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2,880,177

LUBRICATING GREASES THICKENED WITH BENZIDINE DIAZO COMPOUNDS

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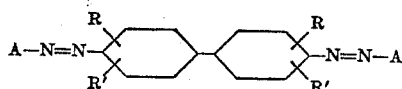
9 Claims. (Cl. 252-49.9)

This invention relates to lubricating greases and to a

novel class of thickening agents therefor. More particularly it relates to lubricating greases thickened with compounds of a class of high melting diazo compounds.

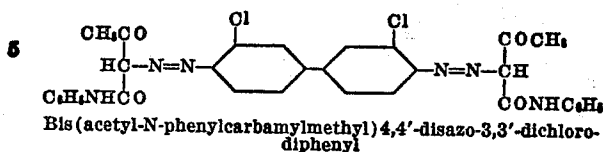
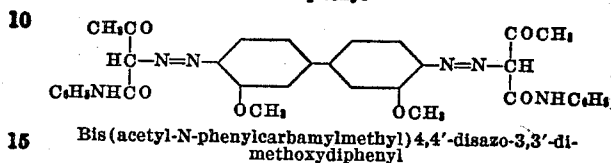
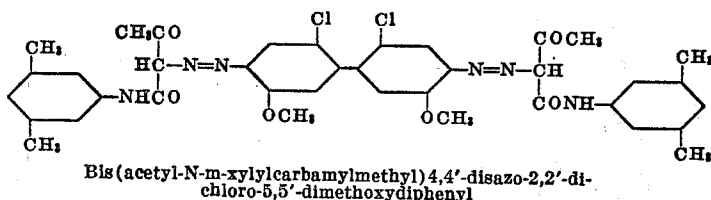
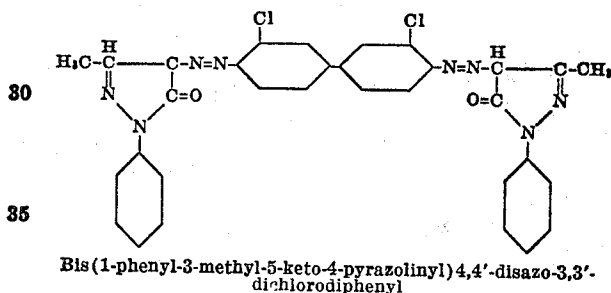
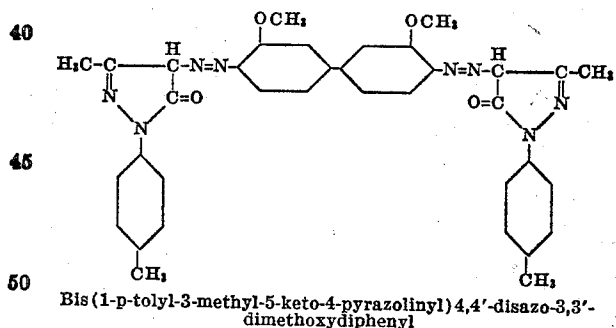
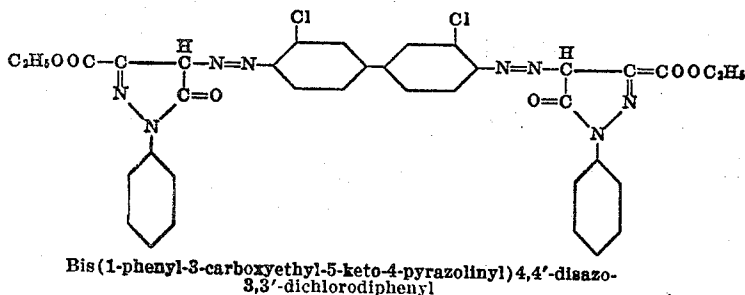
We have found that compounds of a class of diazotized benzidine derivatives form stable gels of grease-like consistency, having very superior lubricating properties, when they are dispersed in lubricating oils in suitable proportions. In particular, high temperature performance properties are obtained in these compositions which are greatly superior to those obtainable in the conventional soap-thickened greases, and also to those obtainable in other non-soap thickened greases of the prior art, containing finely divided solids of other types having the property of thickening lubricating oils to a grease consistency.

