10). An ideal molecule of a polyorgano siloxane having this analysis is as follows:



The heat-treated polyaryl urea which was used in the composition shown in Table I was prepared according to the following procedure. An aryl amine solution was formed by dissolving 44 grams (0.22 mole) of p,p'-oxydianiline and 6.35 grams (0.05 mole) of p-chloroaniline in 300 ml. of a 2:1 mixture of acetone:methanol. The aryl amine solution thus formed was added slowly with stirring to a dispersion of 66 grams (0.25 mole) of 3,3'-dimethylbiphenylene-4,4'-diisocyanate in 500 ml. of acetone. A precipitate of the polyaryl urea product formed immediately. The reaction mass thus formed was stirred

6

The long performance life of a composition of the invention at a high rotational speed and a high temperature is self-evident from the above data.

Other lubricating compositions within the scope of the invention are illustrated in Table II. The "Cab-O-Sil" employed in the compositions shown in Table II is a finely-divided amorphous silica marketed by Godfrey L. Cabot, Inc. This silica is a submicroscopic particulate silica prepared in a hot gaseous environment (1100° C.) by the vapor-phase hydrolysis of a silicon compound. On a moisture-free basis, this silica is 99.0 to 99.7 percent silicon dioxide which is practically free from contaminating metallic salts. Gravimetric analyses fail to detect the presence of any calcium or magnesium. The iron content has been found to be about 0.004 percent and volatile matter removed on ignition at 1000° C. amounts to less than 1 percent. "Cab-O-Sil" is an extremely fine silica with particles ranging in size from 0.015 to 0.020 micron.

TABLE II

Composition, Percent By Weight	B	C	D	E	F
Lubricating Oil QF-6-7024	75	80	85	85	89
Heat-Treated (450° to 600° F.) Polyaryl Urea:					
1,4-Diisocyanato benzene:p-phenylenediamine (mole ratio 1:1)	25	20			
2,4-Tolylene diisocyanate:p-toluidine (mole ratio 1:2)					
3,5-Diisocyanato-t-butyl-benzene:p-anisidine:1,2,4-benzenetriamine (mole ratio 3:3:1)			15		
1,3,5-Trisocyanato benzene:p-chloroaniline:p-toluidine (mole ratio 1:1:2)				10	
Diphenylmethane-4,4'-diisocyanate:p,p'-oxydianiline:p-chloroaniline (mole ratio 4:4:1)					10
Auxiliary Thickener:					
Ameline				5	
Finely-divided silica					1
Mole ratio of aryl isocyanate:aryl amine	1:1	1:2	1:1.33	1:3	1:1.25
Ratio of isocyanate:amine groups	1:1	1:1	1:1	1:1	1:1.125

¹ Cab-O-Sil.

for about ½ hour. The reaction mass was then filtered, the filter cake being washed with 2:1 acetone:methanol. The product thus obtained was dried. The dried product was a fine white powder of polyaryl urea having a melting point of about 335°-34° C.

The polyaryl urea thus obtained was placed in a stainless steel beaker and heated at 450° F. with intermittent stirring until no more vapors evolved. This required a period of about 15 hours. The temperature was then raised slowly to 600° F. where it was held for an additional 48 hours. The product thus obtained was a dark-brown powder comprising heat-treated polyaryl urea having a melting point above about 400° C. The yield was 65 percent. The total weight loss during the heat-treatment was thus 35 percent.

In preparing the illustrative lubricating composition, the oil and the polyaryl urea were mixed at room temperature for a period of 10 to 30 minutes. The slurry thus formed was passed twice through a Premier Colloid Mill set at a stator-rotor clearance of 0.0015 inch. The approximate make-up and properties of the thickened lubricating composition thus prepared are set forth in Table I.

TABLE I

Composition, percent by weight:	A
Lubricating oil	
QF-6-7024	86.7
Heat-treated (450° to 600° F.) polyaryl urea 3,3'-dimethylbiphenylene-4,4'-diisocyanate:p,p'-oxydianiline:p-chloroaniline (mole ratio 4:4:1)	13.3
Mole ratio of aryl isocyanate:aryl amine	1:1.25
Ratio of isocyanate:amine groups	1:1.125
Inspection:	
Penetration, D-1403—	
Unworked (conv. to D217)	355
Worked (conv. to D217)	355
Dropping point, ° F.	800+
Performance life, hours—	
Average results of two tests at 20,000 r.p.m. and 600° F.	57

While our invention has been described with reference to various specific examples and embodiments, it will be understood that the invention is not limited to such examples and embodiments and may be variously practiced within the scope of the claims hereinafter made.

