United States Patent Office 3,730,895 Patented May 1, 1973

3,730,895

CORROSION INHIBITING COMPOSITIONS

Manley Kjonaas, Hammond, Ind., assignor to Atlantic Richfield Company, New York, N.Y.

No Drawing. Filed Oct. 21, 1970, Ser. No. 82,800
Int. Cl. C10m 5/22, 5/14
U.S. Cl. 252—18 32 Claims

ABSTRACT OF THE DISCLOSURE

Greases thickened with conventional grease thickeners and containing a cloudy-type overbased alkali metal or alkaline earth metal sulfonate or carboxylate dispersant and a water-soluble corrosion inhibiting salt.

Corrosion inhibiting concentrates are also set forth which comprise lubricating oil, cloudy-type over-based dispersants, and water-soluble corrosion inhibiting salts.

This invention relates to grease compositions which have improved corrosion inhibiting properties. More particularly, it relates to greases which include highly dispersed water-soluble salts in amounts effective to inhibit corrosion.

Certain water-soluble salts have been recognized as efficient corrosion inhibitors for lubricants. A problem encountered with these compositions has been the inability to disperse the salt in sufficiently fine particles throughout the lubricant. Greases which contain large solid particles can harm the mechanical systems to which they are added. Federal Standard 291–3005 (Dirt Count Test) requires that a lubricant be completely free of solid particles greater than 125 microns in size. Prior art compositions, however, contained much of the corrosion inhibitor as large particles so that although the grease was effectively corrosion inhibited, the large particles caused the composition to be abrasive while in use. To be completely acceptable, greases should contain very few solid particles over 25 microns in size, with the great majority of the particles being less than 5 microns.

Many dispersants have been used in attempting to reduce the size of solid particles in greases. Included among the dispersants that have been used are: water gelling agents (U.S. Pat. 3,098,849); the reaction product of an imidazoline and a fatty acid (U.S. Pat. 3,291,494); and calcium mahogany sulfonates (U.S. Pat. 2,820,009). However, none of these dispersants are able to produce a completely acceptable solid particle size range in lubricants. U.S. Pat. 2,820,009 teaches the use of calcium mahogany sulfonates to disperse an aqueous solution of water-soluble corrosion inhibitor in grease. However, since water evaporates at elevated temperatures or under vacuum, the presence of water in the final grease product (as in the compositions of U.S. Pat. 2,820,009) tends to limit the utility of the composition. When the grease compositions of U.S. Pat. 2,820,009 are dehydrated, unacceptably large crystalline corrosion inhibitor particles may form. The problem presented is to provide a grease composition which is effectively corrosion inhibited and contains solid corrosion inhibitor particles of a completely acceptable size.

Therefore, one major object of the present invention is to provide a grease composition with improved corrosion properties. Other objects and advantages of the invention will become apparent hereinafter.

It has now been discovered that a grease composition comprising lubricating oil thickened to grease consistency, at least one cloudy type overbased alkali or alkaline earth metal dispersant and a corrosion inhibiting amount of water-soluble salt is corrosion inhibited and substantially all the solid particles of the water-soluble corrosion inhibitor contained in this grease composition are less than

about 5 microns in size. One embodiment of the present invention is a grease composition comprising: (1) a major amount of a lubricating oil thickened to grease consistency; (2) at least one cloudy type overbased alkali and/or alkaline earth metal dispersant in an amount from about 0.01% to about 15%, preferably from about 0.01% to about 5%, by weight of the total composition; and (3) at least one water-soluble salt in a corrosion inhibiting amount. It is preferred that the water-soluble corrosion inhibitor be present in the grease composition in an amount from about 0.1% to about 5.0%, most preferably between about 0.1% and about 2.0%, by weight of the total composition. The grease composition of the present invention has corrosion inhibiting properties without detrimentally affecting any of the lubricating qualities of the grease composition. It is, of course, understood that more than one overbased dispersant and/or corrosion inhibitor can be used in combination in a single grease and such a grease composition is within the scope of the present invention. The proportions given apply to the total amounts of dispersants and/or water-soluble corrosion inhibitors regardless of how many of each are used.

