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2,851,418

LUBRICATING GREASES THICKENED WITH 3-N-ARYL - CARBAMYL - 2 - HYDROXY - 1 - NAPHTHYLENAZOARENES

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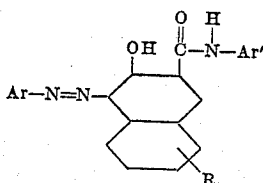
No Drawing. Application December 28, 1956
Serial No. 631,031

8 Claims. (Cl. 252—49.6)

This invention relates to improved lubricating greases, and more particularly to lubricating greases thickened with compounds of a class of high melting azo compounds.

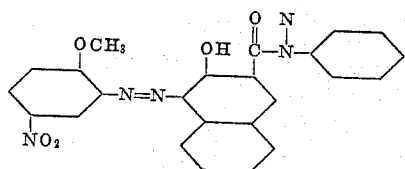
We have found that compounds of a class of arylazonaphthol compounds, which are more specifically described as 3-N-arylcarbaryl-2-hydroxy-1-naphthaleneazoarenes, form gels of grease-like consistency and very superior lubricating properties generally when they are dispersed in lubricating oils in suitable proportions.

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

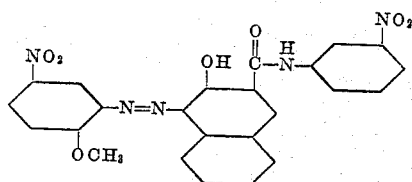


wherein Ar and Ar' are aryl groups, preferably phenyl or naphthyl groups, or substituted aryl groups, and R represents hydrogen or one or more substituent radicals. Substituents represented by R, and which may also be present in the aryl groups represented by Ar and Ar', are preferably substantially neutral, non-salt forming groups such as, for example, alkyl, aryl, alkaryl, ether, ester, aldehyde, amino, hydroxy, nitro groups and halogens.

The compounds of the above class are high melting solids, having the properties of pigments. They are either commercially available or readily produced by well known methods involving coupling diazotized arylamines with arylides of 3-hydroxy-2-naphthoic acids (Naphthol AS). Particularly suitable compounds which are commercially available include the following:

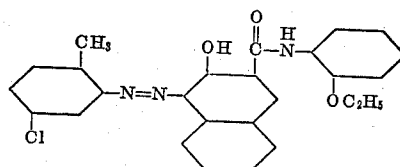


3-N-phenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-methoxy-5'-nitrobenzene

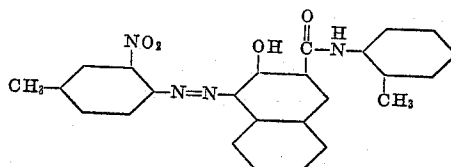


3-N-m-nitrophenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-methoxy-5'-nitrobenzene

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3-N-o-ethoxyphenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-methyl-5'-chlorobenzene



3-N-o-methylphenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-nitro-4'-methylbenzene

Additional examples of suitable compounds of this class which may be mentioned include the following: 3-N- α -naphthylcarbaryl-2-hydroxy-1-naphthaleneazobenzene; 3-N-p-ethylphenylcarbaryl-2-hydroxy-6,7-dichloro-1-naphthaleneazo-2',5'-dichlorobenzene; 3-N-phenylcarbaryl-2-hydroxy-5-nitro-1-naphthaleneazo- α -naphthene; and 3-N-o-chlorophenylcarbaryl-2-hydroxy-5-methyl-7-nitro-1-naphthaleneazo-2',4',6'-trimethylbenzene.

The above compounds may be employed either in pure form or in the form of the so-called reduced toners, wherein the compounds are precipitated upon particles of inert inorganic materials such as SiO_2 , Al_2O_3 , TiO_2 , BaSO_4 , 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.

The greases of this invention comprise essentially a lubricating oil containing sufficient amounts of a thickening agent of the class 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.