We claim:

1. A lubricating composition comprising a dispersion in a major amount of a liquid polyorgano siloxane of a small amount, sufficient to thicken the polyorgano siloxane to a grease consistency, of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of an aryl isocyanate having the formula:



where R is selected from the group consisting of arylene and C₁ to C₄ alkyl substituted arylene radicals containing not more than 12 cyclic carbon atoms and n is an integer of 2 to 3 and an aryl amine having the formula:



where R₁ is selected from the group consisting of aryl, alkaryl, aminoaryl, hydroxyaryl, cyanoaryl, haloaryl, alkoxyaryl, aryloxyaryl and aminoaryloxyaryl radicals wherein the alkyl portions of said alkaryl and alkoxyaryl radicals contain from 1 to 4 carbon atoms and m is an integer of 1 to 3 and wherein said reaction product is prepared by reacting the aryl isocyanate and the aryl amine in amounts such that the ratio of the isocyanate groups to the amine groups is within the range of about 1:1 to about 1:2.

2. The lubricating composition of claim 1 wherein the heat-treated polyaryl urea comprises about 10 to about 25 percent by weight of the total composition.

3. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the poly-

7

organo siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of an aryl isocyanate having the formula:



where R is selected from the group consisting of arylene and C₁ to C₄ alkyl substituted arylene radicals containing not more than 12 cyclic carbon atoms and *n* is an integer of 2 to 3 and an aryl amine having the formula:



where R₁ is selected from the group consisting of aryl, alkaryl, aminoaryl, hydroxyaryl, cyanoaryl, haloaryl, alkoxyaryl, aryloxyaryl and aminoaryloxyaryl radicals wherein the alkyl portions of said alkaryl and alkoxyaryl radicals contain from 1 to 4 carbon atoms and *m* is an integer of 1 to 3 and wherein said reaction product is prepared by reacting the aryl isocyanate and the aryl amine in amounts such that the ratio of the isocyanate groups to the amine groups is within the range of about 1:1 to about 1:2 and about 0.5 to about 5 percent by weight of an auxiliary thickening agent selected from the group consisting of finely-divided silica, p-polyphenyl, and ammeline.

4. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of 1,4-diisocyanato benzene and p-phenylenediamine in a mole ratio of 1:1, respectively.

5. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of 2,4-tolylene diisocyanate and p-toluidine in a mole ratio of 1:2, respectively.

6. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of

8

about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of 3,5-diisocyanato-t-butyl-benzene; p-anisidine; and 1,2,4-benzenetriamine in a mole ratio of 3:3:1, respectively.

7. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of 1,3,5-triisocyanato benzene; p-chloroaniline; and p-toluidine in a mole ratio of 1:1:2, respectively.

8. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of diphenylmethane-4,4'-diisocyanate; p,p'-oxydianiline; and p-chloroaniline in a mole ratio of 4:4:1, respectively.

9. A lubricating composition comprising a liquid polyorgano siloxane thickened to a grease consistency with about 10 to about 25 percent by weight of a polyaryl urea which prior to being incorporated into the polyorgano siloxane has been heated to a temperature of about 450° to about 600° F. for a time sufficient to reduce the weight of the polyaryl urea by about 20 to about 40 percent, said polyaryl urea being the reaction product of 3,3'-dimethylbiphenylene-4,4'-diisocyanate; p,p'-oxydianiline; and p-chloroaniline in a mole ratio of 4:4:1, respectively.

10. The lubricating composition of claim 9 wherein the heat treatment at 450° to 600° F. is for a time sufficient to reduce the weight of the polyaryl urea by about 35 percent.

References Cited

UNITED STATES PATENTS

2,710,839	6/1955	Swakon et al.	252—51.5
2,710,840	6/1955	Swakon et al.	252—49.6
3,269,945	8/1966	Hedenburg et al.	252—50

DANIEL E. WYMAN, *Primary Examiner*.

I. VAUGHN, *Assistant Examiner*.