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3,002,928

REACTION PRODUCT OF A DIISOCYANATE AND AN ALKYL AMINE SALT OF AN ALKYL AMIDE OF ALKYL ORTHO PHOSPHORIC ACID AND LUBRICATING OIL THICKENED WITH SAME

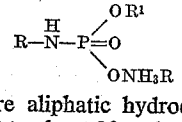
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15 Claims. (Cl. 252—49.9)

This invention relates to new additive agents for high temperature lubricants and grease compositions containing the same. More particularly this invention pertains to compositions of matter suitable for use as gelation or thickening agents in thermally stable greases for use under high temperature conditions and greases thickened with the same.

As lubricating greases are required for use at higher and higher temperatures because of increased speeds of engines and machines, the advent of jet propulsion, atomic energy as a power source, etc. it has become increasingly difficult to prepare greases fulfilling such requirements. In attempting to provide high temperature greases the art has progressed from the use of petroleum lubricant vehicles thickened with metal soaps of long chain fatty acids, eg. lithium hydroxy stearate, to more thermally stable synthetic lubricating oils such as the aliphatic diesters of dicarboxylic acids, silicone polymers, etc., thickened with soaps or inorganic materials such as silica gels. The more thermally stable oleaginous lubricant vehicles developed in recent years are able to withstand high working temperatures because of their thermal stability and relatively low volatility. However, the progress of grease thickener research has not in general kept pace with the development of lubricant vehicles. At temperatures as high as 400–450° F. there are few, if any, greases available which will retain their consistency for a substantial period of time.

I have found certain new compositions which are useful as grease thickeners in lubricant oils and which provide a high degree of thermal stability to greases, thereby allowing them to retain their consistency at temperatures as high as about 250 to about 450° F. In accordance with the present invention the new compositions of matter provided are reaction products of a diisocyanate with an alkyl amine salt of an alkyl amide of alkyl ortho phosphoric acid, hereinafter referred to as "alkyl amine salt." Such "alkyl amine salts" have the following formula:



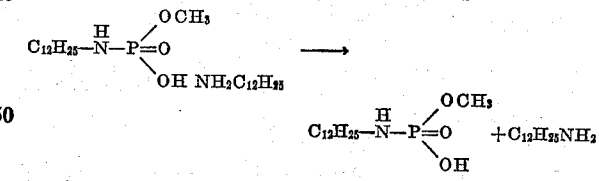
Wherein the R's are aliphatic hydrocarbon substituents having from about 8 to about 20 carbon atoms and preferably from about 12 to about 18 carbon atoms and R^1 is an organic water solubilizing substituent such as an alkyl radical having less than 5 carbon atoms, an alcohol or a glycerol. The "alkyl amine salts" useful within this invention are those disclosed by W. H. Woodstock in U.S. Patent 2,406,423. The preparation of the "alkyl amine salts" may be by the method therein disclosed by Woodstock. Of particular preference are the commercially prepared salts such as, for example, "Victamine C," "Victamine D," "Victamine G," and "Victamine K" as produced by the Victor Chemical Works. "Victamine C" is the lauryl amine salt of the lauryl amide of ethyl orthophosphoric acid and "Victamine G" is an analogue of "Victamine C." "Victamine D" is the stearyl amine salt of the stearyl amide of ethyl orthophosphoric acid and corresponds to the above formula wherein the R's are stearyl groups and R^1 is ethyl. "Victamine K" is an analogue of "Victamine D" and is prepared from a mixture of predominantly saturated C_{18} primary amines so

that the R's of the above formula correspond to saturated C_{18} groups while R^1 represents ethyl.

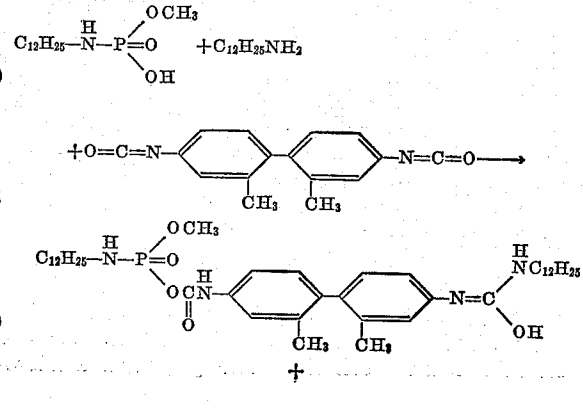
The diisocyanates which are used to react with the alkyl amine salts above to form the reaction products of the invention are those compounds which have at least 2 isocyanate radicals. Examples of suitable diisocyanates are toluene diisocyanate, p,p'-diisocyanate biphenyl, 1,4 - diisocyanate - benzene, p,p' - diisocyanate - diphenylmethane, 1,6 - diisocyanate - hexane, 1,12 - diisocyanate-dodecane, 1,3,5-benzene-triisocyanate, naphthylene diisocyanate, bitolylene diisocyanate, tris-p-isocyanate-phenylmethane, etc.

