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3,736,256

NITRITE CONTAINING CORROSION-INHIBITING GREASE COMPOSITIONS

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ABSTRACT OF THE DISCLOSURE

This invention concerns synergistic combinations of inorganic nitrites and certain amines which when incorporated into alkali-metal soap and/or alkaline earth metal soap based greases inhibit corrosion.

This invention concerns nitrite-containing, corrosion-inhibiting greases and their preparation. More particularly, this invention concerns grease compositions incorporating combinations of inorganic nitrites with certain amines as their corrosion-inhibiting entity.

The use of corrosion-inhibiting compositions in oils and greases to minimize corrosion in moving parts such as bearings is well known in the lubricating art. In the absence of these compositions, metal parts, particularly those fabricated from the ferrous metals and their alloys, rapidly become oxidized in an environment of heat, moisture and free acidity. Once oxidized, these parts function unsatisfactorily, and prematurely require maintenance and/or replacement.

Corrosion inhibitors can be of different types or classes. Some are oil-soluble while others are oil-insoluble. Illustrative of the former type of inhibitors are the metal sulfonates and naphthenates, while the latter are exemplified by inorganic nitrite and borate salts. Generally, the oil-insoluble (water-soluble) type of corrosion-inhibitors are preferred for static or quiescent operational conditions while the oil-soluble inhibitors have been favored in situations where the grease film is being constantly sheared and displaced (as in bearings). However, for applications where the greases are challenged by an environment of elevated temperatures and high humidity, neither the oil-soluble salts or the metal nitrites alone have been entirely satisfactory, and novel and more effective combinations of inhibitors is sought. This is particularly the case in lithium soap-based greases where sodium nitrite alone in moderate amounts does not provide the desired degree of anti-corrosive protection. Increasing the quantity of nitrite is undesirable since, in many instances, it adversely affects the physical characteristics and stability of the grease. In view of this shortcoming much development work has been done to find materials which, when combined with the nitrites, will synergize or potentiate their corrosion inhibition. In U.S. 3,459,683, the use of an aromatic amine is disclosed to improve the anti-corrosive effect of alkali metal nitrites, while in U.S. 3,098,848 and 2,971,911 certain heterocyclic amines are shown to potentiate sodium nitrite containing greases in their anti-corrosive properties. Unfortunately, other aromatic and heterocyclic amines have been shown to be ineffective. Similarly, certain aliphatic amines have been found to potentiate the effect of the nitrite component

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while others have little effect or an adverse effect on corrosion-inhibition. In short, the selection of potential synergists for nitrite salts as anti-corrosive compositions is an empirical task and ordinarily cannot be predicted. After considerable evaluation of potential synergists, the applicants have found that the amines disclosed infra are effective as corrosion-inhibitors when utilized in conjunction with nitrites while others, seemingly equally operable, are ineffective.

It is an object of this invention to provide a selection of amines, empirically derived, which, when employed in an alkali-metal soap-based lubricating grease together with alkali metal and/or alkaline earth metal nitrites, provide superior protection from corrosive attack compared to greases incorporating the nitrite or amine component alone.

Another object of this invention is to provide anti-corrosive compositions which can be added to alkali-metal soap-thickened greases to substantially increase their resistance to corrosion.

Further objects can be gleaned by those skilled in the art from an examination of this application including the several embodiments and examples.

In practice, the above objects can be achieved by the inclusion of from about 2.0 to 5.0 parts by weight of an anti-corrosive composition comprising:

(a) From about 0.5 to 4.0 parts by weight of inorganic nitrite selected from the group consisting of calcium nitrite, barium nitrite, strontium nitrite, sodium nitrite, potassium nitrite, lithium nitrite, and mixtures thereof, and

(b) From about 0.5 to 5.0 parts by weight of at least one amine selected from the group consisting of N-oleyltrimethylene diamine, aniline, bis-p-aminophenylethane, mixtures of tertiary aliphatic primary amines ranging from C₁₂-C₁₅ and having a molecular weight averaging 185-213, and mixtures of these, for each 100 parts by weight of alkaline earth metal soap and/or alkali metal soap based grease.

