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GREASE COMPOSITIONS CONTAINING MAGNESIUM SALTS OF UNSATURATED FATTY ACIDS AS RUST INHIBITORS

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ABSTRACT OF THE DISCLOSURE

Grease compositions providing improved rust resistance comprising a major amount of an oil of lubricating viscosity, a minor amount, sufficient to thicken the oil to the consistency of a grease thickener, and a minor portion of a magnesium salt of an unsaturated unsubstituted or hydroxy-substituted fatty acid of 14 to 24 carbon atoms.

BACKGROUND OF THE INVENTION

Field of the invention

With the increased use in recent years of greases which have the facility of lubricating for extended periods at elevated temperatures, the need has increased for improved rust prevention with these greases. In contrast to ordinary corrosion, which is generally caused by attack of acidic oxidation products of the grease itself, rust attack is usually caused by contact with excessive humidity and, in particular, salt water and vapors therefrom, etc.

The problem of rusting is particularly acute in such applications as grease-lubricated bearings of various automotive or marine components which by virtue of their particular use will be exposed to water, often salt water. A particular example of this application is in the lubrication of the bearings in automotive or marine electric alternators or generators.

In the past, a wide variety of materials have been used in greases to impart rust prevention properties. Typical materials which have been used include sulfonates, lead soaps, amines, amine salts, metallic sulfonates and naphthenates, various esters and nonionic surfactants, etc.

While many of the above-mentioned inhibitors have been employed successfully in inhibiting rust formation with various greases, in general, results have been obtained under relatively mild conditions, and there is a definite need for an inhibitor which will impart increased resistance to rust formation and will be compatible with a wide variety of grease compositions. The importance of the last point is that many of the previously employed inhibitors have had adverse effects upon particular types of lubricants. For example, sulfonates, if they contain a metal radical different from that of the thickener, may tend to weaken the grease structure. Similar effects are attributed to various esters and amines. Some inhibitors are known to have a degelling effect upon bentonite thickened lubricating greases.

An additional problem is that certain amines employed as rust inhibitors react with and destroy paint films with which they come in contact.

DESCRIPTION OF THE PRIOR ART

U.S. Pat. No. 3,077,450, teaches the use of alkaline earth metal soaps of C_{14}–C_{30} mono-unsaturated fatty acids in salt-soap lubricants. The alkaline earth unsaturated acid salt is employed in the compositions in the ratio of 1:100 to 1:1000 relative to the salt. It is said that by the use of the unsaturated acid stable dispersions may be formed, and the use of the unsaturated acid moiety rather than the saturated one results in softer compositions. Thus, larger amounts of metal may be included in the lubricant and may thus have higher load-bearing capacities. The salt portions are usually calcium acetate, and the soap material is preferably a calcium salt.

SUMMARY OF THE INVENTION

Greases having superior antirust properties are provided, the greases comprising a major portion of an oil of lubricating viscosity, a minor portion of a grease thickener sufficient to thicken said oil to the consistency of a grease and a second minor portion, from 0.1 to 10, preferably 0.5 to 8.0 percent by weight of a magnesium salt of an unsaturated, unsubstituted or hydroxy-substituted, fatty acid of from 14 to 24, preferably from 16 to 22 carbon atoms. An example of a preferred salt is the magnesium salt of ricinoleic acid.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

Thus, examples of the acids from which the rust inhibitors of the invention are derived include ricinoleic, ricinolenic, elaidic, oleic, linoleic, linolenic, etc. It may be noted that the above materials are all naturally derived. These materials are preferred because of convenience; however, synthesized materials are also suitable. Polycarboxylic acids may also be used.

As previously mentioned, the thickeners and the grease compositions of the invention may be of a wide variety of types. Thus, the rust inhibitors are compatible with soap-type thickeners, inorganic thickeners, complex soap thickeners, and a variety of non-soap thickeners of organic origin. A comprehensive description of the types of thickeners which are used to prepare various greases may be found in Boner, "Manufacture and Application of Lubricating Greases," Reinhold, 1954.

The thickener is employed in an amount sufficient to thicken the base oil to grease consistency. Usually 5 to 50% by weight, more preferably, 10 to 40% by weight will be employed.

Illustrations of various soap greases include those thickened by soaps of aluminum, barium, calcium, lithium, lead, strontium, and of lesser significance those thickened with soaps of sodium, potassium, cesium, indium, gallium, beryllium, zinc, cadmium, boron, tin, zirconium, cerium, vanadium, antimony, bismuth, arsenic, copper, mercury, silver, etc.

Mixed metal soap base lubricating greases are also commonly employed. Examples of these include sodium-barium soap, lithium-calcium soap, magnesium-aluminum soap, aluminum-calcium soap, aluminum-lithium soap, etc. Many other combinations have been employed. The complex of lubricants include various hydrated soaps, such as hydrated calcium soaps, hydrated aluminum, hydrated barium, hydrated lithium, hydrated sodium, hydrated strontium, etc.