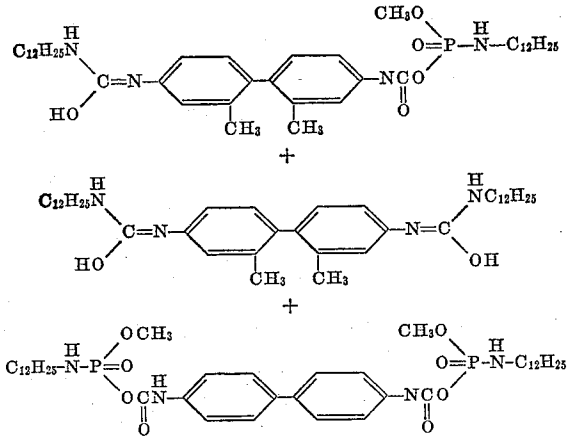
The reaction products of this invention are prepared by admixing the "alkyl amine salt" with an oleaginous lubricant vehicle or solvent or diluent and slowly heating the mixture to a temperature above about 100° F., advantageously in the range of about 150° F. to about 450° F. and preferably in the range from about 200° F. to about 350° F. and then adding about 0.5 to about 2.0 and preferably from about 0.8 to about 1.2 moles of the diisocyanate per mole of salt. The reaction mixture is maintained within the above temperature range until the reaction is complete. The reaction proceeds rapidly within a short period of time. We have found that 10 minutes is usually sufficient within the preferred reaction temperature range; however, much longer reaction times must be used if needed. The reaction mixture is then cooled and milled.

Although I do not wish to be held to any theories regarding the reaction between an alkyl amine salt of an alkyl amide of alkylorthophosphoric acid and a diisocyanate I believe that the reaction is explained by the following typical example: approximately equimolar amounts of bitolylene diisocyanate and the lauryl amine salt of the lauryl amide of methyl orthophosphate are charged to a solvent extracted mineral lubricating oil in a reaction vessel and heated to about 150° F. for 10 minutes. A mixture of reaction products of unknown structure is formed. Although the structures of the products are not known, it is believed the reaction proceeds in two steps to form products which may resemble those structures set out below. In the first step, it is believed that the amine salt of the lauryl amide of methyl orthophosphate may decompose into a primary amine and a phosphate ester with an acidic —OH group as follows:



In the second step, the primary amine and the phosphate ester may then react with the two isocyanate groups of the bitolylene diisocyanate to form a mixture of products such as those shown by the unbalanced equation below:

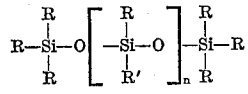




The reaction is advantageously carried out in the presence of a sufficient amount of an oleaginous lubricant vehicle to form a thickened grease containing from about 2 to about 25, and preferably from about 5 to about 15 weight percent of the reaction product thickening agent. Therefore, from about 75 to about 98, and preferably from about 85 to about 95, weight percent of an oleaginous lubricant vehicle is advantageously used in the reaction mixture.

Oleaginous lubricant vehicles which can be used in accordance with this invention to form grease products can be 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 shown as "Fluorolube" (made by Hooker Chemical Company), the trifluoroethylene polymers, and other lubricant vehicles.

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 diethoxysilanes with a suitable chain stopper, e.g. a trisubstituted monochlorosilane. 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 either the phenylmethylsilicone or the chlorophenylmethylsilicone 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 Saybolt Universal viscosity at 100° F. of about 300 to about 400 seconds. Another suitable silicone polymer is a chlorophenylmethylsilicone marketed as GE 81406 by General Electric Company.

Other oleaginous vehicles which may be empolyed 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 ethers 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 by the reaction products of the present invention to produce excellent greases. Polyfluoro derivatives of organic compounds, particularly hydrocarbons, and dibacic acid esters of $H(CF_2)_nCH_2OH$, in the lubricating oil viscosity range can be thickened with compounds of the present invention. Other synthetic oils, such as esters of aliphatic carboxylic acids and polyhydric alcohol, e.g. trimethylolpropane pelargonate, pentaerythritol hexanoate, can be used as suitable oil vehicles. Where the grease product is to be employed under high temperature conditions lubricating oils which are stable, i.e. do not decompose, at the temperatures to be encountered should be used as the lubricant vehicle. For such uses, it is preferred to use oils such as silicone polymers, fluorocarbons and the like.

