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RUST PREVENTIVE GREASE CONTAINING A
POLYVALENT METAL SULFONATE AND A
WAX OXIDATION PRODUCTGeorge W. Eckert, Glenham, and Theodore W.
Langer, Buffalo, N. Y., assignors to The Texas
Company, New York, N. Y., a corporation of
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This invention relates to lubricating greases having superior rust preventive properties which are imparted by a novel combination of additives which they contain. More particularly it relates to lubricating greases containing both an oil-soluble polyvalent metal sulfonate and a synthetic acid product obtained by the partial oxidation of petroleum wax.

It is an object of this invention to provide an improved rust preventive grease for the protection of ferrous metal surfaces. Another object of the invention is to provide a grease suitable for the lubrication of gears, bearings, roller paths and so forth under severe rusting conditions. A still further object of the invention is to provide a grease containing a novel combination of additives which act cooperatively to impart superior rust preventive properties to the grease without substantial impairment of other lubricating properties.

In accordance with our invention a lubricating grease having exceptional rust preventive characteristics and otherwise satisfactory properties for the lubrication of bearings and other metal surfaces exposed to severe rusting conditions is obtained by incorporating in a base grease of any suitable type a combination of additives comprising a small amount in the order of about 0.5 per cent to about 5 per cent of a preferentially oil-soluble polyvalent metal sulfonate and a small amount in approximately the same order of a synthetic acid product obtained by the partial oxidation of petroleum wax. We have found that a higher degree of rust preventiveness is obtained by means of this combination of additives than can be obtained by corresponding amounts of either of the two additives alone, and with the further advantage that other properties of the base grease are not undesirably affected.

It has already been proposed to employ sulfonates, and particularly the oil-soluble polyvalent metal sulfonates as rust inhibitors in lubricating compositions. For example, Duncan et al., U. S. 2,480,638, disclose polyvalent metal sulfonates suitable for use as rust preventive agents in mineral oils, which polyvalent metal sulfonates are prepared from the so-called "mahogany" acids obtained by treating heavy petroleum fractions with concentrated sulfuric acid, or from other preferentially oil-soluble sulfonic acids such as may be obtained by sulfonating olefins, aliphatic fatty alcohols or their esters, alkylated aromatics or their hydroxy derivatives, partially hydrogenated aromatics, and so forth, with sulfuric acid or other sulfonating agents.

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The use of the polyvalent metal salts of the mahogany acids as rust inhibiting agents in lubricating oils and greases, including calcium, aluminum, barium, magnesium, zinc, sodium, and lithium base greases, is also disclosed by Bray, U. S. 2,453,690 and Butcosk, U. S. 2,445,936.

While compounds of the above type have been found to impart a mild degree of rust preventiveness to lubricants, they are not sufficiently effective by themselves to produce lubricants which are suitable for use under severe rusting conditions, i. e., under conditions of high humidity and the presence of rust promoting salts, such as are encountered for example in the operation of marine installations. Furthermore, the use of these compounds in large amounts in greases is frequently undesirable because of such effects as high water absorption, increased low temperature torque and changes in grease consistency which they impart.

The sulfonates which are suitable for forming our additive combinations are the oil-soluble polyvalent metal sulfonates in general which act as anti-rust agents in lubricating compositions, as disclosed in the above cited patents. They are preferably those obtained from the mahogany acids resulting from the action of a sulfonating agent such as concentrated or fuming sulfuric acid on heavy petroleum fractions. The metallic element of these salts is preferably an alkaline earth metal, most suitably calcium, although other polyvalent metals such as Al, Zn, Sn, Co, and so forth, may also be employed.

The mahogany acids which constitute the preferred material for forming the sulfonates of our additive combination are obtained as before stated by treating a heavy oil, which may be a distillate fraction from a paraffinic, naphthenic or mixed base crude, with concentrated sulfuric acid, fuming sulfuric acid or other suitable sulfonating agent. After removal from the acid treated products of the acid sludge which contains the water-soluble, so-called "green" acids, the mahogany acids may be separated and converted to the desired polyvalent metal salts by any convenient method such as by neutralizing them with an alkali metal oxide or hydroxide, extracting the salts thus formed from the oil with a solvent such as an aqueous alcohol solution and converting the extracted salts to the desired polyvalent metal salts by double decomposition between the alkali metal sulfonates and a suitable polyvalent metal salt. They may also be obtained by extracting the mahogany acids with a solvent and neutralizing the extracted

acids directly with a suitable polyvalent metal base.

