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LUBRICATING COMPOSITION

Max J. Wisotsky, University Park, Pa., and Norman R. Odell, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y., a corporation of Delaware

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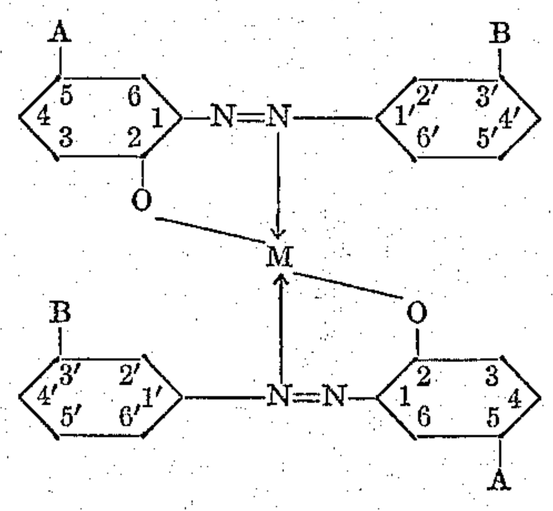
This invention relates to a lubricating grease composition and to a novel class of thickening agents therefor. More particularly, the present invention relates to a lubricating grease composition thickened with a particular class of metal chelates of substituted 2-hydroxyazobenzenes.

We have found that certain copper and nickel chelates of halo- or methoxy-substituted 3'-halo-2-hydroxyazobenzenes form stable grease compositions having excellent lubricating properties in synthetic base oils, such as silicone polymer oils and diester oils.

The copper and nickel chelates of the halo- or methoxy-substituted 3'-halo-2-hydroxyazobenzenes which are employed as grease thickening agents of the present invention are represented by the general formula:



wherein A is a member selected from the group consisting of methoxy and halogen, preferably chlorine, and B is a halogen, preferably a chlorine, and wherein M is a member selected from the group consisting of copper and nickel and wherein when M is nickel, A is a halogen, preferably chlorine.

Particularly suitable azobenzene compounds to prepare the copper or nickel chelate thickening agents include 5,3'-dichloro-2-hydroxyazobenzene and 5 methoxy-3' - chloro - 2 - hydroxyazobenzene. The particular metal chelating azo compounds employed in the lubricating greases of the present invention as the thickening agents include the copper and nickel chelates of 5,3'-dichloro-2-hydroxyazobenzene and the copper chelate of 5-methoxy-3' - chloro - 2 - hydroxyazobenzene. It is indeed surprising that these particular chelates are effective thickening agents in lubricating greases when other chelate compounds, such as the copper or nickel chelate of 5,4'-dichloro-2-hydroxyazobenzene, the nickel chelate of 5-methoxy-3'-chloro-2-hydroxyazobenzene and the nickel chelate of 5-chloro-2'-methoxy-2-hydroxyazobenzene are not satisfactory grease thickening agents in synthetic base oils, such as a silicone polymer base oil or in a diester base oil.

The grease compositions of the present invention comprise a synthetic base oil having a viscosity in the lubricating oil viscosity range, containing a copper or nickel chelate of 5,3'-dichloro-2-hydroxyazobenzene or the copper chelate of 5-methoxy-3'-chloro-2-hydroxyazobenzene, in an amount sufficient to thicken said base oil to a grease consistency. In general, the composition contains from about 55 to 85 percent of base oil and from 15 to 45 percent of the metal chelate, based on the weight of the composition. The grease compositions of the invention usually also contain from 0.5 to about 5% by weight of a corrosion inhibitor and in addition, may

contain from about 0.5 to 5% by weight of an amine oxidation inhibitor.

As is understood in the grease art, the grease compositions may additionally contain minor amounts of conventional lubricity agents, coloring materials, extreme pressure agents and the like, including combinations of these materials.

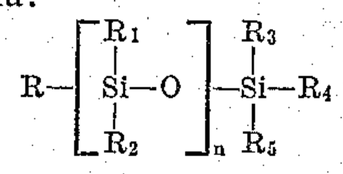
A preferred lubricating grease composition comprises from about 59 to 69% by weight of a synthetic silicone polymer oil having a viscosity in the lubricating oil viscosity range, from 30 to 40% by weight of copper or nickel chelate of 5,3'-dichloro-2-hydroxyazobenzene, 0.5% of diphenyl-para-diphenylenediamine as an oxidation inhibitor, and 0.5% N-cocoylsarcosine as a corrosion inhibitor where cocoyl denotes the acyl component derived from coconut oil acids.

