United States Patent Office 3,269,951 Patented August 30, 1966

3,269,951

HIGH TEMPERATURE GREASE

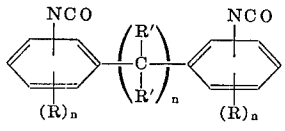
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No Drawing. Filed Feb. 3, 1964, Ser. No. 342,273
12 Claims. (Cl. 252—49.6)

This invention relates to lubricant greases and particularly relates to a novel grease thickener for lubricant greases destined for high temperature service.

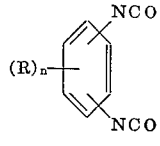
I have now discovered that greases possessing outstanding high temperature properties and mechanical stability may be prepared with a thickener comprising the reaction product of an aromatic diisocyanate and a phenyl azoaniline compound. Such preparation is advantageously effected in the presence of a lubricant base or vehicle, and a particular advantage of the inventive composition is that a wide variety of lubricant bases may be employed therewith.

The aromatic diisocyanate reactant may be any one of the diisocyanates having at least one aromatic ring in the molecule. Biphenylene diisocyanates having the following structural formula:



constitute particularly desirable aromatic diisocyanates. In the foregoing formula *n* is an integer of 0–4, R is an alkyl group of 1 to 18 carbon atoms, a phenyl group, halogen, or mixtures thereof, and R′ is hydrogen or an alkyl group of 1–4 carbon atoms. Examples of biphenylene diisocyanates include bitolylene diisocyanate (3,3′-bitolylene - 4,4 - diisocyanate), diphenylmethane-4,4′-diisocyanate, 3,3′-dimethylidiphenylmethane-4,4′-diisocyanate, xylenyl diisocyanate, diphenylxylenyl diisocyanate, etc. Substituted diphenylene diisocyanates such as dianisidine diisocyanate and dichloroxenylene diisocyanate may also be employed. The preferred aromatic diisocyanate reactant is bitolylene diisocyanate (3,3′-bitolylene-4,4′-diisocyanate).

Monophenylene diisocyanates may similarly be used. These compounds have the general formula

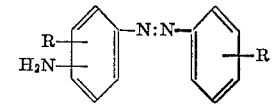


where R is an alkyl group of 1–4 carbon atoms and *n* is 0–4. The R's may be the same or different alkyl groups. Examples of monophenylene diisocyanates include the tolylene diisocyanates, which are available as 65 percent of the 2,4 isomer and 35 percent of the 2,6 isomer, as 80 percent of the 2,4 isomer and 20 percent of the 2,6 isomer, or 100 percent of the 2,4 isomer. Other monophenylene diisocyanates include metaphenylene diisocyanate, 2,4-tolylene diisocyanate dimer, and xylylene diisocyanate. Substituted monophenylene diisocyanates are also suitable, and these include methoxyphenylene diisocyanate, phenoxyphenylene diisocyanate, and chlorophenylene diisocyanate.

Polynuclear aromatic diisocyanates such as naphthalene diisocyanates may also be employed.

Phenyl azoaniline compounds are the other reactants necessary for preparing the inventive compositions. These

compounds generally have the following structural formula:



wherein R is hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen, or mixtures thereof. Examples of alkyl phenyl azoalkylaniline compounds include 4-(o - tolylazo) - o - toluidine, p-tolylazo-4-o-toluidine, p-ethylphenylazo-4-m-toluidine, o-ethylphenylazo-4-o-toluidine, 4-phenylazo-1-naphthylamine, etc.

Oleaginous lubricant vehicles or bases which can be thickened with the inventive reaction products can be any of the known lubricants. In one embodiment the lubricant is advantageously prepared by reacting the aromatic diisocyanate with the phenyl azoaniline compound in situ in such a lubricant base. The reaction product can conveniently be prepared in this manner by making separate solutions or dispersions of diisocyanate in lubricant base and phenyl azoaniline compound in another portion of the base material. The two separate solutions are then brought into contact in the presence of a catalyst material. Suitable catalysts are trialkyl amines having the following formula:

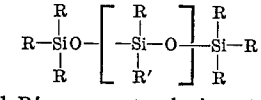


wherein R is an alkyl group of 1–8 carbon atoms. Catalysts of this type include amine compounds such as trialkyl amines, e.g. triethyl amine which is preferred. In addition to amines, heterocyclic amines, such as pyridine, may be employed; phosphines may also be employed as catalyst materials. The reaction is carried out over a wide variety of conditions. For reasons of convenience the reaction may advantageously be carried out at room temperature and atmospheric pressure. The reactants are suitably reacted in proportions to give a ratio of 1 to 2 moles of phenyl azoaniline compound to 1 mole of aromatic diisocyanate. Preferably the reactants are contacted with each other in the ratio of 1 mole of phenyl azoaniline compound to 1 mole of aromatic diisocyanate.

Lubricant vehicles suitable for use according to the present invention are silicone polymer oils, mineral lubricating oils, synthetic hydrocarbon lubricating oils, synthetic lubricating oils such as the 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," etc. may be used.

