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LITHIUM SOAP GREASES CONTAINING A RUST INHIBITOR

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The present invention relates to lithium base greases having improved rust inhibiting properties. More particularly, the present invention relates to lubricating greases thickened with a lithium soap and containing a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product.

Lithium base greases have been used in large amounts for several years. This is due primarily to the fact that they have properties which make them more nearly suitable as an "all purpose" grease. In other words, they have a combination of properties which render them useful in a wide variety of lubrication needs.

As is well known, greases comprise a base oil and a thickening agent which, in the case of lithium greases, is generally a lithium soap. In addition, greases contain numerous additive agents to improve specific properties. For example, extreme pressure agents are used to increase the load carrying properties of a grease. In addition, corrosion inhibiting agents are used to increase the resistance of greases to rust and corrosion. For example, U.S. Patent No. 2,812,306 to Hubert J. Liehe describes a lithium base grease which contains, in addition to other materials, a combination of a petroleum oxidation product and sperm oil. The patent teaches that this specific combination is necessary in order to pass the anti-rust test.

Lead naphthenate has been used in greases heretofore; however, to my knowledge it has usually been used as a lubricity agent. Also to my knowledge, the combination of lead naphthenate and a petroleum oxidation product has not heretofore been used in lithium base greases.

It has been my experience that the use of a petroleum oxidation product alone in a lithium base grease does not result in a grease which will consistently pass the rust test. Also, it has been my experience that the use of lead naphthenate alone in a lithium base grease does not result in a grease which will consistently pass the rust test. Unexpectedly, I have found that a combination of a petroleum oxidation product and lead naphthenate results in a grease which will consistently pass the rust test.

In addition, it has been my experience that most rust inhibitors known to the prior art when added to greases have a softening effect. Unexpectedly, I have found that a combination of lead naphthenate and a petroleum oxidation product, when added to a lithium base grease, does not soften the grease but generally exhibits a thickening effect in addition to acting as a rust inhibitor.

It is an object of the present invention to provide improved lithium base lubricating greases.

It is another object of the present invention to provide lithium base lubricating greases having improved rust inhibiting properties.

It is still another object of the present invention to provide lithium base lubricating greases which do not soften upon the addition of a rust inhibitor.

Broadly stated, the present invention relates to lithium base lubricating greases containing as a rust inhibitor a combination of lead naphthenate and a petroleum oxidation product.

More particularly, the present invention relates to lithium base lubricating greases comprising a liquid lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination

of lead naphthenate and a petroleum oxidation product.

The liquid lubricating oil which is used in the lithium base greases of my invention can be either a mineral lubricating oil or a synthetic lubricating oil. Of these, the mineral lubricating oils are preferred. These can be derived from naphthenic or paraffinic base crude oils, and can be either residual or distillate oil or a mixture thereof, depending on the particular grease which is being prepared. For example, in an automotive grease lubricant, a blend of a residual oil with a distillate oil has been found particularly suitable in meeting the viscosity requirements for the various grade.

The term synthetic lubricating oil, as used herein, refers to materials derived synthetically which are suitable as lubricants. Examples of suitable synthetic lubricants include the silicones, polyalkylene glycols, fluorocarbons, esters of dicarboxylic acids, esters of long-chain carboxylic acids, and complex esters. It is to be understood that the type of lubricating oil used in my greases is not critical, and that any of the lubricating oils which have heretofore been used to prepare lithium base greases are suitable.

As is well known, the lithium base lubricating greases are produced by preparing a dispersion of a lithium soap in the liquid lubricating oil. Usually, a calculated amount of soap, which will be defined more precisely hereafter, is added to the liquid lubricating oil base followed by heating at an elevated temperature, for example, from about 350 to about 450° F., for sufficient time to disperse the soap. Subsequently, the hot dispersion is cooled to provide the final grease product. Mixing or milling can be provided, as desired, during any of the preparation steps. Various soaps or admixtures of soaps can be employed in the lithium base greases. However, preferably the soaps are hydroxy fatty acid soaps of lithium. A particularly desirable base grease is obtained through the employment of soaps derived from mixtures of a hydroxy fatty acid and a hydrogenated fatty material, for example, hydrogenated fish oil, castor oil, and the like. Further details concerning the latter greases and their method of preparation are set forth in U.S. Patent No. 2,475,589.