Rather than preparing the grease thickeners of this invention as component parts of a thickened grease, it may be desirable to prepare grease thickener addition agents. Such addition agents are readily prepared by using a solvent or diluent which is capable of being removed after the reaction in lieu of using the oleaginous lubricant vehicle recited above. After the reaction, the solvent or diluent is removed leaving the thickening agent. Such addition agents may also be prepared from the above prepared thickened greases; accordingly, the thickened grease prepared above is washed with a solvent such as hexane or heptane to remove the lubricating oil leaving the reaction product as an insoluble. It may be desirable to produce such thickening agents with the oleaginous lubricant vehicle removed for purposes of storing, such as where space is limited. The addition agents may then later be added to oleaginous lubricant vehicles in amounts of about 2 to about 25 weight percent and preferably from about 5 to about 15 weight percent to form a finished grease.

Also concentrates of greases containing the grease thickener may be formed by reducing the amount of oleaginous lubricant vehicle in the reaction mixture to provide a thickener concentration within the range of from about 25 to about 65 weight percent of the total reaction mixture. If the reaction mixture is too thick for convenient handling, a suitable solvent or diluent may be added and later removed after the reaction. Such concentrates of greases may be used to prepare grease compositions containing the amounts of thickener set out above by dilution of the concentrate with an oleaginous lubricant vehicle.

The grease products containing the grease thickener and concentrates thereof can contain one or more well known addition agents suitable under the conditions of use to impart desired properties thereto, such as, by way of example, antioxidants, extreme pressure agents, corrosion inhibitors, anti-leak agents, anti-foam agents, graphite, molybdenum sulfide, etc.

To further illustrate this invention the following specific examples of thickened grease compositions were prepared and tested as indicated below for suitability of use at high temperatures.

Example 1

4.5 g. of "Victamine K" were admixed with 93.5 g. of a phenol extracted SAE 40 mineral lubricating oil. The mixture was slowly heated in a reaction vessel to a temperature ranging from 300 to 310° F. and 2.0 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature ranging from 300 to 310° F. for about 10 minutes. The resulting material was cooled and milled to produce a finished grease product.

Example 2

4.0 g. of "Victamine K" were admixed with 94.0 g. of Dow-Corning Silicone Oil 550. The mixture was slowly heated in a reaction vessel to a temperature ranging from 300° to 310° F. and 2.0 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature ranging from 300 to 310° F. for about 10 minutes. The resulting material was cooled and milled to produce a finished grease product.

Example 3

6.0 g. of "Victamine K" were admixed with 91.0 g. of Dow-Corning Silicone Oil 550. The mixture was slowly heated in a reaction vessel to a temperature ranging from 300° to 310° F. and 3.0 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature ranging from 300 to 310° F. for about 10 minutes. The resulting material was cooled and milled to produce a finished grease product.

Example 4

5.0 g. of "Victamine K" were admixed with 93.0 g. of a phenol extracted SAE 40 mineral lubricating oil. The mixture was slowly heated in a reaction vessel to a temperature ranging from 300 to 310° F. and 2.0 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature ranging from 300 to 310° F. for about 10 minutes. The resulting material was cooled and milled to produce a finished grease product.

Example 5

7.0 g. of "Victamine C" were admixed with 85 g. of diethyl hexyl sebacate. The mixture was slowly heated in a reaction vessel to 300° F. and 8.0 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature of about 300° F. for five minutes. The resulting mixture was cooled and milled to produce a finished grease product.

Example 6

11.6 g. of "Victamine C" were admixed with 85 g. of trimethylol propyl pelargenate. The mixture was slowly heated in a reaction vessel to 300° F. and 3.4 g. of bitolylene diisocyanate were added. The reaction mixture was maintained at a temperature of about 300° F. for five minutes. The resulting mixture was cooled and milled to produce a finished grease product.

Example 7

4.9 g. of "Victamine D" and 93.0 g. of a phenol extracted SAE 40 mineral lubricating oil were mixed in a beaker. The mixture was heated to 310° F. 2.1 g. of bitolylene diisocyanate were then added and the reaction mixture was held at about 310° F. for 5 minutes. The resulting mixture was cooled and roll milled to produce a finished grease product.

Example 8

4.9 g. of "Victamine D" and 93.0 g. of a phenol extracted SAE 40 mineral lubricating oil were mixed in a beaker. The mixture was heated to 200° F. and 2.1 g. of bitolylene diisocyanate were added. The reaction mixture was held at about 200° F. for 5 minutes, cooled and roll milled to produce a finished grease product.

The unworked and worked penetration values for the above example were determined by ASTM Method 217–52T and the drop points of the examples were determined by ASTM Method D566–42. The data from the two ASTM tests are reported in Table 1.

TABLE 1

Example	Unworked Penetration [1]	Worked Penetration [1]	Drop Point, ° F.
1	346	369	470+
2	342	356	470+
3	293	289	465+
4	337	333	470+
5	329	337	400+
6	349	357	400+
7	288	292	400+
8	308	312	400+

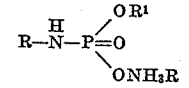
[1] Penetrations determined on a ¼ size cone and converted.