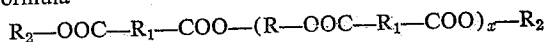
The grease preparation may be carried out by merely mixing together the thickener and any additives employed with the lubricating oil, employing any convenient means such as milling in a colloid mill or in a paint mill to obtain a thorough dispersion of a thickener and additives in the lubricating oil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

The lubricating oils employed may be 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 having viscosities in the range from about 80 seconds SU at 100° F. to about 225 seconds SU at 210° F., and preferably those having viscosities in the range from about 100 to about 600 seconds SU at 100° F. For preparing high temperature greases, synthetic oils of various types, including particularly silicone oils and polyesters are preferably employed. Such oils may very advantageously comprise from about 50 up to 100 percent of the oil component of the grease, the remainder being mineral oil or other oil of a different type.

A particularly suitable class of synthetic polyester oils

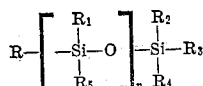
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are those disclosed by R. T. Sanderson in U. S. 2,628,974, obtained by reacting dibasic aliphatic acids with glycols and end-blocking the reaction products with monohydric aliphatic alcohols or monocarboxylic aliphatic acids. The preferred materials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



wherein R is an aliphatic hydrocarbon or an aliphatic ether group containing from 4 to 12 carbon atoms, R₁ and R₂ are aliphatic hydrocarbon groups 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, R₁, R₂, R₃, R₄ and R₅ represent 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 about 100 to 600 pounds SU at 100° F. Suitable compounds of this type include dimethylsilicone polymer, diethylsilicone polymer, methylcyclohexylsilicone polymer, diphenylsilicone, methylphenylsilicone polymer, methylethylsilicone polymer, methyltolylsilicone polymer, etc. These materials may be prepared by various methods, including hydrolysis of hydrolizable 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, etc. Suitable oxidation inhibitors include particularly those of the amine type, such as diphenylamine, α-naphthylamine, β-naphthylamine, p-phenylenediamine and 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. An oil-soluble phosphorus acid ester may be very advantageously employed in conjunction with an amine of this type in amounts from about 1 to 10 percent by weight based on the weight of the composition, to serve as a solvent and carrier for the amine. Also, additional thickening agents may be employed in minor amounts, such as other finely divided solids of various types and metal soaps of high molecular weight fatty acids, such as are commonly employed in lubricating greases.

Greases which are representative of the greases of this invention are described in the following examples:

EXAMPLE 1

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

Solid thickener	20
Lubricating oil	80

The solid thickener employed was the substantially pure compound 3-N-m-nitrophenylcarbonyl-2-hydroxy-1-naphthaleneazo-2'-methoxy-5'-nitrobenzene in finely divided form, having a particle size of about 1.5 microns and a measured surface area of 49 square meters per gram.

The mineral oil was a refined naphthenic distillate oil having a viscosity of about 300 seconds SU at 100° F.

The grease preparation was carried out by mixing together 225 grams of the solid thickener and 900 grams of the lubricating oil at room temperature, employing an electric mixer, and then milling with two passes through a Premier colloid mill at 0.002 inch clearance.

A soft, smooth grease was obtained having very

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superior lubricating properties generally, including excellent shear stability, oxidation resistance, and water resistance, as shown by the following tests.

Dropping point, °F ----- 420

Working stability:

ASTM Penetration at 77° F.—

After 60 strokes ----- 351

After 100,000 strokes ----- 341

ASTM bomb oxidation test: 100 hours at 210° F.

lbs. pressure drop ----- 4

Dynamic water resistance test: percent loss ----- 6.3

Water absorption test:

Water absorption, percent ----- 100+

ASTM worked penetration after test ----- 322

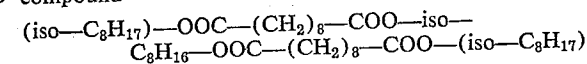
EXAMPLE 2

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

Solid thickener	25.0
Diphenyl-p-phenylene diamine	1.0
Tricresyl phosphate	3.0
Lubricating oil	71.0

The solid thickener was the same as that employed in the grease of Example 1.

