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3,113,107

LUBRICANT GREASE

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6 Claims. (Cl. 252—51.5)

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 lubrican 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.

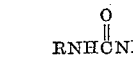
Recently, it has been discovered that certain arylcarbamyl compounds are outstanding grease thickeners, particularly when used in conjunction with special lubricant vehicles such as the silicone oils (Swakon and Brannen, U.S. Patents 2,710,839, 2,710,840, and 2,710,841). Arylcarbamyl-thickened greases have been widely accepted for high temperature and high load and speed service conditions. However, these thickeners are expensive, which has mitigated 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 a polymerized unsaturated fatty acid, for example a polymerized linoleic acid. By such treatment, greases having equivalent ASTM penetration may be prepared with a substantially reduced content of arylcarbamyl thickening agent.

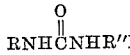
Arycarbamyl compounds suitable as grease thickeners are the high melting aromatic ureas, di-ureas, amides, and di-amides, all of which contain at least one



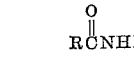
radical, wherein R is an aryl radical. Suitable arylcarbamyl compounds have the following empirical structures:



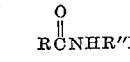
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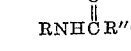
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In the above formulae, R, R' and R'' represent unsubstituted or substituted aryl or alkyl aryl radicals containing no more than 12 carbon atoms. With the exception that R'' is necessarily a divalent radical, e.g. phenylene, biphenylene, naphthylene, 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-diphenyl-urea; 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 monoisocyanates, as described in U.S. 2,710,840.

Normally liquid lubricant vehicles, also termed "oleaginous bases," 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 of 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 yield-improving additive, as noted earlier, is a polymerized unsaturated fatty acid, preferably one which is oil-soluble and has a molecular weight in the range of from about 300 to about 2000. These are advantageously employed in the free acid form, since it has been found that compounds of polymerized unsaturated fatty acids are markedly inferior to the free acid.

The polymerized fatty acids or polymerization products of the unsaturated fatty acids are those such as may be obtained by the polymerization of natural or synthetic mono-carboxylic acids which generally will have 16 to 26 carbon atoms, most frequently 18 carbon atoms, but if synthetic unsaturated fatty acids are used they may have a lesser or greater number of carbon atoms. Examples of the natural fatty acids are those such as linoleic, linolenic, ricinoleic (which upon heating forms linoleic acid), linoleaidic, elaido-linolenic, eleostearic, arachidonic, eicosatrienoic, cetoleic, docosatrienoic and the like. The free fatty acids can be polymerized either thermally or with the assistance of catalysts. A method of thermally polymerizing free fatty acids (see U.S. 2,482,761) consists of hydrolyzing a fat or an oil, adding a small portion of water, and heating in a pressure vessel until substantially all of the di- and tri-unsaturated fatty acids present polymerize. The resultant product is then heated at a reduced pressure to distill off vaporizable constituents, leaving behind the polymerized unsaturated fatty acids. The polymerization reaction is carried out at a temperature of about 300° to 360° C. for about 3 to 8 hours at a pressure varying between 75 and 500 p.s.i.g. The polymerization product may consist of monomers, dimers, trimers, and higher polymers of the unsaturated fatty acids. The various fats or oils which may be hydrolyzed to produce the free fatty acids used in the above thermal polymerization are those such as sardine oil, linseed oil, soybean oil, castor oil, peanut oil, palm oil, olive oil, cottonseed oil, sunflower seed oil, and the like.

Another method of preparing the polymerized fatty acids consists of subjecting fats and oils such as have been listed supra (without previous hydrolysis) to a thermal or catalytic polymerization to cause polymerization of the esters of the unsaturated carboxylic acids to the dimers, trimers, and higher polymerization products thereof followed by hydrolysis to yield the corresponding polymers of the acids. A large source of the polymerized unsaturated fatty acids are those residual acids obtained by methanolysis (see U.S. 2,450,940) of the semi-drying or drying type oils such as castor oil, soybean oil, and others listed supra, polymerizing the methyl esters, removing unpolymerized compounds, saponifying the residual esters and freeing polymerized acids therefrom. The products of catalytic polymerization of semi-drying oils such as the BF_3 polymerization products of soybean oil, cottonseed oil, or the like also produce polymers suitable for use in the invention.

It should be understood that while various polymerized unsaturated fatty acids may be used, they do not all provide the same effect, and indeed there may be pronounced differences when used in the composition of this invention. A highly preferred source of the polymerized unsaturated faty acids is obtained as a by-product still residue in the manufacture of sebacic acid by the dry distillation of castor oil in the presence of sodium hydroxide. A method of obtaining such by-product still residues in the manufacture of sebacic acid is described in U.S. 2,470,849 issued to W. E. Hanson May 24, 1949. The mixture of high molecular weight unsaturated fatty acids comprises monomer, dimer, trimer and higher polymers in the ratio of from about 45% to about 55% of a monomer and dimer fraction having a molecular weight in the range of from about 300 to 600 and from about 45% to about 55% of a trimers and higher polymer fraction having a molecular weight in excess of 600. The fatty acid polymers result in part from a thermal polymerization of fatty acid type constituents of the castor oil, and in part from other reactions such as the inter-molecular esterification of such acid to form high molecular weight products. The acid mixture, which is mainly a mixture of polymeric long chain polybasic carboxylic acids, is further characterized by the following specifications:

Acid No.	150 to 164
Saponification No.	175 to 186
Free fatty acids—percent	75 to 82
Iodine value	44 to 55
Non-saponifiables —percent	2.5 to 5

A fatty acid mixture such as above described is marketed under the trade name Hardesty "D–50 Acids" and also as "VR–1 Acids."