In a further embodiment, the present invention involes a composition of matter comprising: (1) a lubricating oil in an amount from about 30% to about 95% by weight of the total composition; (2) at least one cloudy type overbased alkali and/or alkaline earth metal dispersant in an amount from about 0.5% to about 30%, preferably from about 0.5% to about 20% by weight of the total composition; and (3) at least one water-soluble salt present in an amount such that when the total composition is added to a grease, the resulting grease will have a corrosion inhibiting amount of said water-soluble salt, such amount of water-soluble salt being within the range of from about 0.5% to about 65%, preferably about 20% to about 65%, by weight of the total composition. This embodiment of the invention can be used as a corrosion inhibitor concentrate which can be added to a base grease composition to produce a corrosion inhibited grease. The manufacture of a corrosion inhibitor concentrate, such as noted above, permits a grease composition to be corrosion inhibited and receive the other benefits of the invention with a minimum of inconvenience and disruption of standard grease production. This is so, because the concentrate can be produced entirely independent of the base grease composition (which is made in the conventional manner). The concentrate and base composition are then simply blended together in the desired proportion. The concentrates in which the water-soluble salt is between about 20% and about 65% by weight of the total composition are preferred since only small amounts of these concentrates need be added to the base grease in order to render the product grease corrosion inhibited. This feature in turn adds to the convenience of using the concentrates.

The oils used in the compositions of the present invention are those conventionally used in grease manufacture. These lubricating oils include those having viscosity within the range of about 50 SUS to about 2000 SUS at 100° F. These oils may be refined or otherwise processed to produce an oil having the desired quality. Although mineral oils are preferred, the oil may be synthetic in nature. Typical of the oils used in the present invention is a mineral oil having a viscosity of about 1100 SUS at 100° F. Combinations of two or more different oils in a single grease composition are within the scope of the present invention.

The cloudy type overbased alkali and alkaline earth metal (i.e., sodium, potassium, lithium, magnesium, strontium, barium and calcium) dispersants useful in the present invention comprise: (1) alkali and alkaline earth

metal salts of organic acids selected from the group consisting of sulfur acids, carboxylic acids, and mixtures thereof; and (2) solid particles of at least one oil-insoluble alkali and alkaline earth metal carbonates.

Specific examples of the metal salts of organic acids useful in the present invention are those derived from sulfur acids such as sulfonic, sulfamic, sulfinic and sulfenic acids. Of these, the salts derived from sulfonic acids which include about 12 to about 200 carbon atoms are of particular usefulness in the present invention. Among the sulfonic acids are the following: mahogany sulfonic acids, petrolatum sulfonic acids, mono- and poly-wax substituted naphthalene sulfonic acids, phenol sulfonic acids, diphenyl ether sulfonic acids, diphenyl ether disulfonic acids, naphthalene disulfide sulfonic acids, naphthalene disulfide disulfonic acids, diphenyl amine disulfonic acids, cetyl-phenol mono-sulfide sulfonic acids, cetoxy caprylbenzene sulfonic acids, di-cetyl thianthrene sulfonic acids, such as cetyl chloro-benzene sulfonic acids, cetyl-phenol sulfonic acids, cetyl-phenol disulfide sulfonic acids, cetyl-phenol mono-sulfide sulfonic acids, cetoxy capryl-benzene sulfonic acids, di-cetyl thiathrene sulfonic acids, di-lauryl beta-naphthaol sulfonic acids and di-capryl nitronaphthalene sulfonic acids, aliphatic sulfonic acids such as paraffin wax sulfonic acids, unsaturated paraffin wax sulfonic acids, hydroxy substituted paraffin wax sulfonic acids, tetraisobutylene sulfonic acids, tetra-amylene sulfonic acids, chloro-substituted paraffin wax sulfonic acids, nitroso paraffin wax sulfonic acids, etc., cyclo-aliphatic sulfonic acids, such as petroleum naphthene sulfonic acids, cetyl-cyclopentyl sulfonic acids, lauryl-cyclohexyl sulfonic acids, bis-(diisobutyl)-cyclohexyl sulfonic acids, mono- and poly-wax substituted cyclohexyl sulfonic acids, etc.