The lubricating oil was a mixture of synthetic ester with about 7.1 percent by weight of a mineral lubricating oil, which was a highly refined paraffinic distillate oil having a viscosity of about 335 seconds SU at 100° F. The synthetic ester was obtained by reacting sebacic acid, 2-ethylhexane-1,3-diol and 2-ethylhexanol in about 2:1:2 ratio respectively, and consisted predominately of the



The grease preparation was carried out as described in Example 1, employing a grease mixture consisting of 300 grams of the thickener, 12 grams of the amine inhibitor, 36 grams of tricresylphosphate, 795 grams of the synthetic ester and 57 grams of the mineral lubricating oil. The amine inhibitor was added to the mixture in solution in the tricresylphosphate.

The following tests were obtained upon this grease.

Dropping point, °F ----- 500+

Working stability:

ASTM penetration at 77° F.—

After 60 strokes ----- 283

After 100,000 strokes ----- 279

ASTM bomb oxidation test: 100 hours at 210° F.

lbs. pressure drop ----- 9

Dynamic water resistance test: percent loss ----- 5.0

Water absorption test:

Water absorption, percent ----- 75

ASTM worked penetration after test ----- 269

Copper corrosion, MIL-L-3545, 24 hours ----- pass

High temperature performance test: hours at

400° F ----- 210

The high temperature performance test of the foregoing table is a test for determining the performance characteristics of greases in anti-friction 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 Normal Hoffman ABEC No. 3 grade, and are mounted on a spindle approximately 5/8 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 con-

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sists 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 counterwise 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 two 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."

The high temperature performance life of the grease of this invention in the above test was far in excess of that obtainable in the conventional soap thickened greases, which are ordinarily unsuitable for use at temperatures above about 300° F. In addition, it was considerably higher than that obtainable by employing solid thickeners of the prior art in lubricating oils of the ester type. For example, a copper phthalocyanine thickened grease of the same composition otherwise ran for only 119 hours at 400° F. in this test.

EXAMPLE 3

As an additional example of the greases of this invention, a grease was prepared employing as the thickening agent the compound 3-N-o-methylphenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-nitro-4'-methylbenzene. This was a commercial pigment having a particle size of about 0.1 to 0.2 by 1.5 microns and a measured surface area of 76 square meters per gram. The grease consisted of 30 percent by weight of this material in a refined paraffinic distillate oil having a viscosity SU at 100° F. of about 335 seconds.

The grease preparation was carried out by mixing together the oil and thickener and finishing with one pass through a Premier colloid mill at 0.002 inch clearance. A smooth glossy grease was obtained having an ASTM unworked penetration of 321. It had a high dropping point of over 500° F. and very good shear stability, as shown by an ASTM penetration of 352 after 60 strokes and of 330 after 100,000 strokes in the ASTM Worker Test.

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Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore, 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 selected from the class consisting of 3-N-arylcarbaryl-2-hydroxy-1-naphthaleneazoarenes and substituted derivatives thereof which are free from oil-solubilizing groups and from salt-forming groups.

2. The composition according to claim 1 wherein the said lubricating oil comprises in major proportion at least a dicarboxylic acid polyester.

3. The composition according to claim 1 wherein the said lubricating oil is a silicone polymer.

4. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with 3-N-m-nitrophenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-methoxy-5'-nitrobenzene.

5. A lubricating grease consisting essentially of a dicarboxylic acid polyester having a viscosity in the lubricating oil viscosity range thickened to a grease consistency with about 15 to 35 percent by weight based on the weight of the composition of 3-N-m-nitrophenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-methoxy-5'-nitrobenzene.

6. The composition according to claim 5 containing about 0.5 to 5.0 percent by weight of an amine oxidation inhibitor.

7. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with a compound selected from the class consisting of 3-N-arylcarbaryl-2-hydroxy-1-naphthaleneazoarenes and substituted derivatives thereof wherein the substituent groups are chosen from the class consisting of lower alkyl groups, lower alkoxy groups, halogens and the nitro group.

8. A lubricating grease consisting essentially of a lubricating oil thickened to a grease consistency with 3-N-o-methylphenylcarbaryl-2-hydroxy-1-naphthaleneazo-2'-nitro-4'-methylbenzene.

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