With regard to the amount of soap which is used in the preparation of the base grease, I have found that an amount in the range of about 1 to about 25 percent, by weight, is suitable, with an amount in the range of about 5 to about 10 percent, by weight, being preferable.

The lead naphthenate which is used in the rust inhibiting combination employed in my greases can be obtained from any commercially available source. Generally, a commercial grade of lead naphthenate contains in the neighborhood of about 30 percent, by weight, lead.

The petroleum oxidation product which is a component of the rust inhibiting combination used in my greases is a mixture of aliphatic oxygen-containing compounds of petroleum origin obtained by the controlled oxidation of hydrocarbons, or mixtures of hydrocarbons, such as occur in or associate with petroleum oils. The controlled oxidation is carried out in the liquid phase at elevated temperatures under super-atmospheric pressures. The resultant oxidation product is a mixture of aliphatic alcohols, ketones, alcohol-ketones, lactones, and esters, together with some unoxidized hydrocarbons. The method of obtaining these oxygen-containing aliphatic compounds and the compositions thereof are described in U.S. Patents 1,690,768; 1,690,769; 1,863,004, and others issued to A. W. Burwell. As shown in U.S. 1,863,004, a typical analysis of such oxidation products shows the following approximate composition:

	Weight percent
Saturated aliphatic carboxylic acids	23–40
Neutral lactones and esters from said acids	7–50
Unsaponifiable, non-acidic oxygen-containing aliphatic compounds	25–40

Products of the type suitable for use in the present invention are marketed by the Alox Corporation under the trade name of "Alox" compounds. Compounds marketed as "Alox 125," "Alox 152," "Alox 350," "Alox 1727," and "Alox 2028" are suitable for this purpose. These compounds have the following properties:

	Alox 125	Alox 152	Alox 350	Alox 1727	Alox 2028
Mean Mol. Wt.	450–500	400–425	500–550	500–525	500–525
Acid No. (ASTM D-974-52T)	115–125	17–25	28–35	3–7	3–7
Sap. No. (ASTM D-94)	270–289	125–135	125–135	12–18	60–67
Percent Unsaponifiable	20–25	30–35	30–25	45–55	55–65
Percent Ash	1 0.1	1 0.1	1 0.1	0.3–0.4	0.5–0.6
Specific Gravity at 150° F., about	0.89	0.86	0.89	0.93	0.92
Weight per Gallon (Lbs.), about	7.4	7.2	7.4	7.8	7.7
Melting Point, °F. (ASTM D-127-45), about	190	105	108		98
Flash (O.C.), ° F., about	325	250	310	365	345
Fire (O.C.), ° F., about	325	290	370	450	365

1 Maximum.

For reason of simplicity, these compounds will be referred to herein as "petroleum oxidation products." Of the Alox compounds, I prefer to use either "Alox 125" or "Alox 1727."

With regard to the amounts of lead naphthenate and petroleum oxidation product employed in my invention, I have found that a 1:1 ratio (weight) of the two materials is optimum, although it is suitable to use a petroleum oxidation product to lead naphthenate ratio (weight) as high as 2:1, or even higher. Expressed in another manner, a suitable amount of lead naphthenate is in the range of about 0.50 to about 5.0 percent (weight) with a suitable amount of petroleum oxidation product being in the range of about 0.50 to about 5.0 percent (weight) of the total grease composition. Preferably, the lead naphthenate is used in an amount in the range of about 0.75 to about 2.5 percent (weight), while the petroleum oxidation product is used in an amount in the range of about 0.75 to about 2.5 percent (weight).