In the preferred practice a lithium soap thickened, paraffin based distillate oil containing grease having superior anti-corrosion properties is prepared by admixing the following components:

(a) From about 95 to 99 parts by weight of a lithium soap thickened grease comprising:

(1) From about 90 to 95 parts by weight of a paraffinic distillate oil having a SUS viscosity at 100° F. of between 1000 and 1200 and API gravity of between 22 and 26,

(2) From about 3.5 to 6.0 parts by weight of a lithium soap selected from the group consisting of the lithium salts of stearic acid, the lithium salt of 12 hydroxy stearic acid.

(b) From about 1 to 5 parts by weight of anti-corrosive composition comprising:

(1) From about 1.0 to 4.0 parts by weight of sodium nitrite, and

(2) From about 0.5 to 3.0 parts by weight of N-oleyltrimethylene diamine.

In order to more clearly disclose the inventive concept, the following supplemental information is supplied:

(A) Alkaline earth metal or alkali metal soap-based greases. The term grease as used herein refers to solid or semi-fluid lubricants comprising a major amount of at least one oil of lubricating viscosity and a minor amount of at least one alkaline earth metal soap and/or alkali metal soap, as well as a minor amount of additives or

modifying agents generically referred to as grease adjuvants. The grease components are as follows:

(1) Oil of lubricating viscosity.—the lubricating oils to be employed as the major component of the inventive corrosion-inhibiting greases include any of the hydrophobic oils of lubricating viscosity derived from synthetic or natural (mineral or fossilized) sources or mixtures of these oils. The former include the aliphatic diesters such as bis-2-ethyl sebacate, bis-dinonyl adipate, alkyl (methyl, ethyl, hexyl, etc.) and mixed alkyl esters of pentaerythritol, alkyl silicates, polyoxyalkylene monomers and polymers such as polyoxyethylene glycols and polyoxypropylene glycols, alkyl silicanes, alkyl and aryl phosphates such as trioctyl phosphate, tributyl phosphate, tricresyl phosphate and the like.

The naturally derived oils utilized in this invention may be either naphthenic, paraffinic or asphaltic in type, or blends of one or more of these having a viscosity ranging from about 50 SSU to about 2000 SSU at 100° F., preferably between about 300 and 1200 SSU at 100° F. The viscosity index of the oil or oils can vary from below 0 to about 100 or higher. The oil may be relatively crude or highly refined by processess as diverse as solvent refining or distillation.

These oils, whatever their origin, comprise from about 75 to 97 parts by weight, preferably from about 85 to 96 parts by weight, of each 100 parts by weight of the grease.

The soaps utilized as the principal thickening agents for the grease compositions comprise the alkali metal and/or alkaline earth metal salts of aliphatic fatty acids or hydroxylated fatty acids containing about 10 to 30 carbon atoms, preferably 12 to 18 carbon atoms. Illustrative acids include stearic, oleic, myristic and palmitic acids as well as their hydroxylated derivatives. The glycerides or lower alkylesters may be employed instead of the fatty acids. The alkali metal soaps are preferred particularly the lithium soap of 12-hydroxystearic acid. Ordinarily the metal soap(s) is used in amounts ranging between 3 to 25 parts by weight of the finished grease with from 4 to 15 parts by weight representing the preferred amount.

(B) Inorganic nitrite.—The nitrites which, together with certain selected amines, form the corrosion-inhibiting compositions of this invention are selected from the alkaline earth metal nitrites and the alkali metal nitrites and mixtures thereof.

The alkali metal nitrites are the favored nitrites with the preferred nitrite being sodium nitrite. If the nitrites are to be added to the grease or grease components in solid form, it is desirable that they should be finely particulated; preferably from about 90 to 95% of them should have a particle size less than 40 microns, most preferably a particle size range of about 0.5 to 5.0 microns. The nitrites can be ground to order using the usual blenders, ball mills, colloid mills and the like. Particle size can be determined by electron or light microscopy or similar techniques.

As will be demonstrated infra there are several methods of incorporating the inorganic nitrite into the grease. However, the preferred method, especially when sodium nitrite is the nitrite used, is to prepare a dispersion of sodium nitrate in a mineral oil base using a dispersant such as polyalkylene polymer or a sulfonate. This dispersion is then added to the preformed grease or its component parts. The preparation of the nitrite-oil dispersion is described below under "Embodiment A." The preparation of an illustrative preformed grease thickened by a lithium soap is described under "Embodiment B" which follows "Embodiment A."