The only slight variations between unworked penetration and worked penetration in the above tests demonstrates the consistency of the greases hereinabove described The high drop points obtained demonstrate the suitability of such greases for use at temperatures even up to about 450° F.

It is evident from the above disclosure and illustrations that I have provided grease thickening agents, thickened grease compositions and a method for their preparation, which thickened grease compositions have excellent penetration characteristics and a high drop point enabling their use for excellent lubrication at elevated temperatures.

Therefore, I claim:

1. As a composition of matter, the product obtained by reacting at a temperature in the range between about 100° F. and about 450° F. from about 0.5 to about 2.0 moles of an organic diisocyanate with one mole of a compound corresponding to the formula:



wherein R is an alkyl radical having from about 8 to about 20 carbon atoms and R^1 is a water solubilizing radical.

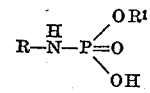
2. The composition of claim 1 wherein said diisocyanate and said compound are reacted in a mole ratio of from about 0.8:1.0 to about 1.2:1.0, diisocyanate: said compound.

3. The composition of claim 1 wherein the diisocyanate is bitolylene diisocyanate and R has from about 12 to about 18 carbon atoms.

4. The composition of claim 3 wherein R has 12 carbon atoms.

5. The composition of claim 3 wherein R has 18 carbon atoms.

6. As a composition of matter, the lubricating grease product obtained by reacting an alkyl amine and a compound corresponding to the formula:



wherein R is an alkyl radical having from 8 to about 20 carbon atoms and R^1 is a water solubilizing radical selected from the class consisting of an alkyl radical having less than 5 carbon atoms, an alcohol and a glycerol with an organic diisocyanate at a temperature in the range of from about 150° F. to about 450° F. in the presence of a normally liquid oleaginous lubricant vehicle for a period of time sufficient to form a reaction product of said alkyl amine and said compound with said diisocyanate in said oil.

7. The composition of claim 6 wherein said reaction product constitutes from about 2 to about 25 weight percent of the composition.

8. The composition of claim 6 wherein said normally liquid oleaginous lubricant vehicle is an ester lubricating fluid.

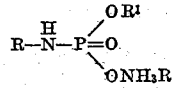
9. The composition of claim 6 wherein said diisocyanate and said compond are in a molar ratio of from about 0.8:1.0 to about 1.2:1.0, diisocyanate: said compound.

10. The composition of claim 6 wherein the organic diisocyanate is bitolylene diisocyanate.

11. The composition of claim 10 wherein R has 12 carbon atoms.

12. The composition of claim 10 wherein R has 18 carbon atoms.

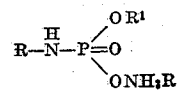
13. As a composition of matter, the lubricating grease concentrate obtained by reacting in admixture with a normally liquid oleaginous lubricant vehicle a compound corresponding to the formula:



wherein R is an alkyl radical having from about 8 to about 20 carbon atoms and R^1 is a water solubilizing alkyl radical having from 1 to 4 carbon atoms inclusive with an organic diisocyanate at a temperature in the range of from about 200° F. to about 350° F. to obtain a reaction product of said compound and said diisocyanate in said oil, wherein the mole ratio of said diisocyanate to said compound in from 0.8:1.0 to about 1.2:1.0 and the total weight of said reaction product is from about 35 weight percent to about 75 weight percent of the total composition.

14. The composition of claim 13 wherein said oil is a silicone lubricating oil.

15. The method of thickening lubricating oils to form lubricating grease compositions having excellent consistency and high temperature drop point properties, which method comprises admixing with a normally liquid lubricating oil a compound corresponding to the formula:



wherein R is an alkyl radical having from about 8 to about 20 carbon atoms and R^1 is a water solubilizing group, subjecting the resulting mixture to a temperature in the range of from about 100° F. to about 450° F., adding from about 0.5 to about 2.0 moles of an organic diisocyanate to said mixture per mole of said compound, mainaining the resulting reaction mixture at a temperature in the range of from about 100° F. to about 450° F. for a period of time sufficient to form a reaction product of said compound with said diisocyanate in said oil, cooling said reaction product in said oil, and milling said reaction product in said oil whereby said lubricating grease composition is formed.

References Cited in the file of this patent

UNITED STATES PATENTS

2,406,423	Woodstock	Aug. 27, 1946
2,898,300	Norton et al.	Aug. 4, 1959

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 3,002,928 October 3, 1961

Stephen J. Zajac

It is hereby certified that error appears in the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 7, line 28, for "in" read -- is --.

Signed and sealed this 3rd day of April 1962.

(SEAL)
Attest:

ERNEST W. SWIDER
Attesting Officer

DAVID L. LADD
Commissioner of Patents