LUBRICATING GREASES THICKENED WITH ALIZARIN LAKES

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This application relates to lubricating greases thickened with alizarin lakes in finely divided form.

Alizarin lakes, commonly known as madder lakes, are resins products of alizarin with aluminum hydroxide or with both aluminum hydroxide and a reactive compound of a different polyvalent metal such as a salt or hydrate of calcium, barium, iron, tin, etc. They apparently comprise both adsorption complexes of alizarin with aluminum hydrate and salts of alizarin with aluminum or other polyvalent metal, wherein the ratio of aluminum hydrate to alizarin residues is at least 2:1, and commonly up to about 12:1, and the ratio of hydrogen equivalents of salt forming metal atoms to alizarin residues is from about 1:1 to 2:1 for divalent metals, and about 1:1 to 3:1 for trivalent metals. These compounds are employed extensively as pigments in compositions of various types.

We have now found that compounds of the above type form stable gels of very superior lubricating properties generally when they are dispersed in lubricating oils in suitable proportions. These compositions have high temperature properties which are greatly superior to those obtained in the conventional soap thickened greases, and in addition they are much superior to solids thickened greases of the prior art in their water resistance and other properties.

The greases of this invention comprise essentially a lubricating oil containing sufficient amounts of a thickening agent of the above class to impart at least substantial thickening. Ordinarily the composition will contain from about 5 to about 45 percent by weight of the alizarin lake, and preferably from about 15 to about 35 percent by weight of the lake, based on the weight of the composition. The lake is employed in the form of particles below about 5 microns in diameter, and preferably below about 2 microns in diameter.

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 Saybolt Universal at 100° F. to about 225 seconds Saybolt Universal at 210° F., preferably 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 polyesters are preferably employed. Such oils may very advantageously comprise from about 50 to 100 percent of the oil component of the grease, the remainder being a mineral oil or other oil of a different type. A particularly suitable class of synthetic polyester 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 or monocarboxylic aliphatic acids.

The preferred materials of this character are products obtained by reacting mono- or polynuclear glycols with dicarboxylic acids and monohydric alcohols, represented by the formula

$$R_2-OOC-R_1-COO-(R-OOC-R-COO)_x-R_2$$

wherein R is an aliphatic hydrocarbon or an aliphatic ether group containing from 4 to 12 carbon atoms, R_1 and R_2 are aliphatic hydrocarbon groups containing from 1 to 12 carbon atoms and x is an integer from 1 to 5. 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, alphaphthylamine, beta-phenylenediamine, para-phenylenediamine and N,N'-diphenyl-para-phenylenediamine. A composition of this type may suitably be present in amounts from about 0.5 to about 5 percent by weight, based on the weight of the composition. The inhibitor composition described in U.S. 2,663,691, comprising N,N'-diphenyl-para-phenylenediamine dissolved in about three times its weight of tricresyl phosphate, may very advantageously be employed. 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 conventionally employed in lubricating greases.

The alizarin lakes which are employed as thickening agents in these greases are commercially available or obtainable by well known methods, which involve prolonged boiling of alizarin and aluminum hydrate or phosphate, employing at least two mols of aluminum per mol of alizarin. The preferred method comprises boiling alizarin with an excess of aluminum hydrate in a neutral or slightly acid aqueous solution in the presence of an excess of alkaline earth metal salt or hydrate. The solution may very suitably contain about 3–8 mols of aluminum hydrate (as Al(OH)₃) per mol of alizarin and about 1–2 mols of a calcium salt such as calcium chloride. The aluminum hydrate may be either prepared before mixing it with alizarin, or precipitated in the presence of the alizarin. A higher fatty acid such as Turkey red oil, obtained by treating castor oil with concentrated sulfuric acid, or tannic acid, is advantageously employed in the reaction mixture, suitably in amounts from about 0.05 mol to about 2 mols and phosphates may also be employed, suitably in amounts from about 2 to 10 mols per mol of alizarin. Depending upon the proportion of reactants employed, the lake produced will comprise from about 10 to 50 percent by weight of alizarin, the remainder being inorganic material and sometimes small amounts of higher fatty acids employed in the reaction. Under the preferred conditions, employing a ratio of alizarin to aluminum hydrate in the ratio of about 1:3 to 1:8 and an excess of an alkaline earth metal compound, the product will contain about 15–40 percent by weight of alizarin, the ratio of alizarin residues to aluminum and to alkaline earth metal atoms being about 1.3–8; 0.5–1 respectively.