Satisfactory arylamine oxidation inhibitors include diphenylamine, phenyl-alpha-naphthylamine, para-phenylenediamine, and N,N'-diphenyl-para-phenylenediamine.

Satisfactory corrosion inhibitors include lead naphthenate and the sarcosines including the N-acylsarcosines containing from 8 to about 20 carbon atoms in the acyl group such as N-cocoylsarcosine, N-laurylsarcosine and N-stearylsarcosine.

The synthetic base oil may be a silicone polymer base fluid or an aliphatic diester fluid.

The silicone polymer base fluids used to form the greases of the present invention are compounds having the general formula:



wherein R, R_1, R_2, R_3, R_4, and R_5 are methyl, phenyl, or chlorinated phenyl groups, preferably at least about 35% thereof being methyl groups and with sufficient chlorinated phenyl groups to give a chlorine content of at least about 3% by weight to the polymer, and wherein *n* is an integer of sufficient size to give a polymer having a viscosity in the lubricating oil viscosity range. The preferred silicone oils are those having a viscosity of from about 100 to 600 seconds Saybolt Universal at 100° F. and contain about 4 to 12 percent by weight of chlorine. A particularly suitable silicone polymer material is the commercial product sold under the trade name "Versilube F–50," having an average molecular weight of about 3,233, a viscosity of about 180 to 280 seconds Saybolt Universal at 100° F., and containing about 33.6% silicone and 7.18% of chlorine by weight. Another suitable silicone polymer base fluid, sold under the trade name "Dow F–60," also can be used in the grease compositions of the invention.

The methylchlorophenylsilicone polymer oil can be employed as the sole oil component, or it may be employed in admixture with minor amounts of other oils, particularly other synthetic oils, such as, polyethers, polyglycols, diesters, polyesters, or mixtures of such oils.

The aliphatic ester type base fluids for use in the grease compositions include the diesters of primary alcohols and aliphatic dicarboxylic acids. The dicarboxylic acid component usually contains from 6 to 12 carbon atoms, but glutaric and succinic acids are also included. From the standpoint of cost and availability, the preferred acids are adipic, sebacic, and azelaic. The primary aliphatic alcohol used to form the diester base fluid usually contains at least 4 carbon atoms and may contain 30 or more carbon atoms. C_6 to C_{18} alcohols are most commonly used. Specific examples of the dialkyl esters of aliphatic dicarboxylic acids which are the preferred base fluid bases for use in the grease composition of the invention are as follows: dibutyl azelate, di-2-ethylhexyl azelate, didodecyl azelate, ditridecyl azelate, dihexyl

sebacate, di-2-ethylhexyl sebacate, dihexadecyl sebacate, di-2-ethylhexyl adipate, and diisooctyl adipate. A particularly preferred aliphatic diester base fluid oil is ditridecyl sebacate.

The aliphatic diester base oil can be employed as the sole oil component in the grease compositions of this invention, or the diester can be employed in admixture with minor amounts of other oils, particularly other synthetic oils, such as a silicone polymer oil, a polyether oil, a polyglycol oil, a polyester oil, or mixtures of said oils.

Specific details for the preparation of the copper or nickel chelate chloro- or methoxy-substituted 3'-chloro-2-hydroxyazobenzene compounds will be readily apparent to those skilled in the art from the following examples.

EXAMPLE A

The 5,3'-dichloro-2-hydroxyazobenzene starting material to prepare the copper or nickel chelate thereof was prepared in a known manner by diazotizing meta-chloroaniline and reacting the resulting diazotate with parachlorophenol.

EXAMPLE B

The reaction product of Example A above in an amount of 467 grams was reacted with 175 grams of cupric acetate monohydrate in 500 milliliters of water, 1500 milliliters of dioxane and 1500 milliliters of methanol by heating the mixture with stirring on a steam plate for 3 hours. The resulting reaction product was filtered, washed with dioxane and with methanol. The copper chelate of 5,3'-dichloro-2-hydroxyazobenzene product was a rust-red powder. The yield was 84% (439.8 grams). The copper chelate had a melting point of 294–297° C. On analysis, the copper content was found to be 9.91% by weight.