A second type of complex soap lubricating grease which may be employed in the compositions of this invention is the soap-salt complex grease. These materials, in general, comprise a complex of a metal soap and a metal salt of the same or different metal. The organic acids from which the salts are derived are generally of low molecular weight, usually containing less than 7 carbon atoms per molecule and being either mono or dicarboxylic acids such as acetic, propionic, butyric, pentanoic, hexanoic, succinic, glutaric, adipic, etc.

Thus, various combinations of soaps and salts are employed in the complexes. In a typical example, the first metal is an alkaline earth metal and the second is an alkali or alkaline earth metal. Illustrative examples of these greases are calcium-sodium complex greases with acetic acids supplying the acid moiety of the salt and various other combinations.

The inorganic thickeners employed in the greases include inorganic gels, particularly silica gel, and various clays. The most commonly used clay thickened grease is one thickened with organophilic bentonite. These thickeners and related types are disclosed in U.S. Pat. 2,531,427; greases thickened with the materials are disclosed in U.S. Pat. 2,531,400. Other clay-type materials which have been employed include zeolite, modified clays, such as amine-treated bentonite, etc., and attapulgite clay.

Other non-soap thickened greases include various products of organic bases, carbohydrates and proteins, organic polymers, and phthalocyanine derivatives.

The numerous products of organic bases which have been employed as grease thickeners and are effective in the compositions of this invention include neutral anilides of fatty acids, toluides of fatty acids, combinations of these materials with metallic soaps, amides such as stearamides, and a particularly useful group of materials, the arylureas.

U.S. Pat. No. 3,242,210 described polyureas which are particularly useful. These materials are of the formula:

$$R'NH-\left(\overset{O}{\overset{\|}{C}}NHR'''NH\overset{O}{\overset{\|}{C}}NHRNH\right)_x-\overset{O}{\overset{\|}{C}}NHR'''NH\overset{O}{\overset{\|}{C}}NHR''$$

wherein x is an integer of from 1 to 3, R and R''' may be the same or different and are hydrocarbylene of from 2 to 30 carbon atoms (hydrocarbylene is a divalent organic radical composed solely of carbon and hydrogen which may be aliphatic, alicyclic or aromatic or combinations thereof, e.g., alkaryl, aralkyl, etc., having its two free valences on different carbon atoms); R' and R'' may be the same or different and are hydrocarbyl of from 1 to 30 carbon atoms (hydrocarbyl is a monovalent organic radical composed solely of carbon and and hydrogen which may be aliphatic, aromatic, or alicyclic or combinations thereof, e.g., aralkyl, alkaryl, etc.).

Greases containing materials of this general type are disclosed and claimed in U.S. Pat. No. 3,243,372.

In order to illustrate the improved rust resistance imparted to the compositions of this invention by the magnesium salts of the particular unsaturated acids, rusting tests were performed employing various additives in several greases.

The rusting tests which were used included ASTM Rusting Test (D–1743) and modified forms of the test. The ASTM test is specifically entitled "Standard Method of Test for Rust Preventative Properties of Lubricating Greases" (D–1743–64). Briefly the test involves lubricating clean, new Timken roller bearings (cone No. 09074 and cup No. 09196) with the subject lubricant, running the bearings for 60 seconds under a light thrust-load in order to distribute the lubricant in the bearing, and storing the bearings in a sealed glass jar for two weeks at 77° F. and 100% relative humidity. The jar contains 5 ml. of distilled water. At the end of the test period, the lubricant is removed from the bearing with a "Solvent Rinse Solution," which is a mixture of Stoddard solvent and isopropyl alcohol. The bearing is then dried and examined for evidence of corrosion, which is defined as any surface damage (pitting, etching, rusting, etc.) of the cup raceway and rollers or black stains thereon.

For the purposes of testing greases which are to be used in applications where more serious rusting conditions are encountered, the ASTM Test, which will be called Test A, was modified to produce two new tests as follows:

Test B.—In this test the basic ASTM (D–1743) procedure was followed, except that exposure of the bearing was carried out at 125° F. for 24 hours, and instead of distilled water, a mixture of 95% distilled water and 5% synthetic sea water was used. The synthetic sea water was prepared according to ASTM D–665.

Test C.—This test was run in the same manner as Test B except that the humidity-imparting liquid was 100% synthetic sea water.

In both tests a modified rating system was employed. A rating of 1 or 2 generally corresponds to the ASTM rating, i.e., the grease passes with little or no bearing corrosion evident. 3 or 4 indicate definite evidence of rusting and thus indicates failure of the grease. 4 indicates severe corrosion and pitting.