The diazo compounds which are employed as thickening agents in the greases of this invention are compounds represented by the general formula



wherein A is chosen from the group consisting of acylacet-arylamine and N-arylpyrazolone radicals and their substituted derivatives, and R and R' are hydrogens or —CH₃, —OCH₃, or Cl substituents. The acylacet-arylamine and N-arylpyrazolone radicals may contain sub-

able compounds which are commercially available include the following:



stituents of various types such as alkyl, aryl, alkaryl, aralkyl groups, —OR'', —COOR'', —OH, —NO₂, —NH₂, —NHR'', —NR''R''', halogens, etc., where R'' and R''' are alkyl or aryl groups.

The above class of compounds includes the familiar Benzidine Yellows and Vulcan Fast Reds, which are employed extensively as rubber pigments. Particularly suit-

Additional examples of compounds of this class which may be employed as thickening agents in accordance with this invention include the following:

Bis(acetyl-N-phenylcarbamylmethyl) 4,4'-disazodiphenyl; bis(acetyl-N-phenylcarbamylmethyl) 4,4'-disazo-3,3'-dichlorodiphenyl; bis(propionyl-N-phenylcarbamylmethyl) 4,4'-disazo-3,3'-dimethoxydiphenyl; bis(butyryl-

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N-phenylcarbamylnmethyl)4,4'-disazo-3,3'-dichlorodiphenyl; bis(acetyl-N-o-chlorophenylcarbamylnmethyl)4,4'-disazodiphenyl; bis(acetyl-N-1-naphthylcarbamylnmethyl)4,4'-disazo-3,3'-dichlorodiphenyl; bis(acetyl-N-o-bromophenylcarbamylnmethyl)4,4'-disazo-3,3'-dimethoxydiphenyl; bis(acetyl-N-m-xylylcarbamylnmethyl)4,4'-disazo-3,3'-dimethoxydiphenyl; bis(acetyl-N-o-tolylcarbamylnmethyl)4,4'-disazo-3,3'-dimethyldiphenyl; bis(acetyl-N-2,5-dichlorophenylcarbamylnmethyl)4,4'-disazodiphenyl; bis(acetyl-N-xenylcarbamylnmethyl)4,4'-disazo-3,3'-dichlorodiphenyl; bis(acetyl-N-o-nitrophenylcarbamylnmethyl)4,4'-disazo-3,3'-dimethoxydiphenyl; bis(acetyl-N-o-methoxyphenylcarbamylnmethyl)4,4'-disazo-3,3'-dichlorodiphenyl; bis(acetyl-N-2,4,6-trimethylphenylcarbamylnmethyl)4,4'-disazo-3,3'-dichlorodiphenyl; bis(acetyl-N-phenylcarbamylnmethyl)4,4'-disazo-2,2',5,5'-tetrachlorodiphenyl; bis(acetyl-N-o-chlorophenylcarbamylnmethyl)4,4'-disazo-2,2'-dichloro-5,5'-dimethoxydiphenyl; bis(1-phenyl-3-methyl-5-keto-4-pyrazolynyl)4,4'-disazo-3,3'-dimethyldiphenyl; bis(1 α -naphthyl-3-ethyl-5-keto-4-pyrazolynyl)4,4'-disazo-2,2'-dichloro-5,5'-dimethyldiphenyl; bis(1-phenyl-3-carboxymethyl-5-keto-4-pyrazolynyl)4,4'-disazo-3,3'-dimethyldiphenyl; bis(1-p-ethylphenyl-3-methyl-5-keto-4-pyrazolynyl)4,4'-disazo-3,3'-dimethoxydiphenyl; bis(1-m-xylyl-3-butyl-5-keto-4-pyrazolynyl)4,4'-disazo-2,2',5,5'-tetrachlorodiphenyl; bis(1-o-chlorophenyl-3-phenyl-5-keto-pyrazolynyl)4,4'-disazodiphenyl; bis(1-p-bromophenyl-3-ethyl-5-keto-4-pyrazolynyl)4,4'-disazodiphenyl; bis(1-o-hydroxy-p-nitrophenyl-3-methyl-5-keto-4-pyrazolynyl)4,4'-disazo-3,3'-dichlorodiphenyl.

The above compounds are either commercially available or readily obtainable by well known methods involving diazotizing benzidine or a substituted benzidine and then coupling the diazotized product with a suitable acylacetarlamide or N-arylpyrazolone, as described for example in German Patent 251,479 (1912).