EXAMPLE C

Following the procedure for Example B above, the nickel chelate of 5,3'-dichloro-2-hydroxyazobenzene was prepared from nickelous acetate tetrahydrate and the product of Example A above. The chelate was obtained in 68% yield; M.P. 293–296° C.

EXAMPLE D

Following the procedure of Example B above, the copper chelate of 5-methoxy-3'-chloro-2-hydroxyazobenzene was prepared from cupric acetate monohydrate and 5-methoxy-3'-chloro-2-hydroxyazobenzene. The yield was 54.4%; M.P. 252–257° C.; 8.7% copper; 8.1% nitrogen.

EXAMPLE 1

A grease was prepared by blending 1,723 parts of a water slurry of the copper chelate of 5,3'-dichloro-2-hydroxyazobenzene prepared in a manner similar to Example B above, 485 parts of silicone polymer oil (Versilube F–50), and heating the blend at 250° F. for 2 hours with stirring. The slurry contained 417 parts of the chelate and 1,306 parts of water. The resulting blended grease was milled twice in a Premier colloid mill having a rotor-stator clearance of 0.002 inch. The resultant product was a buttery, glossy grease. Inspection tests on this grease are shown in the table below.

EXAMPLES 2 TO 4 INCLUSIVE

Following the procedure of Example 1 above, various greases were prepared from a silicone polymer oil, Versilube F–50, using as thickening agents various copper and nickel chelates. The compositions of these greases and the particular chelate thickeners are shown in the table below.

EXAMPLE 5

A synthetic ester grease was prepared by blending 460 parts of ditridecyl sebacate with 2,365 parts of a water slurry of the copper chelate of 5,3'-dichloro-2-hydroxyazobene prepared in a manner similar to Example B above and the resulting blend was heated to a temperature of 250° F. The slurry contained 460 parts of the chelate and 1,905 parts of water. When the blend had attained this temperature, heating was discontinued and 7.45 parts of diphenyl-paraphenylenediamine oxidation inhibitor and 7.45 parts of Sarkosyl LC corrosion inhibitor were added to the heated blend with mixing. The resulting heated blend was milled for 2 passes through a Premier colloid mill having a clearance of 0.002 inch. Inspection tests on the resulting grease are shown in the table below.

Table

	Example 1	Example 2	Example 3	Example 4	Example 5
Composition, wt. percent:					
Versilube F50	69.1	60.0	58.9	60.0	
Formamide [1]			1.0		
Diphenyl p-phenylenediamine.					0.6.
Sarkosyl LC					0.6.
Ditridecyl sebacate					60.4.
Chelate*	A—30.9	A—40.0	B—40.1	C—40.0	A—38.4.
Product inspections:					
Penetration, unworked [2]	242	189	272	249	264.
Worked, 60 strokes	249	328	384	290	281.
105 strokes	294	289	400+		
Dropping point, ° F	500+	500+	500+	450	500+.
Dynamic H_2O resist., percent loss.	5.0	0	0	0	0.
Water absorb., percent abs	60	20	20	10	20.
Oil separation, 30 hrs., 450° F., percent loss.	5.5	0.6	3.9		
Oil evaporation, 22 hrs., 400° F., percent loss.	0.65	1.47	1.33		
ASMT bomb ox., 100 hrs., 250° F., p.s.i. drop.	2	0	2	(210° F.) 0	(210° F.) 1.
Copper Corrosion	Pass (clean)	Pass (clean)			
Storage Stability—Penetration unworked (worked): [2]					
Original	285 (317)				272 (305).
1 week				(326)	215 (287).
1 month	(253)	(334)	(343)	(313)	257 (283).
3 months	(257)	(317)	(371)		
6 months	(315)				

[1] Flocculation agent. [2] ¼ cone, ⅓ worker.
*A—Copper 5,3'-dichloro-2-hydroxyazobenzene.
*B—Nickel 5,3'-dichloro-2-hydroxyazobenzene.
*C—Copper 5-methoxy-3'-chloro-2-hydroxyazobenzene.