EMBODIMENT A

A suitable stirred reactor is charged with 225 gallons of distilled water and 1886 pounds of solid sodium nitrite and heated to 150–170° F. The nitrite solution is stirred at this temperature for an hour and 540 gallons of a

paraffinic distillate oil,¹ 220 lbs. of emulsifiable polyethylene,² and 35 lbs. of 25% by weight caustic are added. Nitrogen gas is passed into the stirred mixture to purge out oxidants and the temperature is raised to 230° F. and kept at this temperature for one hour. At the end of this time the temperature is gradually raised to 325° F. over a period of 8–10 hours. The mixture is held at this temperature for two more hours with a continuous flow of nitrogen into the system. The mixture is then allowed to cool to a gel.

EMBODIMENT B

A grease kettle equipped with heating, cooling and stirring means is charged with 23.46 parts by weight water and 3.48 parts by weight lithium hydroxide monohydrate. This mixture is stirred and heated to 120° F. at which time 141 parts by weight of base oil³ and 23.45 parts by weight 12-hydroxy-stearic acid are added. The batch is stirred and heated to 200° F. and held at this temperature for ½ hour. The batch is then heated to 300° F. and 70 parts by weight of the base oil is added. Heating and stirring are continued until the batch reaches a temperature of about 400° F. At about 400° F., when the batch is molten, heating is stopped and the cooling cycle is initiated. Immediately 38 parts by weight base oil are added to the stirred, cooling grease. When the batch temperature reaches 375° F., jacket cooling of the kettle is stopped and the stirred grease batch is allowed to continue cooling to about 300° F. with stirring. When the temperature of the batch reaches 300° F. another 127 parts by weight portion of the base oil is added at the rate of 2 parts by weight per minute. The temperature of the batch is not allowed to fall below 220° F. during this stage. While the temperature is at 200–220° F., any additives are added while stirring for 30 minutes more. After the addition is complete, the batch is cooled to 180° F. and milled to grease consistency.

EMBODIMENT C

Suitable amines.—The selection of the amines which are used in conjunction with inorganic nitrites to provide corrosion inhibition for the grease is made empirically. These amines are selected from the members of the group consisting of n-oyleyltrimethyldiamine, a mixture of tertiary aliphatic primary amines containing from C₁₂ to C₁₅ carbon atoms and having a mole weight averaging about 185 to 213, a mixture of tertiary aliphatic amines containing C₁₈–C₂₂ carbon atoms having a molecular weight averaging from 269–325, bis-p-aminophenyl ethane, aniline, diphenylamine and mixtures thereof. The basis of choosing useful amines is ASTM-1743-64 method entitled "Rust Preventive Properties of Lubricating Greases." Potentially useful amines are screened by this procedure as shown below. The test is run twice, the duplicate run being designated as "check." In this procedure three clean new bearings are lubricated with the lubricant composition containing sodium nitrite alone, the amine alone and the grease containing an admixture of sodium nitrite and amine. First the lubricated bearings are run under a light thrust load for 60 seconds so as to distribute the lubricant in a pattern that might be found in actual service operation. The bearings are then stored for

¹ The major characteristics of the mineral oil are as follows:

API gravity: 29.3
Flash, COC: 450° F.
Pour point: 5° F.
Viscosity at 100° F.: 342 SUS
Viscosity at 210° F.: 54.3 SUS
Viscosity index: 94

² The polyalkylene polymer used can be characterized as follows: Softening point (ASTM-28) 229° F., Hardness (ASTM D-1321) 100 g./5 sec./77° F., acid number—16, specific gravity at 75° F. 0.94 at 248° F.—0.81, viscosity at 284° F. (cps.)—160 at 248° F.—300.

³ The base oil had the following properties: API gravity 24.4; viscosity 1150 SUS at 100° F. and 84 SUS at 210° F.; flash COC 450° F.; and pour +20° F.

two weeks at 77° F. and 100 percent relative humidity. After cleaning, the bearings are examined for evidence of corrosion and rated as follows according to the degree of corrosion found: A bearing showing no corrosion is rated 1. Incipient corrosion of no more than three spots of a size to be visible to the naked eye is rated 2. Anything more severe is rated 3 and is considered as a failure. If the ratings on two of three of the bearings agree, this number is reported for the sample. If all three ratings are different, the test is repeated. For the purpose of this invention, to be considered passing, both the original and rerun (check) test must give passing results.

