

1

3,010,905

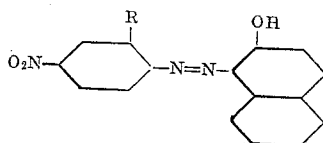
LUBRICATING GREASES THICKENED WITH NITROPHENYL-AZO NAPHTHOL COMPOUNDS

Norman R. Odell, Fishkill, and Joseph F. Lyons, Poughkeepsie, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware
No Drawing. Filed July 10, 1959, Ser. No. 826,109
10 Claims. (Cl. 252—51.5)

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 nitrophenylazo naphthols have the property of thickening lubricating oils to a grease-like consistency when they are dispersed therein in finely divided form, and that the greases thus produced have unexpectedly superior lubricating properties, including particularly the combination of exceptional oxidation resistance and water solubility.

The compounds which are employed as grease thickening agents in accordance with this invention are represented by the general formula



wherein R is hydrogen, or a non-salt forming non-oil solubilizing substituent group, such as a lower aliphatic or lower alkoxy group, containing from 1 to about 3 carbon atoms, a nitro group, an amino group or a halogen. The preferred compounds are those wherein R is a methyl, methoxy or nitro group or a halogen.

Examples of suitable compounds of the above class include the following: 1(4-nitrophenylazo)-2-naphthol; 1(2-chloro-4-nitrophenylazo)-2-naphthol; 1(2,4-dinitrophenylazo)-2-naphthol; 1(2-methyl-4-nitrophenylazo)-2-naphthol; 1(2-methoxy-4-nitrophenylazo)-2-naphthol; and 1(2-amino-4-nitrophenylazo)-2-naphthol. These compounds are commercially available or readily obtainable by well known methods including coupling diazotized nitroanilines with 2-naphthol.

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 as the major component 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 10 to about 45 percent by weight of thickening agent of this type, and preferably about 20 to about 40 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 thickener and additives in the lubricating oil base. The mixing may be carried out at ordinary temperatures or at elevated temperatures such as up to about 300° F. in order to dissolve any difficultly soluble additives.

The lubricating oils employed may be any suitable oils of lubricating characteristics, including the conventional

2

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 Saybolt Universal at 100° F. to about 225 seconds Saybolt Universal at 210° F., and preferably those having viscosities in the range from about 100 to about 600 seconds Saybolt Universal at 100° F. For preparing high temperature greases, synthetic oils of various types, including particularly silicone oils and synthetic esters 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. Suitable synthetic esters include aliphatic diesters, such as di-2-ethylhexyl sebacate, di(secondary amyl) sebacate, di-2-ethylhexyl azelate, di-iso-octyl adipate, etc. A particularly suitable class of synthetic esters are the polyesters described in U.S. 2,628,974, obtained by reacting an aliphatic dicarboxylic acid with a glycol and a monofunctional aliphatic alcohol or acid. Suitable silicone oils include, for example, dimethyl silicone polymer, diethyl silicone polymer, methylcyclohexyl silicone polymer, diphenylsilicone polymer, methylphenyl silicone polymer, methylethyl silicone polymer, methyltolyl silicone polymer, etc., preferably having viscosities in the range from about 100 to about 600 seconds Saybolt Universal at 100° F.

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, alpha-naphthylamine, beta-naphthylamine, para-phenylenediamine, and N,N'-diphenyl-p-phenylenediamine. A compound of this type may be present in an amount from about 0.5 to about 5 percent by weight, based on the weight of the composition. An oil soluble phosphorus acid ester may very advantageously be employed in conjunction with the amine in an amount from about 1 to about 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 as thickening agents in lubricating greases.

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

Example I

A lubricating grease representative of the greases of this invention is obtained by thickening a mineral lubricating oil with 30 percent by weight, based on the weight of the composition of finely divided 1(2-chloro-4-nitrophenylazo)-2-naphthol. The latter is in the form of particles 90 percent of which are in the 0.01–0.05 micron range and the remainder below 0.01 micron, in their largest dimension, and having a measured surface area of about 39 square meters per gram. This material is commercially available from the Hilton-Davis Chemical Company under the trade name of "Flame Toner."

The mineral lubricating oil is a refined naphthenic distillate oil having a Saybolt Universal viscosity at 100° F. of about 330.

The grease preparation is carried out by mixing together the oil and thickener in the proportions disclosed above, employing an electric mixer, and passing the mixture through a Premier colloid mill with two passes at 0.002 inch clearance.

The grease prepared as described above is a smooth N.L.G.I. No. 0 grade grease having a high dropping

point and very superior lubricating properties generally as shown by the following test results:

Dropping point, ° F.....	457
ASTM penetration at 77° F.:	
Unworked.....	
Worked, 60 strokes.....	307
Worked 100,000 strokes.....	342
ASTM bomb oxidation test (100 hrs. at 210° F.),	
lbs. pressure drop.....	3
Dynamic water resistance, percent loss.....	0
Water absorption, percent.....	50
Penetration ¹ before test.....	337
Penetration ¹ after test.....	295

¹ Unworked, converted from ½ size cone.