Inspection of the test data shown in the table above indicate that the grease compositions of the present invention containing the copper and the nickel chelates of 5,3'-dichloro-2-hydroxyazobenzene and copper 5-methoxy-3'-chloro-2-hydroxyazobenzene are satisfactory thickening

agents for silicone polymer and diester base oils to form stable grease.

The grease composition of Example 1 was a buttery No. 3 grade grease that exhibited a high dropping point, excellent oxidation and corrosion resistance and low oil separation and evaporation properties in the tests. The shear stability, water resistance and storage test results were good.

Inspection of the test results shown in the table above, show that the grease composition of Example 2 also exhibited desirable grease properties.

The grease of Example 3 was a No. 2 grade grease having excellent dropping point, water resistance, oil separation and oxidation values in the tests.

The grease composition of Example 4 exhibits good shear stability, oxidation resistance and water resistance. This grease was a No. 3 grade grease having a dropping point of 450° F.

The grease of Example 5 above was a buttery No. 2 grade grease. This grease composition had a high dropping point, good oxidation resistance, water sensitivity, and shear stability as shown in the above table.

Additional experiments were conducted to evaluate other copper and nickel chelates of similarly substituted 2-hydroxyazobenzenes.

The following compounds were tested in Versilube F–50 base oil as grease thickening agents, but the results were completely unsatisfactory. Fluid and semi-fluid systems were obtained using the following chelates in Versilube F–50 base oil.

39.6% of the copper chelate of 5,4′-dichloro-2-hydroxyazobenzene;
39.7% of the corresponding nickel chelate;
39.6% of the nickel chelate of 5-methoxy-3′-chloro-2-hydroxyazobenzene;
39.5 and 39.7%, respectively of the nickel chelate of 5-chloro-2′-methoxy-2-hydroxyazobenzene.

These tests serve to demonstrate the specificity of the particular copper 5-chloro-substituted, copper 5-methoxy-substituted, as well as the nickel 5-chloro-substituted 3′-chloro - 2 - hydroxyazobenzene compounds as thickening agents in the compositions of the invention.

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 composition comprising a synthetic base oil having a viscosity in the lubricating oil viscosity range containing a compound selected from the group consisting of the copper and nickel chelates of 5,3′-dichloro-2-hydroxyazobenzene and the copper chelate of 5-methoxy-3′-chloro-2-hydroxyazobenzene in an amount sufficient to thicken said base oil to a grease consistency.

2. A grease composition as claimed in claim 1 wherein the synthetic base oil comprises from about 55 to 85 percent by weight and the metal chelate thickening agent comprises from about 15 to 45 percent by weight, based on the weight of the composition.

3. A grease composition as claimed in claim 1 wherein the thickening agent is the copper chelate of 5,3′-dichloro-2-hydroxyazobenzene.

4. A grease composition as claimed in claim 1 wherein the thickening agent is the copper chelate of 5-methoxy-3′-chloro-2-hydroxyazobenzene.

5. A grease composition in accordance with claim 1 wherein the thickening agent is the nickel chelate of 5,3′-dichloro-2-hydroxyazobenzene.

6. A grease composition as claimed in claim 1 wherein the synthetic base oil is a silicone polymer oil having a viscosity in the lubricating oil viscosity range.

7. A grease composition as claimed in claim 5 wherein the silicone polymer oil is a methylchlorophenylsilicone polymer oil having a viscosity in the range of from about 100 to 600 seconds, Saybolt Universal at 100° F.

8. A grease composition as claimed in claim 1 wherein the synthetic lubricating oil is ditridecyl sebacate.

9. A grease composition comprising from about 59 to 69 percent by weight of a methylchlorophenylsilicone polymer oil having a viscosity in the lubricating oil viscosity range, thickened to a grease consistency with from 30 to 40 percent by weight of a copper chelate of 5,3′-dichloro-2-hydroxyazobenzene, and containing about 0.5 percent by weight of an amine oxidation inhibitor, and about 0.5 percent by weight of a sarcosine corrosion inhibitor.

10. A grease composition as claimed in claim 9 wherein the amine oxidation inhibitor is diphenyl-paraphenylenediamine.

11. A grease composition as claimed in claim 9 wherein the sarcosine corrosion inhibitor is N-cocoylsarcosine.

References Cited by the Examiner

FOREIGN PATENTS

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DANIEL E. WYMAN, *Primary Examiner.*