Various other additives, such as oxidation inhibitors, lubricity agents, extreme pressure agents, stringiness agents, and the like, may be added to the lithium base greases of my invention. In this connection, I have observed that the presence of other additives has no adverse effect on the rust inhibiting properties of the greases of my invention.

It has been my experience in the past that many rust inhibitors deteriorate the water resistance properties of the lubricating greases to which they are added. Interestingly, I have found that the rust inhibiting combinations of my invention do not deteriorate the water resistance of lithium grease but, on the contrary, improve the water resistance.

The test procedure employed in evaluating rust inhibition in connection with the greases of my invention was ASTM Procedure D–1743–60T. Briefly, this test can be described as follows. Three clean new bearings are lubricated with the test grease and then run under a light thrust load for 60 seconds so as to distribute the lubricant in a pattern that might be found in service. The bearings are then stored for two weeks at 77° F. and 100 percent relative humidity, after which time they are examined visually for evidence of corrosion. The following rating system is employed.

Rating No. 1—No corrosion,

Rating No. 2—Incipient corrosion, no more than three spots of a size just sufficient to be visible to the naked eye,

Rating No. 3—Anything more severe than No. 2.

The following exception to the standard ASTM Procedure was made in the tests run. Instead of using three bearings per grease sample, only two bearings were used. This was due to the fact that a large number of grease samples were tested. In reporting the results of the test, ratings for each of the two bearings are given. For example, a rating of 1,1 means that both bearings had a No. 1 rating; whereas a 1,3 rating indicates that one bearing had a No. 1 rating and the second bearing had a No. 3 rating.

The following examples are presented in illustration of the invention.

Example 1

This example illustrates the cooperative rust inhibiting effect shown by the combination of lead naphthenate and petroleum oxidation product as compared to the rust inhibiting properties of each of the materials used alone.

In this example, two base greases are employed. Base grease A employed a gelling agent consisting of 100 percent lithium 12-hydroxy stearate soap. Base grease B employed a gelling agent consisting of about 75 percent by weight of lithium 12-hydroxy stearate soap and about 25 percent by weight lithium stearate soap. In both base grease A and base grease B a medium viscosity mineral lubricating oil was employed. The gelling agent was present in the preferred range as defined previously. The results of blending varying amounts of "Alox 125" and of lead naphthenate in these two greases are shown in the table below.

Base Grease	Weight Percent Additive in Base Grease		ASTM D-1743 Rust Rating
	"Alox 125"	Lead Naphthenate	
B	1.0	None	3.3 Fail.
B	1.5	None	3.3 Fail.
B	2.0	None	1,3 Borderline.
A	2.0	None	3.3 Fail.
B	None	2.0	1.3 Borderline.
A	None	2.0	1,3 Borderline.
B	None	2.5	3.3 Fail.
A	None	2.5	1,3 Borderline.
B	0.5	0.5	3,3 Fail.
B	0.5	1.5	1.1 Pass.
B	1.0	0.5	3.3 Fail.
B	0.78	1.0	1,1 Pass.
B	1.0	1.0	1.1 Pass.
B	0.5	1.0	1,1 Pass.

Example 2

This example illustrates still further that lead naphthenate used alone does not provide adequate rust inhibiting properties. The base greases were the same as used in Example 1.

Base Grease	Weight Percent Lead Naphthenate in Base Grease	ASTM D-1743 Rust Rating
A	2.0	1,3 Borderline.
A	2.5	1,3 Borderline.

Example 3

This example illustrates the cooperative rust inhibiting effect shown by the combination of lead naphthenate

and petroleum oxidation products, other than used in Example 1. The base greases were the same as used in Example 1.