The polymerization products of the unsaturated fatty acids may have a molecular weight between about 400 and 2000. Those polymers having a molecular weight higher than about 500, and especially those having molecular weight averaging about 800 or higher are particularly preferred for use in this invention. The polymerization products may consist primarily of dimers and trimers of linoleic acid, for example Emery 955 dimer acid which contains 85% of the dimer, 12% of the trimer, and 3% of the monomer of linoleic acid may be used. Especially preferred polymerized unsaturated fatty acids are the polymerization products of acids such as linoleic acid having a molecular weight between about 300 and 2000, wherein the polymerization products consist predominantly (50% or more by weight) of the dimer, with lesser amounts of monomer, trimer, etc. A commercially available predominantly-dimer polymerized linoleic acid is Empol 1022, manufactured by Emery Industries, Inc.

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 polymerized unsaturated fatty acid. It has been found that grease yield increases markedly with increasing acid 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 polymerized unsaturated fatty acid.

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 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 may be cooled to about 150–250° F., whereupon the polymerized unsaturated fatty acid is 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 heated portions of lubricant vehicle and then mixing the portions.

As an example of the present invention, several greases are prepared utilizing a phenyl methyl silicone polymer (Dow-Corning 550 Silicone Fluid) which has a viscosity at 100° F. of about 300 to about 400 SSU. The greases are thickened with an arylcarbamyl compound composed of equimolar amounts of bitolylene diisocyanate, p-toluidine, and p-chloroaniline, which are reacted in situ at a temperature of about 400–500° F. and permitted to react for about three hours. When the grease is cooled to 200° F., the desired amount of Empol 1022 polymerized linoleic acid is added, and the final grease is milled. The following results are obtained:

Sample—	ASTM penetration, unworked
Grease	300
Grease+0.5% acid	214
Grease+1.0% acid	203
Grease+2.0% acid	192

It will be observed that the addition of about 0.5–2.0 weight percent acid decreased the penetration by approximately one-third. In other words, by means of the present invention, greases of the same penetration can be made with one-fourth less arylcarbamyl compound.

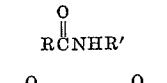
In addition to its function as a yield improver or extender for arylcarbamyl thickeners, the polymerized unsaturated fatty acid increases the thermal and high-load stability of the grease and also serves as an antirust compound.

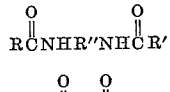
The greases of the present invention may contain added constituents such as additional antirusts, antioxidants, oiliness agents, extreme pressure additives, etc., without in any way departing from the scope of the present invention.

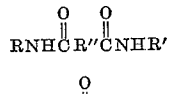
While the invention has been described in conjunction with certain specific embodiments thereof, it will be evident that many alternatives, modifications, and variations will be apparent to those skilled in the art in light of the foregoing description. Accordingly, it is intended to embrace all such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

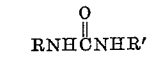
I claim:

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:

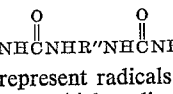








and



wherein R and R′ represent radicals containing no more than 12 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 an oil soluble polymer of an unsaturated fatty acid having from 16 to 26 carbon atoms, said polymer having a molecular weight below about 2,000.

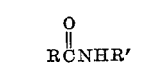
2. The grease of claim 1 wherein said amount is in the range of about 0.005–2.5 weight percent.

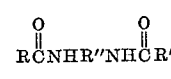
3. The grease of claim 1 wherein said polymer of an unsaturated fatty acid is a polymer of linoleic acid.

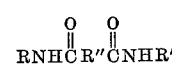
4. The grease of claim 3 wherein said polymer of linoleic acid is predominantly the dimer.

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

6. The method of decreasing the ASTM penetration 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:

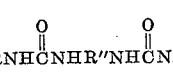








and



wherein R and R′ represent radicals containing no more than 12 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 comprises incorporating therein a small amount, effective to decrease the ASTM penetration, of an oil soluble polymer of an unsaturated fatty acid having from 16 to 26 carbon atoms, said polymer having a molecular weight below about 2,000.

References Cited in the file of this patent

UNITED STATES PATENTS

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

OTHER REFERENCES

"Manufacture and Application of Lubricating Greases," by Boner, Reinhold Pub. Corp., New York, 1954, pages 46–49 and 142.