Example II

Another grease representative of the greases of this invention is obtained by thickening a silicone polymer oil with 29.4 percent by weight of the solid thickener described in Example I. The silicone oil is a methylchlorophenyl silicone oil, sold by the General Electric Company under the tradename of Versilube F-50. Typical inspection tests upon this oil include molecular weight of 2760, a silicone content of 33.6 percent and a chlorine content of 7.2 percent. The grease also contains 1.0 percent by weight of a commercial rust inhibitor, which is a reaction product of sodium sarcosinate with coconut oil fatty acid chlorides. The grease preparation is carried out as described in Example I.

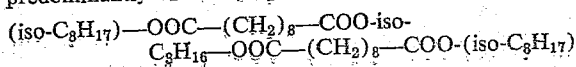
The grease prepared as described above is a smooth N.L.G.I. No. 2 grade grease having a high dropping point and very superior lubricating properties generally as shown by the following test results:

Dropping point, ° F.....	411
ASTM penetration at 77° F.:	
Unworked.....	
Worked, 60 strokes.....	247
Worked, 100,000 strokes.....	270
ASTM bomb oxidation test (100 hrs. at 250° F.),	
lbs. pressure drop.....	2
Dynamic water resistance, percent loss.....	0
CRC bearing protection test.....	Pass

The CRC bearing protection test is described in military specification MIL-G-3278A. It consists essentially in immersing a Timken roller bearing which has been coated with the test grease in distilled water and then storing it in a humid atmosphere at room temperature for 14 days. The bearing is then cleaned and inspected for rusting.

Example III

Another grease representative of the greases of this invention is obtained by employing finely divided 1(2-methoxy-4-nitrophenylazo)-2-naphthol, having a particle size below 0.05 micron, as the thickening agent in a synthetic ester oil. The latter is a product obtained by reacting sebacic acid, 2-ethylhexane-1,3-diol and 2-ethylhexanol in about a 2:1:1 ratio respectively, and consisting predominantly of the compound



The grease contains 30 percent by weight of the solid thickener and also 1.0 percent of diphenylparaphenylenediamine and 3.0 percent of tricresyl phosphate. The grease preparation is carried out as described in Example I.

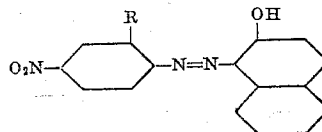
A soft smooth N.L.G.I. No. 0 grade grease is obtained as described above, having a dropping point above 500° F. and suitable for lubrication at elevated temperatures above about 400° F.

In contrast with the results described above, other phenylazonaphthol compounds of the same composition but without the paranitro group of the compounds employed in accordance with this invention were found to have only a very low thickening action in lubricating oils, which was insufficient to form greases.

Obviously many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof and 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 as the major component thickened to a grease consistency with a compound having the formula



wherein R is chosen from the group consisting of hydrogen, lower aliphatic groups and lower alkoxy groups containing 1-3 carbon atoms, the nitro group, amino groups and halogens.

2. A lubricating composition according to claim 1 wherein the said lubricating oil is a mineral oil.

3. A lubricating grease according to claim 1 wherein the said lubricating oil is a dicarboxylic acid ester.

4. A lubricating grease according to claim 1 wherein the said R substituent is a nitro group.

5. A lubricating grease according to claim 1 wherein the said R substituent is a methyl group.

6. A lubricating grease according to claim 1 wherein the said R substituent is a methoxy group.

7. A lubricating grease according to claim 1 wherein the said R substituent is chlorine.

8. A lubricating grease consisting essentially of a mineral lubricating oil thickened to a grease consistency with about 20-40 percent by weight of 1(2-chloro-4-nitrophenylazo)-2-naphthol in finely divided form.

9. A lubricating grease according to claim 8 wherein the said lubricating oil is an aliphatic dicarboxylic acid polyester.

10. A lubricating grease according to claim 8 containing about 0.5-5 percent of an amine oxidation inhibitor.

References Cited in the file of this patent

UNITED STATES PATENTS

2,679,480	Brannen et al.	May 25, 1954
2,848,417	Armstrong et al.	Aug. 19, 1958
2,880,176	Roach et al.	Mar. 31, 1959
2,880,177	Lyons et al.	Mar. 31, 1959
2,915,470	Armstrong et al.	Dec. 1, 1959

**UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION**

Patent No. 3,010,905

November 28, 1961

Norman R. Odell et al.

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 1, line 20, "solubility" read -- stability --.

Signed and sealed this 17th day of April 1962.

(SEAL)

Attest:

ESTON G. JOHNSON

Attesting Officer

DAVID L. LADD

Commissioner of Patents