Base Grease	Petroleum Oxidation Product	Weight Percent Additive In Base Grease		ASTM D-1743 Rust Rating
		Alox	Lead Naphthenate	
A	Alox 152	1.5	None	3,3 Fail.
A	Alox 152	1.5	1.0	1,1 Pass.
B	Alox 152	1.5	1.0	1,1 Pass.
A	Alox 152	1.0	None	3,3 Fail.
B	Alox 350	1.0	None	3,3 Fail.
A	Alox 350	1.5	None	3,3 Fail.
B	Alox 350	1.5	None	3,3 Fail.
A	Alox 350	1.5	1.0	1,1 Pass.
B	Alox 350	1.5	1.0	1,1 Pass.
A	Alox 2028	1.5	None	3,3 Fail.
A	Alox 2028	1.5	1.0	1,1 Pass.
A	Alox 1727	1.5	None	3,3 Fail.
A	Alox 1727	1.5	1.0	1,1 Pass.
B	Alox 1727	1.5	1.0	1,1 Pass.

Example 4

Lithium greases containing the rust inhibiting combination of this invention have been mixed with tap water and then subjected to the ASTM rust test, which they passed. In this test, 75 parts by weight of inhibited grease and 25 parts by weight of tap water were used. The water was difficult to mix in the grease, even when employing high-speed blending equipment, since the inhibited grease is water resistant and does not emulsify water. The admixed non-emulsified water was the external phase of the grease-water blend. Consequently, in the process of packing the test bearings, the bearings contacted the water present in the grease-water blend first. Since the bearings passed the rust test, it is apparent that the grease displaced the water contacting the bearings quite rapidly. The test water employed contained corrosive inorganic compounds, such as alkali and alkaline earth chlorides, carbonates, and sulfates. These tests indicated that the lithium greases of this invention possess excellent rust inhibiting properties, even in the presence of corrosive ions, normally found in water, which can contaminate grease lubricated bearings in actual service conditions.

The data presented in the examples has shown that the use of either a petroleum oxidation product or lead naphthenate alone in a lithium base grease does not result in a grease which will consistently pass the rust test. Still further, the data in the examples has shown that a combination of a petroleum oxidation product and lead naphthenate in a lithium base grease results in a grease which consistently passes the rust test. In addition, the data has shown that several petroleum oxidation products can be used in combination with lead naphthenate to produce a rust inhibiting effect in lithium base greases. It should be noted, also, that I have found that this rust inhibiting effect of the combination of lead naphthenate and petroleum oxidation product is a lasting effect in that samples which were retested after 2 to 11 months still passed the rust test.

Having thus described the invention by providing specific examples thereof, it is to be understood that no undue limitations or restrictions are to be drawn by reason thereof and that many variations and modifications are within the scope of the invention.

I claim:

1. A lithium base lubricating grease comprising a liquid lubricating oil and a grease-forming amount of a lithium fatty acid soap, said grease containing a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, wherein said lead naphthenate is present in an amount in the range of about 0.50 to about 5.0 percent (weight) and said petroleum oxidation product is present in an amount in the range of about 0.50 to about 5.0 percent (weight), said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds obtained by controlled partial oxidation of petroleum hydrocarbons and comprising about 23–40 percent by weight saturated aliphatic carboxylic acids, about 7–50 percent by weight neutral lactones and esters from said acids and about 24–40 percent by weight unsaponifiable non-acidic oxygen-containing aliphatic compounds.

2. A lithium base lubricating grease as defined in claim 1 characterized further in that the lithium fatty acid soap is present in an amount in the range of about 1 to about 25 percent by weight.

3. A lithium base lubricating grease as defined in claim 2 characterized further in that the liquid lubricating oil is a mineral lubricating oil.

4. A lithium base lubricating grease as defined in claim 3 characterized further in that the lead naphthenate is present in an amount in the range of about 0.75 to about 2.50 percent by weight and the petroleum oxidation product is present in an amount in the range of about 0.75 to about 2.50 percent by weight of the grease composition.

