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LUBRICANT GREASE

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This invention relates to lubricant greases, and more particularly concerns a novel ingredient for increasing the yield of certain high temperature greases.

Lubricant greases, comprising a normally liquid lubricant vehicle thickened to grease consistency with normally solid thickening agents, are currently being required to serve under conditions of high temperature and high loads and speeds. Both the lubricant vehicle and the thickening agent must be capable of performing satisfactorily. Until recently, it was the thickening agent rather than the vehicle which had imposed limitations on grease performance.

Recently, it has been discovered that certain arylcarbamyl compounds are outstanding grease thickeners, particularly when used in conjunction with special lubricant vehicles such as the silicone oils (Swakon and Brannen, U.S. Patents 2,710,839, 2,710,840, and 2,710,841). Arylcarbamyl-thickened greases have been widely accepted for high temperature and high load and speed service conditions. However, these thickeners are expensive, which has militated somewhat against their more widespread adoption. It is accordingly a major object of the present invention to provide a yield improver for arylcarbamyl-thickened greases, and hence decrease their cost and increase their availability.

In accordance with the invention, it has now been discovered that the yield of arylcarbamyl greases may be improved substantially by incorporating therein a small amount of trimethylol propane phosphite. By such treatment, greases having equivalent ASTM penetration may be prepared with a substantially reduced content of arylcarbamyl thickening agent or, conversely, greases of equivalent thickening agent content will have substantially lower ASTM penetrations.

Arylcarbamyl compounds suitable as grease thickeners are the high melting aromatic ureas, di-ureas, amides, and di-amides, all of which contain at least one

$$\mathrm{RNH}\overset{O}{\overset{\|}{C}}\text{—}$$

radical, wherein R is an aryl radical. Suitable arylcarbamyl compounds have the following empirical structures:

$$\mathrm{RNH}\overset{O}{\overset{\|}{C}}\mathrm{NHR'} \qquad (1)$$

$$\mathrm{RNH}\overset{O}{\overset{\|}{C}}\mathrm{NHR''NH}\overset{O}{\overset{\|}{C}}\mathrm{NHR'} \qquad (2)$$

$$\mathrm{R}\overset{O}{\overset{\|}{C}}\mathrm{NHR'} \qquad (3)$$

$$\mathrm{R}\overset{O}{\overset{\|}{C}}\mathrm{NHR''NH}\overset{O}{\overset{\|}{C}}\mathrm{R'} \qquad (4)$$

$$\mathrm{RNH}\overset{O}{\overset{\|}{C}}\mathrm{R''}\overset{O}{\overset{\|}{C}}\mathrm{NHR'} \qquad (5)$$

In the above formulae, R, R′ and R″ represent unsubstituted or substituted aryl or alkyl aryl radicals containing no more than 12 carbon atoms. 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. The compound should have a melting point in excess of 250° F.

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′-dibenzoylbenzidine, 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 aroyl halide, e.g. benzoyl chloride. Diamides such as may be prepared by reacting an aromatic monoamine, e.g. aniline, with an aroyl halide such as a phthalyl chloride, 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 are p-carboxy-1,3-diphenylurea; p-chloro-1,3-diphenylurea; 1,3-di-(1-naphthyl)urea; 4,4′-bis-[3-(p-biphenylyl)-ureido]-biphenyl; 1-(p-carboxyphenyl)-3-(p-biphenylyl)-urea; 1-(p-carboxyphenyl) - 3 - (o-biphenylyl)-urea; 1,3-di-(p-biphenylyl)-urea; 1,3-di-(o-biphenylyl)-urea; 4,4′-bis-(3-phenylureido)-3,3′-dimethoxy biphenyl; p-phenylurethan-1,3-diphenyl-urea; p-cyano-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, phenylenediamine, etc. with an isocyanate of benzene, diphenyl, etc. It should be understood that the specific aryl 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.

Superior arylcarbamyl-thickened greases are those ureas (Formula 1 above) and di-ureas (Formula 2 above) which are prepared from a mixture of two different amines and one diisocyanate or a diamine and two mono-isocyanates, as described in U.S. 2,710,840. An especially preferred grease is made from bitolylene diisocyanate, p-chloroaniline, and p-toluidine.