The synthetic acid product comprising the second component of our additive combination is obtained by the partial oxidation of a petroleum wax, such as crude scale wax, slack wax, petrolatum or heavy lubricating oil fractions by any of the well known methods of wax oxidation such as by blowing with air or oxygen at increased temperatures or by chemical oxidation. It may be obtained for example by the method of U. S. 1,909,945, whereby crude scale wax is oxidized with air at atmospheric pressure and at 260-330° F. for a period of about 16 hours. The product obtained by such oxidation processes is of indefinite composition and has properties which differ from those of the fatty acids by reason of the other oxygen-containing groups such as hydroxy, keto and ester groups which it contains. In particular, such materials have special properties which make them desirable components of lubricating compositions, and they have been used in lubricating oils as stabilizers, wax suppressors, detergents, oiliness agents, and so forth. We have found that small amounts of these materials, such as about 0.5 per cent to about 5 per cent, impart a considerable increase in rust preventiveness to greases, although not sufficient to form a grease suitable for use under extreme rusting conditions, as determined by the familiar salt spray rusting test. Additional amounts of the material added to the grease yield no appreciable increase in rust preventiveness and impart an undesirable degree of acidity to the composition.

The amount of synthetic acid product which may be employed in the rust preventive greases of our invention depends chiefly upon the neutralization number and other properties of the product which will vary according to the conditions of manufacture such as the severity and duration of the oxidation process and the starting material. In any case, the maximum amount which may be employed will be limited by the permissible neutralization number of the finished grease. Thus where the maximum permissible neutralization number of the finished grease is 2.5, approximately 2.5 per cent of a synthetic acid product having a neutralization number of 100 may be employed, or approximately 5 per cent of a synthetic acid product having a neutralization number of 50, where the grease contains no other acidic compounds. We have found that the maximum effectiveness of this additive is also within this general range, so that our preferred range is from about 1 per cent to about 3 per cent for synthetic acid products having neutralization numbers ranging from about 50 to about 200. On the other hand, larger amounts, for example 5 per cent or more, may be employed if desired where the neutralization number of the grease is not critical; and smaller amounts, such as 0.5 per cent or less, may be used in some cases. The sulfonate additive is preferably employed in amounts ranging from about 0.5 per cent to about 5 per cent by weight based on the weight of the finished grease, although amounts as low as 0.1 per cent or as high as 10 per cent or more may be used if desired.

The base grease into which our additives are incorporated preferably comprises a mineral base thickened with about 5-40 per cent and preferably 7-25 per cent of a metal soap of a long chain fatty acid, such as an acid or a mixture of acids of C₁₂ to C₂₂ carbon atoms. The metal com-

ponent of the soap may be any of the metals commonly employed as grease bases, such as sodium, potassium, lithium, calcium, barium, magnesium, aluminum, zinc, lead, and so forth, or mixtures of these. In addition to the rustproofing additives of our invention, the grease may contain other addition agents such as extreme pressure agents, oxidation inhibitors, corrosion inhibitors, anti-bleeding agents, and so forth. It is desirable, although not necessary, to add a small amount, such as from about 1 per cent to about 5 per cent, of a glyceride such as tallow, lard oil, castor oil, or hydrogenated vegetable oil, the same constituting a third element of our rustproofing combination.