5. A lithium base lubricating grease consisting essentially of a mineral lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, said lead naphthenate being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of petroleum hydrocarbons and having the following properties:

Mean molecular weight	450–500
Acid number (ASTM D–974–52T)	115–125
Saponification number (ASTM D–94)	270–280
Percent unsaponifiable	20–25
Percent ash, maximum	0.1
Specific gravity, at 150° F., about	0.89
Melting point (ASTM D–127–45), about ° F.	100
Flash (O.C.), about ° F.	325
Fire (O.C.), about ° F.	325

6. A lithium base lubricating grease as defined in claim 5 characterized further in that the lithium fatty acid soap is derived from a hydroxy fatty acid and hydrogenated castor oil, and is present in an amount in the range of about 1 to about 25 percent by weight.

7. A lithium base lubricating grease as defined in claim 6 characterized further in that the hydroxy fatty acid is 12-hydroxy stearic acid.

8. The grease of claim 7 characterized further in that the lithium fatty acid soap is present in an amount in the range of from about 5 to about 10 percent by weight, the lead naphthenate is present in an amount in the range of from about 0.75 to about 2.5 percent by weight, and the petroleum oxidation product is present in an amount in the range of from about 0.75 to about 2.5 percent by weight.

9. A lithium base lubricating grease consisting essentially of a mineral lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, said lead naphthenate being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained

by controlled partial oxidation of petroleum hydrocarbons and having the following properties:

Mean molecular weight	500–525
Acid No. (ASTM D–974–52T)	3–7
Saponification number (ASTM D–94)	12–18
Percent unsaponifiable	45–55
Percent ash	0.3–0.4
Specific gravity at 150° F., about	0.93
Flash (O.C.), about ° F.	365
Fire (O.C.), about ° F.	450

10. A lithium base lubricating grease as defined in claim 9 characterized further in that the lithium fatty acid soap is derived from a hydroxy fatty acid and hydrogenated castor oil, and is present in an amount in the range of about 1 to about 25 percent by weight.

11. A lithium base lubricating grease as defined in claim 10 characterized further in that the hydroxy fatty acid is 12-hydroxy stearic acid.

12. A lithium base lubricating grease consisting essentially of a mineral lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, said lead naphthenate being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of petroleum hydrocarbons and having the following properties:

Mean molecular weight	400–425
Acid number (ASTM D–974–52T)	17–25
Saponification number (ASTM D–94)	125–135
Percent unsaponifiable	30–35
Percent ash, maximum	0.1
Specific gravity at 150° F., about	0.86
Melting point (ASTM D–127–45), about ° F.	105
Flash (O.C.), about ° F.	250
Fire (O.C.), about ° F.	290

13. A lithium base lubricating grease consisting essentially of a mineral lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, said lead naphthenate being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained

by controlled partial oxidation of petroleum hydrocarbons and having the following properties:

Mean molecular weight	500–550
Acid number (ASTM D–974–52T)	28–35
Saponification number (ASTM D–94)	125–135
Percent unsaponifiable	30–35
Percent ash, maximum	0.1
Specific gravity at 150° F., about	0.89
Melting point (ASTM D–127–45), about ° F.	108
Flash (O.C.), about ° F.	310
Fire (O.C.), about ° F.	370

14. A lithium base lubricating grease consisting essentially of a mineral lubricating oil, a grease-forming amount of a lithium fatty acid soap, and a rust inhibiting amount of a combination of lead naphthenate and a petroleum oxidation product, said lead naphthenate being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being present in an amount in the range of from about 0.50 to about 5.0 percent by weight, said petroleum oxidation product being a mixture of saturated aliphatic oxygen-containing compounds including alkyl esters, lactones, ketones, alcohols, and alcohol-ketones obtained by controlled partial oxidation of petroleum hydrocarbons and having the following properties:

Mean molecular weight	500–525
Acid number (ASTM D–974–52T)	3–7
Saponification number (ASTM D–94)	60–67
Percent unsaponifiable	55–65
Percent ash	0.5–0.6
Specific gravity at 150° F., about	0.92
Melting point (ASTM D–127–45), about ° F.	98
Flash (O.C., about ° F.	345
Fire (O.C.), about ° F.	365

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