Normally liquid lubricant vehicles, also termed "oleaginous bases," "fluids," etc. which are thickened with the foregoing arylcarbamyl compounds to form greases illustratively include the silicone polymer oils, mineral lubricating oils, synthetic hydrocarbon lubricating oils, synthetic lubricating oils such as polyalkylene glycols and their derivatives, high molecular weight esters of dicarboxylic acids, polyfluoro derivatives or organic compounds such as the trifluorovinyl chloride polymers known as "Fluorolube" and the trifluorochloroethylene polymers known as "Kel-F," and other lubricant vehicles.

The silicone polymer oils which may be employed in conjunction with the present invention are those falling substantially within the lubricating oil viscosity range, e.g. possessing a viscosity at 100° F. within the range of about 25 to about 3500 SSU. These silicone oils are polyalkyl or polyalkaryl siloxanes such as methyl siloxane or methyl phenyl siloxane. Mineral oils in the lubricating oil viscosity range, e.g. from about 50 SSU at 100° F. to about 300 SSU at 210° F., and preferably solvent extracted to substantially remove the low viscosity index constituents, are also suitable. Similarly, 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 typified by 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, azelaic acid, etc., may be thickened to produce excellent greases. Polyfluoro derivatives of organic compounds, particularly hydrocarbons, and dibasic acid esters of $H(CF_2)_nCH_2OH$, in the lubricating oil viscosity range can also be thickened. Other synthetic oils, such as esters of aliphatic carboxylic acids and polyhydric alcohol, e.g. trimethylolpropane tripelargonate and pentaerythritol hexanoate, can be used as suitable oil vehicles. Where the grease product is to be employed under high temperature conditions, e.g. above 400° F., lubricating oil vehicles which are stable, i.e. do not decompose at the temperatures to be encountered, should be used as the vehicle. For such uses, silicone polymers and diesters of dicarboxylic acids are preferred.

The inventive greases ordinarily contain from about 5 to 70% by weight, preferably from about 8 to about 50%, of the arylcarbamyl compound or compounds, together with from about 0.005 to about 2.5 weight percent of the trimethylol propane phosphite. It has been found that grease yield increases markedly with increasing additive concentration until a concentration of about 0.5% is achieved, whereupon further addition effects only a relatively minor increase in yield (decrease in penetration). Thus, from an economic standpoint, the grease advantageously contains about 0.05 to about 1.0 weight percent trimethylol propane phosphite.

Arylcarbamyl-thickened greases may be prepared by any of the methods known in the art, e.g. those described in U.S. 2,710,839. An especially preferred method, described in U.S. 2,710,841, consists in preparing the arylcarbamyl compound by chemical reaction of its ingredients directly in the lubricating oil vehicle. Thus, for example, an arylcarbamyl grease may be prepared 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 wtih 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 may be cooled to about 150–250° F., whereupon the trimethylol propane phosphite and other additives may be added in the desired amount with stirring or other effective agitation. The grease then is cooled to room temperature and milled. The resulting greases are smooth and buttery in texture and have excellent thermal stability. As alternatives to the procedure outlined above, the amine may be dissolved in the lubricant vehicle and the isocyanate added via the solvent, or a solvent may be dispensed with entirely, as for example by the procedure of separately dissolving the reactants in separate portions of lubricant vehicle.

The invention is illustrated in the ensuing examples, which are for the purpose of illustration and are not considered to be wholly definitive with respect to scope and conditions.

Example I

In this example a silicone base vehicle (Dow Corning QF 4039 Silicone Fluid, a high-phenyl type methyl phenyl silicone) thickened with 23.5% of a thickener prepared by reacting bitolylene diisocyanate, p-chloroaniline, and p-toluidine.

The greases are prepared by mixing 12.5% bitolylene diisocyanate, 5.97% p-chloroaniline, 5.01% p-toluidine, and lubricant vehicle, and forming the greases according to the procedure of U.S. Patent 2,710,840 discussed above. During the manufacturing process when the grease has cooled to about 200° F., 0.67% dodecenyl succinic acid is added and, where used, 1.0% trimethylol propane phosphite. The resulting greases are milled, then tested in an ASTM penetration tester.

The grease prepared without trimethylol propane phosphite has an unworked penetration of 300, while that prepared with 1% trimethylol propane phosphite has a penetration of 183. Thus, the yield is increased by more than one-third.

Example II

In this example, greases are made with a pentaerythritol ester of C_6–C_8 fatty acids (Hercolube A, Hercules Powder Company) thickened with 18.95 weight percent of the reaction product of bitolylene diisocyanate and p-chloroaniline. One sample contains one percent by weight of the inventive trimethylol propane phosphite, while the other does not.