The compounds are employed in finely divided form, ordinarily in the form of particles below about one micron in diameter, and preferably below about 0.5 micron in diameter, which may be obtained either by suitably controlling the crystallization conditions during the preparation, or by fine grinding. They may be employed either in pure form or in the form of the so-called reduced toners, wherein the compounds are deposited upon particles of inert inorganic materials such as SiO₂, Al₂O₃, TiO₂, BaSO₄, clay, etc. Generally such materials will be present only in minor amounts, such as up to about 10 percent by weight, but larger amounts, up to about 25 percent by weight or higher, may be present if desired. In addition, the compounds may contain small amounts, such as up to about 5 percent by weight, of various metal salts, particularly metal chlorides such as zinc chloride, ferric chloride, stannic chloride, and cadmium chloride, which may enter into the crystal structure in some manner which is not entirely understood when such salts are present in the reaction mixture during the crystallization.

The greases of this invention comprise essentially lubricating oils containing sufficient amounts of thickening agents of the type described above to impart at least substantial thickening. Ordinarily the composition will contain from about 5 to about 45 percent by weight of a thickening agent of this type, and preferably about 15 to about 35 percent by weight of such thickening agent, based on the weight of the composition.

The grease preparation may be carried out by merely mixing together the thickener and additives, if any, with the lubricating oil, employing any convenient means to obtain a thorough dispersion of the thickener and additives in the lubricating oil base such as by milling in a colloid mill or in a paint mill. The mixing may be carried out at ordinary or at elevated temperatures up to about 300° F. if desired in order to dissolve any difficulty soluble additives.

The lubricating oils employed in these greases may be

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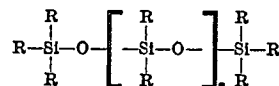
any suitable oils of lubricating characteristics, including the conventional mineral lubricating oils, synthetic oils obtained by various refinery processes, such as cracking and polymerization, and other synthetic oleaginous compounds. Suitable mineral oils include paraffinic and naphthenic oils, particularly those having viscosities in the range from about 100 to about 600 seconds SU at 100° F. The preferred class of lubricating oils are the silicone oils, which may be employed in accordance with this invention to produce greases having superior high temperature performance properties at temperatures above about 400° F. Other synthetic oils, such as high molecular weight ethers and esters, including particularly the dicarboxylic acid esters, may be employed very advantageously to produce greases for operation at moderately elevated temperatures in the range from about 300° F. to about 400° F. Synthetic oils of these types may very advantageously comprise about 50-100 percent by weight of the oil component of the grease, the remainder being mineral oils or other oils of different types.

A particularly suitable class of dicarboxylic acid ester oils are those disclosed by R. T. Sanderson in U.S. 2,628,974, obtained by reacting dibasic aliphatic acids with glycols and end blocking the reaction products with monohydric aliphatic alcohols or monocarboxylic aliphatic acids. The preferred materials of this character are products obtained by reacting a mono- or polyalkylene glycol with a dicarboxylic acid and a monohydric alcohol, represented by the formula



wherein R is an aliphatic group or an aliphatic ether group containing from 4 to 12 carbon atoms, R₁ is an aliphatic group containing from 1 to 12 carbon atoms, and x is an integer from 1 to 5.

The silicone oils are compounds having the general formula



wherein R represents alkyl, aryl, alkaryl or aralkyl groups, which may be the same or different, and n is a number sufficient to give a viscosity in the lubricating oil range to the compound, preferably a viscosity in about the range from 70 to 900 seconds Saybolt Universal at 100° F. Suitable compounds of this type include dimethyl silicone polymer, diethyl silicone polymer, methylcyclohexyl silicone polymer, diphenyl silicone polymer, methylethyl silicone polymer, methyltolyl silicone polymer, etc. These materials may be prepared by various methods, including the hydrolysis of hydrolyzable organic-substituted silanes, as described, for example, in U.S. 2,410,346 and U.S. 2,469,888.

Additives of the usual types may be employed in these greases, such as, for example, oxidation inhibitors, corrosion inhibitors, tackiness agents, extreme pressure agents, and so forth. An oxidation inhibitor is preferably employed, which may be suitably an inhibitor of the amine type, such as diphenylamine, alphanaphthylamine, beta-naphthylamine, p-phenylene diamine, or N,N' diphenyl-p-phenylene diamine. A compound of this type may be present in amounts from about 0.5 to about 5 percent by weight based on the weight of the composition. Very advantageously the composition may also contain about 1-10 percent by weight of an oil-soluble phosphorus acid ester, which may serve as a carrier and dispersing agent for the amine inhibitor. Also, additional thickening agents may be employed, such as other finely divided solids of various types and metal soaps of high molecular weight fatty acids, such as are conventionally employed in lubricating greases.

The following examples are given for the purpose of more fully disclosing the invention.