With respect to the sulfonic acids, it is intended herein to employ the term "petroleum sulfonic acids" to cover all sulfonic acids which are derived at least in part from petroleum products. Additional examples of sulfonic acids and/or the alkali and alkaline earth metal salts thereof which can be employed as starting mateirals are disclosed 508; 2,193,824; 2,197,800; 2,202,791; 2,212,786; 2,213,-360; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,228,598; 2,233,676; 2,239,974; 2,263,312; 2,276,090; 2,276,097; 2,315,514; 2,319,121; 2,321,022; 2,333,568; 2,333,788; 2,335,259; 2,337,552; 2,346,568; 2,366,027; 2,374,193 and 2,383,319.

Metal salts derived from carboxylic acids (i.e., carboxylates) are also useful in the present invention. The carboxylic acids include the fatty acids wherein there are present between about 12 to about 200—preferably about 12 to about 24 carbon atoms per molecule, such as, for example, palmitic, stearic, myristic, oleic, linoleic, etc. acids. The carboxylic acids of the aliphatic type can contain elements in the aliphatic radical other than carbon and hydrogen; examples of such acids are the carbamic acids, ricinoleic acids, chloro-stearic acids, nitro-lauric acids, etc. In addition to the aliphatic carboxylic acids, it is intended to employ the cyclic types such as those containing a benzenoid structure, i.e., benzene, naphthalene, etc., and an oil-solubilizing radical or radicals having a total of at least about 15 to 18 carbon atoms. Such acids are the oil-soluble aliphatic substituted aromatic acids as for example, stearyl-benzoic acids, mono- or polywax substituted benzoic or naphthoic acids wherein the wax group contains at least about 18 carbon atoms, cetyl hydroxy-benzoic acids, etc. The cyclic type of carboxylic acids also includes those which have present in the compound a cyclo-aliphatic group. Examples of such acids are petroleum naphthenic acids, cetyl cyclohexane carboxylic acids, di-lauryl deca-hydronaphthalene carboxylic acids, diooctyl cyclo-pentane carboxylic acids, etc.

The present invention also includes compositions in which the high molecular weight carboxylates, i.e., about C_{12} to about C_{200}, preferably about C_{12} to about C_{24}, are used in conjunction with low molecular weight carboxylates have 1 to about 12 carbon atoms, preferably, about 2 to about 4 carbon atoms per molecule. The more preferred high molecular weight carboxylates for use in the combination of carboxylate salts are mono- and dihydroxy aliphatic carboxylates, while the more preferred low molecular weight carboxylate is acetate. When this combination of carboxylate salts is used, it is preferred that the metal cation be alkaline earth, and in particular calcium. The mol ratio of low molecular weight carboxylate to high molecular weight carboxylate is between about 1 and about 15, preferably between about 3 and about 7. When a carboxylate is used in the practice of the present invention, it is preferred to use the high molecular weight-low molecular weight combination of carboxylates, overbased with solid particles of oil-insoluble carbonate. This combination of overbased carboxylates not only has been found to be an effective dispersant for the corrosion inhibitor, but can also be used as a grease thickener. Therefore, the carboxylate combination can perform a dual function in the grease compositions of the present invention. The carboxylate combination can, however, function solely as a dispersant for water-soluble salts, such as when used to produce corrosion inhibitor concentrates.

The overbased dispersants useful in the present invention are normally prepared and maintained in an oil or other solvent carrier. However, the composition proportions given previously are on a solvent-free basis. Because of their availability and effectiveness as a dispersant in the compositions of the present invention, the preferred dispersants are the cloudy type calcium sulfonates overbased with calcium carbonate.

Calcium sulfonates overbased with calcium carbonate can be obtained by passing carbon dioxide through a mixture of neutral calcium sulfonates, mineral oil, lime and water. The formation of the overbased sulfonates can be aided through the use of "promoters," such as phenols, aromatic amines, sucrose and lower aliphatic alcohols. Many patents have been issued which disclose processes for making calcium carbonate overbased sulfonates. Among these are U.S. Pats. 2,865,956 and 2,956,018. The other dispersants useful in the present invention can be prepared by methods analogous to that given above for the overbased calcium sulfonates.