EMBODIMENT D

Other components of the grease.—In addition to the oil and soap thickeners contained in the corrosion compositions, other modifiers, additives and the like can be present to impart or enhance desirable properties or to eliminate deleterious properties. These optional ingredients are generically referred to as adjuvants and may include other thickeners or fillers such as finely divided asbestos, silica and clay (such as the bentonites), stabilizers such as polymerized dihydroquinoline derivatives, emulsifiers such as polyoxyalkylated fatty alcohols and polyoxyalkylated alkylated phenols, anti-wear agents such as dibenzyl sulfides, viscosity index improvers, extreme pressure agents such as tricresyl phosphate and heavy metal naphthenates and other agents of varying structure and purpose. When any of these optional additives are utilized they can comprise as much as 10 parts by weight for each 100 parts by weight of the final grease composition, but more usually they will comprise from about 0.1 to 7.0 parts by weight per 100 parts by weight of the finished grease. When these grease adjuvants are utilized they are added at the expense of the oil component and unless specified otherwise they are included in the total quantity of oil specified to be in the grease.

While these adjuvants can be introduced into the grease compositions at several different stages, it is preferred to add them during the cooling cycle.

EMBODIMENT E

Ratio of inorganic nitrate to amine and what constitutes an anti-corrosive or corrosion inhibiting amount.—The inorganic nitrite component of the corrosion-inhibiting composition may be present in varying proportions compared to the amine component employed. A weight ratio ranging from about 5:1 to 1:10 represents a range where corrosion inhibition is obtained without compromising the properties of the grease. A narrower range of about 1:1 to 3:1 (nitrate:amine) representing the range where the most significant increase in inhibition of corrosion is obtained. For this reason the latter range of ratios represents the preferred ratio of nitrite to amine in the grease.

A certain minimal concentration of nitrite-amine composition must be present. While this concentration will vary somewhat according to the grease to be protected and the protection desired, it has been found that fair protection against corrosion usually can be obtained when as little as 0.6% by weight of the finished grease comprises the nitrite-amine combination, the nitrite being present in a 1:1 to 3:1 excess. This concentration is referred to as a corrosion-inhibiting or anti-corrosive amount. However, in order to rule out marginal or erratic protection and to assure reproducibility, a concentration of at least 1.33% of the finished grease should comprise the amine-nitrite composition, wherein the nitrite component is present in the above recited excess. The upper concentration of the anti-corrosive composition is not critical being primarily limited by cost and any possible deleterious effect that large quantities of non-lubricants can have

on the physical properties of the finished grease. For most lubrication applications, the amount of anti-corrosive composition should not exceed about 5% by weight of the grease. In view of this, the preferred range of corrosion inhibiting composition is between about 1 and 3% by weight of the finished grease.

EMBODIMENT F

Preparation of the corrosion inhibiting greases

Any one of several methods can be employed. They are as follows:

(1) Using solid nitrite and preformed grease (referred to as Method 1).—In this procedure a grease kettle fitted with cooling, heating and stirring means is charged with a preformed grease preferably with an alkali metal soap-thickened grease, and the grease is heated with stirring to about 125° to 250° F. over a period of about 30 to 90 minutes. During this time, preferably when the temperature is between 190° F. and 220° F. the solid nitrite component of the grease is slowly added to the stirred grease. The heating and stirring are continued for a period ranging from about 15 minutes to 30 hours until a homogeneous grease mixture is obtained. At this time the grease is cooled to about 190 to 220° F. and the amine component along with any other desired additive is incorporated into the stirred grease mixture. After a homogeneous grease blend is made, heating and stirring are stopped and the grease mixture is allowed to cool.

(2) Using a previously prepared ground slurry of nitrite in oil.—In this procedure (referred to as Method 2) the slurry of nitrite in oil, preferably a mineral oil, is added to the grease (which is formed in situ from its component parts) during the cooling cycle, preferably between 190° F. and 220° F. Briefly, the procedure is as follows: A saponifiable material (such as hydrogenated castor oil) is saponified using an alkaline saponifying agent such as caustic in the presence of oil and water. The slurry of nitrite is added to the grease batch after dehydration of the grease during the cooling cycle along with any other desired additives including the amine component.

(3) As an aqueous solution of nitrite.—In this procedure (referred to as Method 3) the aqueous nitrite solution is added to a grease formed from its component parts during the cooling cycle. A mixing kettle equipped as described earlier is charged with a major portion of the oil, saponifiable material and alkaline saponifying agent and heated to between 375 and 400° F. with stirring until the grease is formed. Then during the cooling cycle between about 375 and 325° F. the remainder of the oil is added and the nitrite in the form of an aqueous solution is added while the temperature is held between 230° and 260° F. to dehydrate the grease. The remaining additives as well as the amine are added when the temperature reaches about 200° F.