Example 1

A grease was prepared having the following composition in percent by weight:

Bis(acetyl - N - o - tolylcarbamybmethyl)4,4'-disazo-3,3'-dichlorodiphenyl	20.0
Diphenyl-p-phenylenediamine	1.0
Tricresyl phosphate	3.0
Mineral oil	5.0
Synthetic ester	71.0

The bis(acetyl - N - o - tolylcarbamybmethyl)4,4'-disazo-3,3'-dichlorodiphenyl was a concentrated pigment in the form of a powder having an average particle size of about 0.01-0.15 micron in diameter.

The synthetic ester was obtained by reacting together sebacic acid, 2-ethylhexane-1,3-diol, and 2 ethylhexanol in about a 2:1:2 ratio, respectively, and consisting predominantly of the compound $(\text{iso-C}_8\text{H}_{17})-\text{OOC}-(\text{CH}_2)_8-\text{COO}-\text{iso-C}_8\text{H}_{16}-\text{OOC}-(\text{CH}_2)_8-\text{COO}-(\text{iso-C}_8\text{H}_{17})$.

The mineral oil was a refined paraffinic distillate oil having a viscosity of about 330 seconds Saybolt Universal at 100° F.

The grease was prepared by mixing together the components with an electric stirrer and finishing by milling with two passes through a Premier Colloid Mill at 0.002 inch clearance. The diphenyl-p-phenylenediamine was added to the initial mixture in the form of a solution in the tricresyl phosphate. A smooth yellow grease was obtained having excellent lubricating properties generally, including superior high temperature performance properties, as shown by the following tests:

Dropping point, °F	500+
Working stability, penetration at 77° F.:	
After 60 strokes	311
After 100,000 strokes	341
ASTM bomb oxidation test, 100 hrs. at 210° F., lbs. pressure drop	4
Dynamic water resistance, percent loss	5
High temperature performance test, hrs. at 400° F.	139

¹ $\frac{1}{8}$ size worker, $\frac{1}{4}$ size cone.

The high temperature performance test of the foregoing table is a test for determining the performance characteristics of greases in antifriction bearings at elevated temperatures and high rotative speeds. The test unit consists essentially of a steel spindle supported on ball bearings in an electrically heated housing and driven by an electric motor connected into an electric circuit containing a low amperage fuse 0.1 ampere below that required for full load running. The bearings are Norm-Hoffman ABEC No. 3 grade, and are mounted on a spindle approximately $\frac{5}{16}$ inches apart. A thrust load of 17.5 pounds is applied to the bearings. One bearing is used for test purposes and the second bearing, which is not heated, is used as a guide bearing. The test consists of operating the test bearing for twenty-four hours at 10,000 r.p.m. and at a temperature of from 250° F. to 450° F. followed by a shutdown and cooling period of two hours, and repeating this cycle until the lubricant fails, which is indicated by rupture of the low amperage fuse in the motor circuit. In carrying out the test at 400° F. or above, Marlin Rockwell special heat treated high speed tool steel bearings with silver plated bronze retainers are used. In starting up the test, three grams of the test grease are charged to the test bearing and worked into and around the races and balls. The bearing is next rotated both clockwise and counterclockwise for one minute each at 200 r.p.m. and assembled into the test unit. The heaters and the motor are then started and the test bearing brought up to the test temperature as rapidly as possible, which requires 1.0 to 1.25 hours, while the spindle is rotated at a speed of 10,000 r.p.m.

After 24 hours of operation the heaters and motors are shut off for 2 hours, during which the temperature of the test bearing drops to a minimum of 120-130° F. The total hours of operation, excluding the two hour shutdown periods, to the failure point is recorded as the "hours to failure."

Example 2

A grease was prepared consisting of a silicone polymer oil thickened with 20 percent by weight, based on the weight of the composition, of bis(acetyl-N-phenylcarbamybmethyl)4,4'-disazo-3,3'-dichlorodiphenyl in the form of a powder having an average particle size of about 0.01-0.15 micron in diameter and a measured surface area of about 85 square meters per gram. It contained 1.31 percent of zinc in the form of a soluble zinc salt.

The silicone polymer oil was a commercial product sold by Dow Corning, Inc. under the trade name of DC-550, having a methyl-phenyl ratio of about 0.6 and a viscosity in the range from about 300 to about 400 seconds SU at 100° F.

The grease preparation was carried out by mixing the oil and thickener and finishing by one pass through a Premier Colloid Mill at 0.002 inch clearance. A soft smooth yellow grease was obtained having a dropping point of over 500° F. and an ASTM worked penetration of 345.