The greases in this example are prepared from 9.61 weight percent bitolylene diisocyanate, 9.14% p-chloroaniline, 0.20% of rosin-derived amine, 0.5% phenothiazaine, 0.11% of propylene diamine type metal deactivator, 0.003% blue dye, and the balance Hercolube A.

The ASTM penetration of the grease prepared in the absence of trimethylol propane phosphite is 320; that of the grease prepared with the inventive yield improver is 297.

Example III

Example I is repeated, except that only 0.5% trimethylol propane phosphite is employed. The resultant grease has a penetration of 196.

Thus it is apparent that trimethylol propane phosphite is an outstanding yield improver for arylcarbamyl thickened greases. In addition, the trimethylol propane phosphite imparts excellent high temperature oxidation inhibition to the grease, as well as anti-wear properties and improved lubricity. Furthermore, by permitting a decrease in thickener content, such properties as low temperature apparent viscosity, high-speed high-temperature bearing performance, and steel-on-steel wear characteristics are improved.

The advantages associated with trimethylol propane phosphite are not obtained with other phosphorous compounds. When Example I is repeated with other phosphorous compounds, the resultant grease, which originally has a penetration of 300 without a yield improver, has ASTM penetrations of: 259 with triphenyl phosphite, 276 with dioctodecyl phosphite, 300 with dioctyl phosphite, 241 with phosphoric acid, 293 with dioctyl chloromethane phosphonate.

While the invention has been described in conjunction with specific embodiments thereof, it will be appreciated that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such alternatives, modifications, and variations as fall within the spirit and broad scope of the appended claims.

I claim:

1. A lubricant grease comprising an oleaginous lubricant vehicle thickened to grease consistency with an aryl-carbamyl compound melting above about 250° F., which compound is selected from the group consisting of

$$R\overset{O}{\overset{\|}{C}}NHR'$$

$$R\overset{O}{\overset{\|}{C}}NHR''NH\overset{O}{\overset{\|}{C}}R'$$

$$RNH\overset{O}{\overset{\|}{C}}R''\overset{O}{\overset{\|}{C}}NHR'$$

$$RNH\overset{O}{\overset{\|}{C}}NHR'$$

and

$$RNH\overset{O}{\overset{\|}{C}}NHR''NH\overset{O}{\overset{\|}{C}}NHR'$$

wherein R and R' represent 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 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, and a small amount, effective to decrease the ASTM penetration, of trimethylol propane phosphite.

2. The lubricant grease of claim 1 wherein said amount of trimethylol propane phosphite is in the range of about 0.005–2.5 weight percent.

3. The lubricant grease of claim 1 wherein said aryl-carbamyl compound is prepared from bitolylene diisocyanate and p-chloroaniline.

4. The lubricant grease of claim 1 wherein said aryl-carbamyl compound is prepared from equimolar amounts of bitolylene diisocyanate, p-toluidine, and p-chloroaniline.

5. The lubricant grease of claim 1 wherein said lubricant vehicle is a silicone oil.

6. The lubricant grease of claim 1 wherein said lubricant vehicle is an ester fluid.

7. A method of increasing the yield of a lubricant grease comprising an oleaginous lubricant vehicle thickened to grease consistency with an aryl-carbamyl compound melting above about 250° F., which compound is selected from the group consisting of

$$R\overset{O}{\overset{\|}{C}}NHR'$$

$$R\overset{O}{\overset{\|}{C}}NHR''NH\overset{O}{\overset{\|}{C}}R'$$

$$RNH\overset{O}{\overset{\|}{C}}R''\overset{C}{\overset{\|}{C}}NHR'$$

$$RNH\overset{O}{\overset{\|}{C}}NHR'$$

and

$$RNH\overset{O}{\overset{\|}{C}}NHR''NH\overset{O}{\overset{\|}{C}}NHR'$$

wherein R and R' represent 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 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, which method comprises incorporating in said grease a small amount, effective to decrease the ASTM penetration, of trimethylol propane phosphite.

References Cited in the file of this patent

UNITED STATES PATENTS

2,294,804	Ricketts	Sept. 1, 1942
2,710,839	Swakon et al.	June 14, 1955
2,710,840	Swakon et al.	June 14, 1955
2,710,841	Swakon et al.	June 14, 1955

FOREIGN PATENTS

642,960	Great Britain	Sept. 13, 1950