The grease is finished in the usual manner.

(4) Using a dispersion of nitrate in oil (Method 4).—A grease is formed in situ by saponifying a saponifiable material such as hydrogenated castor oil using an alkaline saponifying agent such as lithium hydroxide, alone, or together with another alkaline material if a mixed soap is desired, in the presence of oil and water. After saponification and dehydration are completed, the dispersion of nitrite and polyalkylene emulsifier in oil (prepared as in Embodiment A) is slowly added to the cooling, stirred mixture. At this time in the cooling cycle or prior or subsequent to it, the amine component of the corrosion-inhibiting composition can be added alone or together with any other desired additives. The grease is finished as before.

(5) Adding particulated nitrite having a critical particle size to a preformed grease.—Here the amine compo-

nent and inorganic nitrite are ground together until the slurry of nitrite and amine is formed in which 90-95% of the nitrite particles have a particle size of less than 40 microns, preferably between 0.5 and 5 microns. The amine and nitrite blend is then blended with a preformed grease disclosed in Method 1.

In order to present this invention in the greatest possible detail, the following illustrative embodiments and examples are submitted. Unless specified otherwise, all percentages and parts are by weight rather than volume.

EXAMPLE 1

Preparation of an illustrative corrosion-inhibiting grease using a preformed lithium soap grease

To an appropriately sized grease kettle equipped with heating, cooling and stirring means is charged 96.34 parts by weight of the preferred lithium soap-thickened grease whose preparation is described under Embodiment B. The grease is heated to about 190° to 220° F. with stirring over a period of ½ hour. At the end of this time a 3.33 parts by weight portion of the dispersion of sodium nitrite¹ (0.99 part by weight) in paraffinic distillate oil is slowly added to the stirred grease mixture. This is followed by the gradual addition of a 0.33 part by weight of N-oleyltrimethylene diamine into the stirred mixture. As the data in Table I indicate, a corrosion-inhibiting grease (as evaluated by ASTM D-1743-64) having generally satisfactory characteristics is obtained.

Substantially similar corrosion-inhibition is obtained in a grease identical in composition to that obtained above except that the lithium soap grease is first formed in situ from its component parts and that both the amine and the sodium nitrite dispersion are added to the grease between 200-220° F. on the cooling cycle.

EXAMPLE 2

Preparation of a lithium soap thickened control grease without either the nitrite or amine component of the inventive corrosion inhibiting composition of Example 1

Using the apparatus, preparative techniques and the preformed lithium soap-thickened grease of Example 1, a control batch of grease used to ascertain the corrosion-inhibiting effect of the preformed grease is prepared as follows: The grease of Example 1 (96.34 parts by weight) is heated with stirring at 190° to 220° F. over a period of ½ hour. The heat is terminated and the stirred grease is allowed to cool to about 180° F. and 3.66 parts by weight of the paraffinic distillate oil used as dispersant for the sodium nitrite in Example 1 is added to the stirred, cooling grease. As can be seen by an examination of the data presented in Table I, while the preformed grease has good general physical characteristics, the corrosion-inhibiting characteristics as measured by ASTM D-1734-64 is unsatisfactory.

EXAMPLE 3

Preparation of lithium soap thickened grease containing only the nitrite component of the corrosion-inhibition composition

Using the apparatus and preparative techniques used in formulating the grease of Example 1, a 3.33 parts by weight portion of the oil dispersion of Example 1 containing 0.99 part by weight of sodium nitrite is added to a stirred 96.67 parts by weight portion of the preformed lithium grease of Example 1. Again, the addition of

¹ The preparation of this dispersion of nitrite in oil is described in Embodiment A.

nitrite component is made at 190° to 220° F. during the cooling cycle, but in this instance no amine component is employed. After finishing the grease as described in Example 1, the grease is evaluated by the ASTM procedure previously described. As the data in Table I indicate, while the general physical characteristics of the grease are satisfactory, corrosion-inhibition as determined by ASTM D-1743-64 is not adequate.