Greases prepared with thickeners of the type described above, particularly those prepared from silicone oil, are exceptionally stable at elevated temperatures.

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 methods, e.g. the hydrolysis of dialkyldichlorosilanes or dialkyldiethoxysilanes with a suitable chain stopper, e.g. a trisubstituted mono-chlorosilane. For purposes of the present invention, those polymers which are high boiling liquids within the lubricating oil viscosity range are suit-

able, these generally possessing a viscosity at 100° F. which is within the range of from about 25 to about 3500 S.S.U. It is preferred, for purposes hereof, to employ such oils as have a viscosity at 100° F. of from about 300 S.S.U. to about 1250 S.S.U. Such products are generally colorless and inert, have a very low volatility and undergo relatively slight change in viscosity for a given change in temperature. Relatively common oils of this type are 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. Also advantageous is Dow-Corning QF–6–7024 fluid typically having a viscosity at 77° F. of 600 S.S.U. and a viscosity of 20 S.S.U. at 210° F.

Other oleaginous vehicles which may be employed herewith are, for example, mineral oils in the lubricating oil viscosity range, i.e. from about 80 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 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. In addition synthetic ester vehicles and polyphenyl polysiloxanes may also be employed.

The lubricant vehicles herein described may be thickened to grease consistency typically by the addition thereto of from about 5 to about 70 percent by weight and preferably from about 5 to about 50 percent by weight of the aromatic diisocyanate-phenyl azoaniline reaction product.

Greases of the present invention may be produced by one of the following methods:

(1) The thickener may be prepared apart from and then admixed with the lubricant vehicle and milled in a colloid mill, 3-roll mill, etc.

(2) The thickener may be formed in situ in the oil by introducing the reactants and the desired amount of lubricant vehicle, heating to about 450° F. for a relatively short time, e.g. from about five minutes to an hour to drive off volatile by-products, and then cooling and milling the mixture.

(3) As a slight modification of method 2 above, a solvent such as dioxane may be employed as a diluent and mutual solvent for the reactants. The solvent is then evaporated and the grease is milled, etc. substantially as set forth.

(4) As a step in any of the above three methods, it has been found, when employing a silicone vehicle, that improved properties may be imparted to the grease by "heat-treating" the grease mixture, i.e. subjecting same to a temperature of about 450° F. for at least about half an hour and preferably longer, e.g. from about 1 to 30 hours. Prolonged heating at such temperature may evaporate a portion of the lubricant vehicle; this loss should be replaced and then the mixture should be milled. If desired, the heating and readdition of vehicle may be repeated before milling.

The thickening compositions of the present invention are surprisingly efficient and they can be used to make greases which are stable at high temperatures. To demonstrate the efficiency of greases thickened with phenyl azoniline-aromatic diisocyanate reaction products a number of grease compositions were prepared and tested. Table 1 sets forth penetration data on the inventive compositions.

TABLE 1

	Thickener			Oil	Grease		
	Reactants		Proportions, mole		Thickener, wt., percent	Penetration*	
	Azo Compound	Diisocyanate				Unworked	Worked
A	4-(o-tolylazo)-o-toluidine	Bitolylene diisocyanate	2:1	DC-550	15	198	
B	do	do	2:1	DC-550	12.5	240	
C	do	do	2:1	DC-550	10.7	272	
D	do	do	2:1	DC-550	9.4	308	
E	do	do	1:1	DC-550	9.5	321	329
F	do	do	1:1	QF-6-7024	10	288	308
G	do	do	2:1	DC-550	9.5	353	361
H	p-Phenylazoaniline	do	1:1	DC-550	15	333	357
I	do	do	2:1	DC-550	15	369	369

*ASTM D-217.

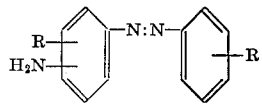
A grease composition was prepared by thickening Dow-Corning 550 fluid with 9.5% of the product of reacting 4-(o-tolylazo)-o-toluidine and bitolylene diisocyanate. The grease was heat treated at 450° F. for 21 hours. Leakage loss for this composition after 24 hours at 450° F. was 6 weight percent. Evaporation loss after 24 hours at 450° F. was 2 weight percent. This composition was also employed to lubricate a lightly loaded antifriction bearing operated at a temperature of 450° F., under 50 pounds radial and 25 pounds axial loads at 10,000 r.p.m. The apparatus and test procedures used were in accordance with Coordinators Research Council test CRC L–35–59, the technique for which was developed and published by The Coordinators Research Council, 30 Rockefeller Plaza, New York 20, New York. In this test the bearing was successfully operated for 583 hours before failure. In addition at 543 hours of operation the bearing was heated to 600° F. for a period in excess of 1 hour. The same bearing test was run on two similar grease compositions prepared in the same manner except that one formulation contained 8 weight percent thickener and the other contained 10 weight percent thickener. Temperature at which the bearing test was conducted on these two compositions was 600° F. At this extremely high temperature the grease containing 8 weight percent thickener ran for 114 hours without failure and the grease containing 10 weight percent thickener ran for 116 hours without failure.