This grease ran for 968 hours at 400° F. in the high temperature performance test described above. This is far in excess of the high temperature performance life obtained with the best solids thickened greases of the prior art. For example, a grease of the same grade, consisting of DC-550 thickened with 30 percent by weight of finely divided indigo, ran for only 378 hours at 400° F. in this test under the same conditions.

Example 3

A grease was prepared consisting of a mineral lubricating oil thickened with 20 percent by weight, based on the weight of the composition, of a pyrazolone pigment, identified as bis(1-phenyl-3-methyl-5-keto-4-pyrazolinyl)4,4'-disazo-3,3'-dimethoxydiphenyl. The mineral lubricating oil was a refined naphthene base distillate oil having a viscosity Saybolt Universal of about 310 seconds at 100° F.

The grease preparation was carried out as described in Example 1. A smooth red grease was obtained giving the following test results:

Dropping point, °F	500+
Working stability, A.S.T.M. penetration at 77° F.:	
After 60 strokes	284
After 100,000 strokes	335
A.S.T.M. bomb oxidation test, 100 hrs. at 210° F., lbs. pressure drop	9-12
Dynamic water resistance, percent loss	0

Example 4

As a further example of the greases of this invention, a grease having the combination of high dropping point, water resistance and superior thermal stability at temperature up to about 400° F. is obtained by means of the following composition in percent by weight:

Bis(1 - phenyl - 3 - methyl - 5 - keto - 4 - pyrazolinyl)4,4' - disazo - 3,3' - dichlorodiphenyl	20.0
Diphenyl-p-phenylenediamine	1.0
Tricresyl phosphate	3.0
Mineral oil	5.0
Synthetic ester	71.0

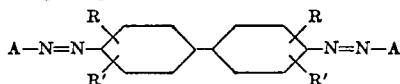
The synthetic ester and mineral oil are as described in Example 1.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and there-

fore, only such limitations should be imposed as are indicated in the appended claims.

We claim:

1. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with a compound having the general formula

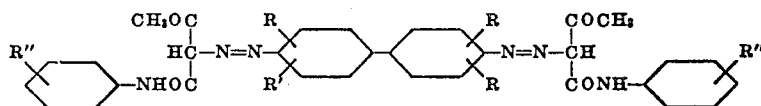


wherein A is chosen from the group consisting of acylacetarlamide, N-arylpyrazolone, and substituted acylacetarlamide and N-arylpyrazolone groups, and R and R' are chosen from the group consisting of hydrogen, methyl, methoxy and chlorine.

2. The grease composition of claim 1 wherein the said lubricating oil comprises a silicone polymer oil having a viscosity in the lubricating oil viscosity range.

3. The grease composition of claim 1 wherein the said lubricating oil consists essentially of a methylphenyl silicone polymer having a viscosity in the range from about 300 to about 400 seconds SU at 100° F.

4. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with a compound having the formula

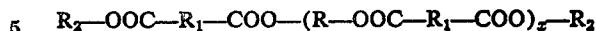


wherein R and R' are chosen from the group consisting of hydrogen, methyl, methoxy and chlorine, and R'' is hydrogen or one or more lower alkyl groups.

5. The grease composition of claim 4 wherein the said lubricating oil comprises about 50-100 percent of a methylphenyl silicone polymer oil having a viscosity in the range from about 70 to about 900 seconds SU at 100° F.

6. The grease composition of claim 4 wherein the said

lubricating oil comprises about 50-100 percent of a polyester represented by the general formula



wherein R is selected from the group consisting of aliphatic groups and aliphatic ether groups containing from 4 to 12 carbon atoms, R₁ is an aliphatic group containing from 1 to 12 carbon atoms, R₂ is an aliphatic group containing from 1 to 12 carbon atoms, and x is an integer from 1 to 5.

7. The grease composition of claim 4 wherein the composition contains about 0.5-5 percent by weight of an amine oxidation inhibitor and about 1-10 percent by weight of an oil-soluble phosphorus acid ester.

8. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with bis(acetyl-N-phenylcarbamyldimethyl)4,4'-disazo-3,3'-dichlorodiphenyl.

9. A lubricating grease consisting essentially of a methylphenyl silicone polymer having a viscosity of from about 300 to about 400 seconds SU at 100° F. thickened to a grease consistency by about 15-35% by weight based on the weight of the composition of bis(acetyl-N-

phenylcarbamyldimethyl)4,4'-disazo-3,3'-dichlorodiphenyl.

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