EXAMPLE 4

Preparation of lithium soap thickened grease containing only the amine component of the corrosion-inhibiting composition

Again the apparatus, preparative technique, preformed grease and amine component of Example 1 are employed. A 0.50 part by weight portion of N-oleyltrimethylene diamine is added to 99.50 parts by weight of the stirred preformed grease at 190° to 220° F. during the cooling cycle. As the data in Table I establishes, the corrosion-inhibition characteristics of the grease, containing only the amine component of the corrosion-inhibiting composition, are not adequate for corrosion inhibition using ASTM D-1743-64 as the criterion.

TABLE I.—CORROSION INHIBITION OF GREASES PREPARED IN EXAMPLES 1 TO 4

Example Number.....	1	2	3	4
Li soap thickened grease, Embodiment A.....	96.34	96.34	96.67	99.50
NaNO ₂ -oil dispersion, Embodiment B.....	3.33		3.33	
N-oleyltrimethyl diamine.....	0.33			0.50
Mineral oil whose properties are described first footnote page 7.....		3.66		
Tests:				
Penetration:				
Unworked.....	318	328	272	270
Worked.....	284	280	270	281
100,000 strokes.....	288	287	280	279
Dropping point, ° F.....	365	384	384	392
Shell roll, 4 hr., room temperature, original penetration.....	265	280		
Points changed.....	-7	-13		
Water absorption, percent.....	125	110		
Original penetration.....	309	317		
Penetration emulsion.....	324	321		
ASTM bomb oxidation, 100 hours, p.s.i. drop.....	10	7, 8		
ASTM wheel bearing, gm. loss.....	Trace	Trace		
ASTM D-1743, bearing protection test.....	1, 1, 1	4, 3, 3	4, 3, 3	4, 3, 3, 3

¹ Contains 1.0% percent by wt. NaNO₂.

² Worked 10,000 strokes.

³ Pass.

⁴ Fail.

EXAMPLES 5 TO 19

Preparation and evaluation of other greases incorporating combinations of inorganic nitrite and amine pairs

In these examples greases are prepared utilizing one of the several formulation methods disclosed on pages 11 to 13 of the specification supra. The greases employed are either the preformed lithium soap-thickened grease disclosed in Example 1 or another grease identical to it in content except the comparable alkaline earth metal or alkali metal is substituted on a weight per weight basis. The greases incorporating amine and nitrite component, in the indicated proportions (based on parts by weight (p.b.w.) of component per hundred parts by weight of finished grease) are evaluated on a pass or fail basis as described in Embodiment C appearing on pages 8 and 9 of the specification. The results are included in Table II.

TABLE II

Example	Soap based grease ¹	Components used in grease formulations—		Ratio amine to nitrite	Method of formulation used	Rating according to ASTM-D-1743-64
		Amine	Nitrite			
5.....	Li	9 PBW p-phenylene diamine.....	1 PBW NaNO ₂	9:1	Method 4.....	Fail.
6.....	Li	9 PBW diphenylamine.....	1 PBW NaNO ₂	9:1	do.....	Pass.
7.....	Li	9 PBW bis-p-aminophenyl ethane.....	1 PBW NaNO ₂	9:1	do.....	Do.
8.....	Li	9 PBW aniline.....	1 PBW NaNO ₂	9:1	do.....	Do.
9.....	Li	9 PBW mix-tertiary C ₁₂ -C ₁₅ amines having mole averaging about 185-223.	1 PBW NaNO ₂	9:1	do.....	Do.
10.....	Li	0.33 PBW triethanolamine.....	1 PBW NaNO ₂	1:3	Method 1.....	Fail.
11.....	Na	9 PBW diphenylamine.....	1 PBW NaNO ₂	9:1	Method 4.....	Pass.
12.....	Na	do.....	1 PBW KNO ₂	9:1	do.....	Do.
13.....	Li	do.....	1 PBW Ca(NO ₂) ₂	9:1	do.....	Do.
14.....	Li	0.33 PBW RNH ₂ mixture ²	1 PBW NaNO ₂	1:3	Method 1.....	Do.
15.....	Li	0.33 PBW N-oleyltrimethylene diamine.....	1 PBW NaNO ₂	1:3	Method 2.....	Do.
16.....	Li	do.....	1 PBW NaNO ₂	1:3	Method 4.....	Do.
17.....	Li	do.....	1 PBW NaNO ₂	1:3	do.....	Do.
18.....	Li	do.....	1 PBW NaNO ₂	1:3	do.....	Do.
19.....	Li	do.....	1 PBW NaNO ₂	1:3	do.....	Do.