A particularly valuable application of our invention is the rustproofing of a lithium base grease prepared from a soap-forming fatty material containing at least a major proportion of a soap-forming hydroxy fatty acid, such as 12-hydroxy stearic acid, or a soap-forming hydroxy fatty acid glyceride, such as hydrogenated castor oil. The lithium soap of the hydroxy fatty acid or the glyceride thereof may constitute the sole thickening agent of the grease; but preferably the lithium soap is formed from a mixture of a major proportion of the hydroxy fatty acid or glyceride with a minor proportion of the order of 10-40 per cent by weight based on the total soap-forming fatty material of a non-hydroxy soap-forming fatty acid, such as stearic acid, or the glyceride thereof. For example, a grease having a lubricant base thickened with the lithium soap of about a 3:1 mixture of hydrogenated castor oil and stearic acid represents a preferred type of product. Greases of this type are particularly useful for the lubrication of aircraft bearings and controls.

However, the rustproofing combination of the present invention is not limited to use in such a lithium base grease, but is of general application to greases of various soap bases where highly effective rustproofing characteristics are desired. Thus the combination of the polyvalent metal sulfonate with the wax acids, or the combination of the polyvalent metal sulfonate with the wax acids and the glyceride, are highly effective in rustproofing sodium or calcium base, or mixed sodium-calcium base, ball and roller bearing lubricants. Likewise, they are highly effective in rustproofing basic or normal barium base greases adapted for lubrication of amphibious craft or other marine application.

The effectiveness of our novel additive combinations in producing rust inhibiting greases is illustrated in the following table showing the results obtained by adding a number of different additive combinations falling within the purview of our invention to two lithium base greases made with two different viscosity oils and subjecting the composition to the salt spray rusting test, which is a test commonly employed to show the rust resisting properties of greases under conditions of high humidity and in the presence of rust accelerating salts such as are present in sea water. According to this test, steel panels are thinly coated with the test grease and maintained in contact with a spray of 4 per cent sodium chloride solution at room temperature and pressure for periods up to 100 hours or longer. Greases which completely resist rusting of the steel panel for a period of at least 20 hours are considered to have fair anti-rusting properties. A good rust-preventive grease for use under severe rusting conditions should permit no rust-

ing or only very slight rusting of the panel during 100 hours exposure to the salt spray.

EXAMPLE

Two lithium base greases were prepared using a low viscosity oil and a high viscosity oil respectively. One grease, designated as A, was prepared having the following composition: 14.7 per cent lithium soap of hydrogenated castor oil, 5.1 per cent lithium stearate, 0.15 per cent stearic acid, 0.5 per cent phenyl alpha naphthylamine, 1.5 per cent glycerine and 78.05 per cent of a mineral lubricating oil of S. A. E. 10 grade having an SUS viscosity of 175 at 100° F. A second grease, designated as B, was prepared having the following composition: 13.09 per cent lithium soap of hydrogenated castor oil, 5.1 per cent lithium stearate, 0.5 per cent phenyl alpha naphthylamine, 0.01 per cent lithium hydroxide, 1.30 per cent glycerine and 80.0 per cent mineral lubricating oil having an SUS viscosity of 50 at 100° F.

To the above greases were added small amounts of sulfonates and of a synthetic wax oxidation product and the resulting compositions subjected to the salt spray rusting test described above. The additives were incorporated evenly into the grease by stirring the mixture vigorously for 15 minutes at a temperature of 150° F. The following table shows the effect of these additives on the rust preventive properties of the greases.

Table

	Percent of surface rusted		
	5 hours	20 hours	100 hours
Grease A.....	15	65	95
Grease A+2.5% Ca sulfonate.....	10		
Grease A+1% wax acids.....		5	
Grease A+2.5% wax acids.....		1	
Grease A+3% wax acids.....		1	10
Grease A+4% wax acids.....		3	20
Grease A+5% wax acids.....		2	15
Grease A+3% wax acids+0.70% Ca sulfonate+3% star tallow.....		0	0
Grease B.....		75	95
Grease B+1.50% Ca sulfonate.....		8	
Grease B+3% wax acids.....		1	10
Grease B+3% wax acids+1.05% Ca sulfonate.....		0	3
Grease B+3% wax acids+2.80% Ca sulfonate.....		0	0
Grease B+3% wax acids+1.05% Al sulfonate.....		0	6
Grease B+3% wax acids+1.05% Ca sulfonate+3% star tallow.....		0	0
Grease B+3% wax acids+1.05% Al sulfonate+3% star tallow.....		0	3
Grease B+1.5% wax acids+0.53% Ca sulfonate+1.5% star tallow.....		0	7
Grease B+2% wax acids+2.10% Ca sulfonate+2% star tallow.....		1	2