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 the thickener and additives in the lubricating oil base. The mixing may be carried out at ordinary temperatures or elevated temperatures up to about 300° F., or higher, if desired, in order to dissolve difficulty soluble additives. Compositions representative of the greases of this invention are described in the following examples.
Example I

A lubricating grease having the following composition in percent by weight:

Alizarin lake ........................................ 30
Lubricating oil ...................................... 70

The alizarin lake is prepared according to the method described by A. W. C. Harrison, "The Manufacture of Lake and Precipitated Pigments," Method B, page 234. The method in detail is as follows: Sodium phosphate (47 parts in 940 parts of water), alizarin (20 percent paste, 66 parts in 660 parts of water), sodium oxide (18 parts in 180 parts of water) and Turkey red oil (9.5 parts in 150 parts of water) are introduced into a precipitation vessel and mixed thoroughly. Aluminum sulphate (18 percent Al₂O₃, 56 parts in 560 parts of water), is then added slowly and after the reaction has subsided, calcium chloride (9 parts in 90 parts of water) is added. The solution is then brought to a boil in three hours and boiled for three hours. The precipitate is filtered, washed, dried and ground to a particle size below two microns in diameter. It contains about 33 percent by weight of alizarin residue, about 21 percent by weight of aluminum and about 6 percent by weight of calcium.

The mineral oil is a refined naphthenic distillate oil having a viscosity of about 300 seconds Saybolt Universal at 100° F.

The grease preparation is carried out by mixing together 300 grams of the alizarin lake and 700 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.

Greases obtained in the above manner are smooth, butty red greases having high dropping points and very superior lubricating property generally. The following tabulation shows typical test results which were obtained upon a grease prepared in this manner.

Dropping point, ° F. .............................. 500-

Working stability, ASTM penetration at 77° F.: .............................. 321
After 100,000 strokes ..................................... 330

ASTM bomb oxidation test, 100 hours at 210° F., lbs. pressure drop .............................. 3
Dynamic water resistance test, percent loss .............................. 2.5

As shown by the above data, the grease of our invention had a dropping point above 500° F., very exceptional shear stability, and excellent resistance to oxidation at elevated temperatures for an uninhibited grease. In addition, it had good water resistance properties as shown by the small amount of loss in the dynamic water resistance test.

Example II

A lubricating grease having the following composition in percent by weight:

Alizarin lake ........................................ 30.0
N,N'-diphenyl-para-phenylenediamine ............. 1.0
Tricresyl phosphate .................................. 3.0
Lubricating oil ...................................... 66.0

The alizarin lake is the same as that employed in the grease of Example I.

The lubricating oil is a mixture of synthetic ester with about 7 percent by weight of a mineral lubricating oil, which is a refined paraffinic distillate oil having a viscosity of about 335 seconds Saybolt Universal at 100° F. The synthetic ester is obtained by reacting sebacic acid, 2-ethylhexane-1,3-diol and 2-ethylhexol in about a 2:1:2 ratio respectively, and consists predominantly of the compound (iso-C₆H₁₃)—OOC—(CH₂)₄—COO—iso-C₆H₁₃—OOC—(CH₂)₈—COO—(iso-C₆H₁₃).

The grease preparation is carried out as described in Example I, the amine inhibitor being added to the mixture in solution in the tricresyl phosphate. The grease prepared as described above is a smooth buttery red grease having a dropping point above 500° F. and improved high temperature performance properties, suitable for use at temperatures up to about 400° F.

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 an alizarin lake in finely divided form, said lake being obtained by boiling an aqueous solution containing alizarin and aluminum hydrate in a molar ratio of from 1:2 to about 1:12, respectively, and at least about 0.5 mol of a water-soluble calcium salt per mol of alizarin.
2. A lubricating grease according to claim 1 wherein the said aqueous solution contains 2–8 mols of aluminum hydrate per mol of alizarin.
3. A composition according to claim 1 wherein the said lubricating oil comprises a high molecular weight diester.

References Cited in the file of this patent

UNITED STATES PATENTS

2,366,191 Jenkins .............................. Jan. 2, 1945