¹ Prepared by the method of Embodiment B.

² An admixture of primary amines wherein R comprises a mixture of isomers containing 18 to 22 carbon atoms having a molecular weight range of 269-325.

NOTE.—PBW=Parts by weight.

As the preceding specification, including the several embodiments and examples indicate, the novel invention is advantageous in several respects. For example, the corrosion-inhibiting compositions comprising inorganic nitrites and certain amines are compatible with mineral and synthetic oils as well as various additives used in grease formulations. In addition, inasmuch as the components of the corrosion-inhibiting compositions are low in cost and function well at low concentration levels, the compositions afford long term protection against corrosion at relatively low cost.

Secondly, this invention is most surprising and unexpected in that the corrosion inhibiting effect obtained in utilizing certain amines with inorganic nitrites in greases is substantially greater than the protection obtained in utilizing these components singly. Similarly, since only certain amines provide this synergistic corrosion-inhibition while seemingly comparable amines do not provide this gain in activity, the inventive process provides unexpected and unobvious results.

What is claimed is:

1. A lubricating grease having superior anti-corrosive properties comprising a homogeneous admixture of the following components in their indicated range of proportions:

- from about 75 to 96 parts by weight of oil of lubricating viscosity thickened to grease consistency with about 3 to 25 parts by weight of soap selected from the group consisting of alkali metal soaps, alkaline earth metal soaps and mixtures thereof, and
- from about 1.0 to 5.0 parts by weight of a corrosion-inhibiting composition comprising:

- at least one inorganic nitrite selected from alkali metal nitrites and alkaline earth metal nitrites,

- at least one amine selected from the group consisting of N-oleyltrimethylene diamine, aniline, bis-p-aminophenyl ethane, diphenylamine, mixtures of tertiary aliphatic primary amines containing C₁₂ to C₁₅ carbon atoms having a mole weight averaging about 185 to 213, a mixture of tertiary aliphatic amines containing C₁₈ to C₂₂ carbon atoms and having a molecular weight averaging 269-325 and mixtures thereof,

said weight ratio of amine to nitrite varying from about 0.5 to 5.0 parts by weight of amine to 0.5 to 4.0 parts by weight of nitrite.

2. The grease of claim 1 wherein the grease contains an emulsifiable polyalkylene polymer as an additive.

3. The grease of claim 1 wherein the nitrite is an alkali metal nitrite and the soap is an alkali metal soap.

4. The grease of claim 1 wherein the nitrite is an alkali metal nitrite and the soap is an alkaline metal soap.

5. A lubricating lithium soap-based grease comprising a homogeneous admixture of the following components in the indicated proportions:

- from about 85 to 96 parts by weight of a mineral oil having a SUS viscosity of 1150 at 100° F., thickened to grease consistency with about 3 to 15 parts by weight of a lithium soap, and
- from about 1 to 5 parts by weight of a corrosion-inhibiting composition comprising

- from about 1.0 to 4.0 parts by weight of sodium nitrite, and
- from about 0.5 to 3.0 parts by weight of N-oleyltrimethylene diamine.

6. The process of claim 5 wherein the lithium soap is the lithium salt of 12 hydroxystearic acid.

7. The process of claim 5 wherein the lithium soap is the lithium salt of stearic acid.

8. The process of claim 5 wherein the mineral oil is a paraffinic distillate.

9. A synergistic corrosion-inhibitor composition which can be incorporated into greases in the proportion of from about 1.0 to 5.0 parts by weight of said inhibitor composition for each 100 parts by weight of finished grease comprising:

- from about 0.5 to 4.0 parts by weight of an inorganic nitrite selected from the group consisting of alkali metal nitrites, alkaline earth metal nitrites and mixtures thereof, and
- from about 0.5 to 5.0 parts by weight of an amine surfactant selected from the group consisting of aniline, N-oleyltrimethylene diamine, and their mixtures.

10. The corrosion-inhibitor composition of claim 8 wherein the inorganic nitrite is an alkali metal nitrite and the composition contains a low molecular weight polyethylene polymer as emulsifier.

11. The corrosion-inhibitor composition of claim 10 wherein the inorganic nitrite is sodium nitrite.

12. The corrosion-inhibitor of claim 9 wherein the amine is N-oleyltrimethylene diamine.

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