The additive referred to in the above table as "wax acids" was a synthetic oxygenated product obtained by the air oxidation of petrolatum stock from a paraffin distillate having an SUS viscosity at 100° F. of about 225. The oxidation was carried out in the presence of 1 per cent manganese naphthenate at 238-250° F., atmospheric pressure and 1.5 cubic feet of air per hour per pound of charge for 72 hours. The oxidate thus obtained had a saponification number of 223, a neutralization number of 95 and an unsaponifiable content of 31.6 per cent. This oxidate was treated with 20 per cent by weight of 40 per cent sulfuric acid at 160° F. to obtain the product employed as an additive in the experiments described above. The product had a saponification number of 184 and a neutralization number

of 79, corresponding to a free fatty acid content of 41.7 (calculated as oleic acid).

The calcium sulfonate additive was prepared from sulfonic acids obtained by treating a furfural extracted, 385 SUS viscosity fraction of a mid-continent crude with fuming sulfuric acid and extracting with aqueous alcohol solution. The alcoholic extract was neutralized with 40° Baumé caustic solution, diluted with a light distillate oil and stripped free of solvent. The solution of sodium sulfonates thus obtained was treated with an aqueous solution of calcium chloride sufficient to convert the sodium sulfonates to calcium sulfonates, which separated out in the form of a brown, curdy precipitate. This precipitate was dissolved in benzene, washed with water, and the solution diluted with a naphthene base distillate oil having an SUS viscosity at 100° F. of about 300. The benzene and any remaining water were finally stripped off and further amounts of distillate oil added to give a 35 per cent solution of the calcium sulfonates.

The aluminum sulfonate additive was prepared by the same method as described above for the preparation of calcium sulfonates except that aluminum sulfate was employed in the double decomposition of the sodium sulfonates instead of calcium chloride.

As shown by the table neither the wax acids nor the sulfonates alone produced a grease of sufficient anti-rusting properties to pass the 20 hour salt spray rusting test. However, by adding small amounts of each of these additives, greases were obtained which passed the 20 hour test and permitted only slight rusting or no rusting at all for periods of 100 hours or longer. The greases thus obtained were noncorrosive according to the copper strip test and had satisfactorily low water absorption and low temperature torque.

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 adapted for the lubrication of high-speed ball and roller bearings under severe rusting conditions comprising essentially a mineral lubricating oil as the predominant constituent thickened to a grease consistency with about 7-25% by weight of the lithium soap of a saponifiable material consisting of a major proportion of a soap forming hydroxy fatty material and a minor proportion of a non-hydroxy soap forming saturated higher fatty acid, said lubricating grease also containing about 0.7-1.05% by weight of a calcium salt of mahogany sulfonic acids, about 2-3% by weight of a synthetic acid product having a neutralization number from about 50 to about 100 obtained by the partial oxidation of petroleum wax, and about 2-3% of tallow, said grease being capable of preventing substantially any rusting of steel panels in the salt spray rusting test for periods up to 100 hours.

2. A lubricating grease adapted for the lubrication of high-speed ball and roller bearings under severe rusting conditions comprising essentially a mineral lubricating oil as the predominant constituent thickened to a grease consistency with about 7-25% by weight of the lithium soap of a saponifiable material consisting of a major proportion of hydrogenated castor oil and about 10-40% by weight based on the total saponifiable material of stearic acid, said lubricating grease

also containing about 0.7-1.05% by weight of calcium mahogany sulfonate, about 2-3% by weight of a synthetic acid product having a neutralization number from about 50 to about 100 obtained by the partial oxidation of petroleum wax, and about 2-3% by weight of tallow, said grease being capable of preventing substantially any rusting of steel panels in the salt spray rusting test for periods up to 100 hours.

GEORGE W. ECKERT.
THEODORE W. LANGER.

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