EXAMPLE 1

Rust inhibition tests with magnesium salts in polyurea grease

Table I following shows results obtained using a variety of additives in a polyurea grease. The grease was prepared in accordance with the procedure of U.S. Pat. No. 3,243,372, employing as reactants 0.65 weight percent ethylene diamine, 3.74 weight percent tolylene diisocyanate and 6.14 weight percent tall oil fatty amine in 89.12 weight percent of a 600 Neutral oil. The composition contained, in addition, 0.35% by weight of phenyl-alpha-naphthylamine and 0.03% by weight of a dye. The thickener was primarily tetraurea.

The grease employed was a commercial material and contained additionally, 0.5% by weight of sodium nitrite and 0.3% by weight of an ethoxylated fatty amine, both materials being conventional rust inhibitors.

TABLE I.—INHIBITION TEST OF POLYUREA GREASE

Additive		Test results		
Type	Concentration, weight percent	Test A	Test B	Test C
Base grease		Pass	Fail	4
Magnesium powder	1.0			4+
Ricinoleic acid	5.0			3
Magnesium ricinoleate	5.0	Pass	Pass	2
Magnesium oleate	5.0		do	
Magnesium stearate	5.0		Fail	

These data show the efficacy of the magnesium salts of unsaturated fatty acids in imparting rust prevention properties to the grease. It may be noted that ricinoleic acid and magnesium powder alone failed, while the magnesium ricinoleate was successful in preventing rust under these conditions.

EXAMPLE 2

Metal salts of ricinoleic acid in rusting tests

Table II following shows the results obtained employing various other metal salts of ricinoleic acid under the severe conditions of Test C in the same grease including supplementary inhibitors as used in Example I.

TABLE II

Rust Test with polyurea grease containing ricinoleate salts

Additive, concentration 0.5% by weight:	Test results, test C
Base grease alone	4
Magnesium ricinoleate	2
Magnesium ricinoleate (duplicate)	2
Zinc ricinoleate	4
Calcium ricinoleate	4+
Lithium ricinoleate	4
Barium ricinoleate	4
Aluminum ricinoleate	3
Sodium ricinoleate	3+
Potassium ricinoleate	4

Rating: 1 and 2, pass 3 and 4, fail.

Note that magnesium ricinoleate was the only salt that passed the severe test. The other alkaline earth metal and alkali metal salts failed to impart proper rust resistance.

EXAMPLE 3

Rust inhibition by magnesium salts in lithium and clay thickened greases

Table III shows Rust Test results obtained employing a lithium hydroxy stearate grease (NLGI Reference A) and an inorganic bentonite thickened grease (NLGI Reference B). The tests show that the magnesium ricinoleate and magnesium oleate at 1% concentration impart anti-rust properties to these greases. Magnesium stearate (from a saturated acid) does not.

TABLE III.—RUST TESTS OF MAGNESIUM SALTS IN LITHIUM AND CLAY BASED GREASES

	Additive		
Grease Composition	Type	Conc. (wt. percent)	Rusting test C
1. Lithium hydroxy stearate thickened grease, NLGI ref. A.	None		Fail.
	Magnesium ricinoleate.	1.0	Pass.
	Magnesium oleate	1.0	Do.
	Magnesium stearate	1.0	Fail.
2. Inorganic bentonite thickened grease, NLGI ref. B.	None	1.0	Fail.
	Magnesium ricinoleate.	1.0	Pass.
	Magnesium oleate	1.0	Do.
	Magnesium stearate	1.0	Fail.

The greases of this invention are formed with a wide variety of oils of lubricating viscosity. Various base oils include naphthenic base, paraffin base and mixed base mineral lubricating oils; synthetic oils, such as polymers of propylene, butylene, etc., propylene oxide polymers, carboxylic acid esters, e.g. isooctyl azelate pentaerythritol caproate or dipropylene glycol dipelagonate; silicon esters, such as tetraethyl silicate hexa-(4-methyl-2-pentoxy)disiloxane, etc.
pentoxy) disiloxane, etc.

In addition to the rust inhibiting additives, the greases may contain other additives such as oxidation inhibitors,

supplementary rust inhibitors, oiliness improvers, and dyes, etc.

I claim:

1. A grease composition consisting essentially of an oil of lubricating viscosity, a grease thickener other than the magnesium salt below in an amount sufficient to thicken said oil to grease consistency, and in an amount of from 0.1 to 10 percent by weight, sufficient to impart rust inhibiting properties to the grease, a magnesium salt of an unsaturated fatty acid or hydroxy-substituted unsaturated fatty acid, wherein said acid contains from 14 to 24 carbon atoms.

2. The composition of claim 1 in which the magnesium salt is present in the amount of from 0.5 to 8.0 percent by weight.

3. The composition of claim 1 in which the unsaturated fatty acid is ricinoleic acid.

4. The composition of claim 1 in which the fatty acid is oleic acid.

5. The composition of claim 1 in which the grease thickener is a polyurea.

6. The composition of claim 3 in which the oil of lubricating viscosity is a mineral oil.

7. The composition of claim 1 in which said fatty acid contains from 16 to 22 carbon atoms.

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