Greases of the present invention may have added there-

to anti-oxidants, oiliness agents, extreme pressure additives, etc., without in any way departing from the scope of the present invention.

Thus having described the invention, what is claimed is:

1. As a new composition of matter the product of reacting a phenyl azoaniline compound having the following structural formula:



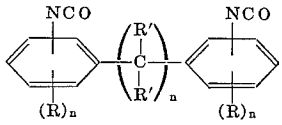
wherein R is selected from the group consisting of hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen and mixtures thereof, with an aromatic diisocyanate in the ratio of from about 1 to about 2 moles of phenyl azoaniline compound per mole of aromatic diisocyanate.

2. The composition of claim **1** wherein said reacting is carried out in the presence of a catalyst having the following formula:

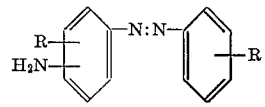


wherein R is an alkyl group of 1–8 carbon atoms.

3. As a new composition of matter the product of reacting an aromatic diisocyanate having the following structural formula:



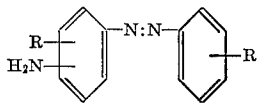
wherein *n* is an integer of 0–4, R is selected from the group consisting of an alkyl group of 1 to 18 carbon atoms, a phenyl group, halogen, and mixtures thereof; and R′ is selected from the group consisting of an alkyl group of 1–4 carbon atoms and hydrogen; and a phenyl azoaniline compound having the following structural formula:



wherein R is selected from the group consisting of hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen, and mixtures thereof, in the ratio of from about 1 to about 2 moles of phenyl azoaniline compound per mole of aromatic diisocyanate.

4. The product of reacting 4-(o-tolyl-azo)-o-toluidine and bitolylene diisocyanate in the ratio of from about 1 to about 2 moles of 4-(o-tolyl-azo)-o-toluidine per mole of bitolylene diisocyanate.

5. A lubricant grease comprising an oleaginous lubricant vehicle thickened to grease consistency with the product of reacting a phenyl azoaniline compound having the following structural formula:



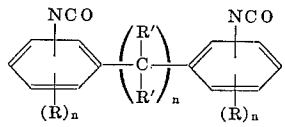
wherein R is selected from the group consisting of hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen and mixtures thereof, with an aromatic diisocyanate in the ratio of from about 1 to about 2 moles of phenyl azoaniline compound per mole of aromatic diisocyanate.

6. The composition of claim **5** wherein said reacting is catalyzed by a catalyst having the following structural formula:

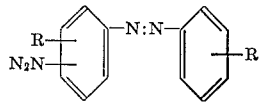


wherein R is an alkyl group of 1–8 carbon atoms.

7. A lubricant grease comprising an oleaginous lubricant vehicle thickened to grease consistency with the product of reacting an aromatic diisocyanate having the following structural formula:

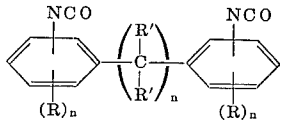


wherein *n* is an integer of 0–4, R is selected from the group consisting of an alkyl group of 1 to 18 carbon atoms, a phenyl group, halogen, and mixtures thereof; and R′ is selected from the group consisting of an alkyl group of 1–4 carbon atoms and hydrogen; and a phenyl azoaniline compound having the following structural formula:

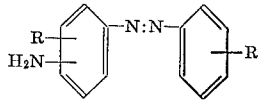


wherein R is selected from the group consisting of hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen, and mixtures thereof, in the ratio of from about 1 to about 2 moles of phenyl azoaniline compound per mole of aromatic diisocyanate.

8. A lubricant grease comprising an oleaginous vehicle thickened with an amount of from about 5 to about 70 percent by weight of the product of reacting an aromatic diisocyanate having the following structural formula:



wherein *n* is an integer of 0–4, R is selected from the group consisting of an alkyl group of 1 to 18 carbon atoms, a phenyl group, halogen, and mixtures thereof; and R′ is selected from the group consisting of an alkyl group of 1–4 carbon atoms and hydrogen; and a phenyl azoaniline compound having the following structural formula:



wherein R is selected from the group consisting of hydrogen, an alkyl group of 1–18 carbon atoms, a phenyl group, halogen, and mixtures thereof, in the ratio of from about 1 to about 2 moles of phenyl azoaniline compound per mole of aromatic diisocyanate.

9. The lubricant grease of claim **8** wherein the oleaginous lubricant vehicle comprises a silicone polymer oil in the lubricating oil viscosity range.

10. A lubricant grease comprising a silicone polymer oil in the lubricating oil viscosity range thickened with from about 5 to about 70 percent by weight of the product of reacting 4-(o-tolyl-azo)-o-toluidine and bitolylene

diisocyanate in the ratio of from about 1 to about 2 moles of 4-(o-tolyl-azo)-o-toluidine per mole of bitolylene diisocyanate.

11. The composition of claim **1** wherein said reacting is carried out in the presence of a heterocyclic amine catalyst.

12. The composition of claim **5** wherein said reacting is carried out in the presence of a heterocyclic amine catalyst.

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