It is essential to the success of the present invention that the overbased dispersant used be of the cloudy type, i.e., the dispersant should include particles, the major portion of which have a maximum dimension greater than about 60 A., and preferably greater than about 100 A., in size, when the dispersant is in an oil carrier. It is preferred to limit the maximum dimension so that the dispersant particles in the final grease product are no larger than about 30,000 A. 3 (microns). With certain of the overbased dispersants, in particular the carboxylates, the entire dispersant (and not just the carbonate) is oil insoluble. These dispersants should have the particle sizes noted herein. The preferred dispersant, i.e. calcium sulfonate overbased with calcium carbonate, may be termed a cloudy type overbased calcium sulfonate. This is so because when the mixture of oil-soluble sulfonate and oil-insoluble carbonate is suspended in mineral oil, the resulting suspension appears cloudy, rather than clear to the naked eye. This cloudiness is a function of the particle size of the oil-insoluble carbonate. As the particle size of the insoluble salt increases, the oil suspension undergoes a gradual change from clarity to cloudiness. In order to obtain a cloudy type overbased calcium sulfonate, a major part of the calcium carbonate particle present must be of a size such that the maximum dimension of the particle is at least 60 A., and preferably at least 100 A., when the dispersant is in an oil carrier. (The term "maximum dimension" as used herein refers to the largest straight line dimension of the particle, be it length, width, diameter or thickness. The term does not refer to the circumference of a spherical or cylindrical shaped particle.) Of course, the calcium carbonate particles should not be so large as

to interfere with the quality of greases into which they are to be incorporated. This maximum size restriction varies from system to system and will depend on the quality of grease desired. For example, there may be certain situations where overbased calcium sulfonates in an oil carrier with major portions of the calcium carbonate particles having maximum dimension greater than about 10,000 A. (1.0 micron) would be disadvantageous. The preferred cloudy type overbased calcium sulfonates have a major part of the calcium carbonate particles in the range of from about 300 A. to about 1200 A. (in an oil carrier). Specific examples of the cloudy type calcium sulfonates preferred for use in the present invention are products which include a major portion of the calcium carbonate particles with a maximum dimension in the range of about 700 A. to about 900 A. (in an oil carrier).

The water-soluble corrosion inhibitors useful in the present invention are well known to the art. Included among these corrosion inhibitors are alkali metal and ammonium nitrites, carbonates, bicarbonates, sulphites, borates, chlorates, perchlorates, hypochlorites, silicates, phosphates, salicylates, citrates, tarnates, lactates, tartrates, oxylates, phthalates, acetates, iodates, arsenites, chromates, molybdates and tungstates, and amine nitrites, phosphates, and iodates. Because of their inexpensive cost and superior corrosion inhibition properties, the alkali metal nitrites and chromates, and mixtures thereof and in particular sodium nitrite, are preferred.

The materials used to thicken the grease compositions of the present invention to grease consistency are conventional and well known in the art. Illustrative of these grease thickeners are alkali metal (e.g., lithium and sodium) and alkaline earth metal (e.g., calcium, magnesium, strontium, and barium) hydroxy fatty acid soaps. These thickeners comprise the soaps of hydroxy fatty acids having about 12 to about 24 carbon atoms per molecule. Other grease thickeners, such as soaps from low molecular weight fatty acids, that are well known in the art, are also applicable to the present novel compositions.

These thickeners are added in an amount effective to give the mineral oil composition a grease-like consistency. In the preferred embodiment of the present invention, these thickeners comprise about 5% to about 25% of the final grease product.

Additional components, such as oxidation inhibitors, detergents and other grease additives well known in the art, may be added to the grease compositions of the present invention.

The following is one method by which the corrosion inhibitor concentrates of the present invention may be produced. The base oil and overbased dispersant are mixed together at a somewhat elevated temperature (130° F. to 200° F.) so that the viscosity of the mixture is sufficiently low to allow efficient blending. After the oil and dispersant are mixed, an aqueous solution of the corrosion inhibiting salt(s) is added and the resulting combination, while being mechanically or otherwise stirred, is heated to about 300–350° F. under sufficient pressure to prevent escape of the water and maintained at these conditions for a period of time (about one hour) to allow the corrosion inhibitor to become completely dispersed. While maintaining an elevated temperature, the pressure is slowly vented and the corrosion inhibitor concentrate is exposed to the atmosphere. This treatment substantially dehydrates the product, leaving the concentrate substantially water-free (substantially dehydrating the concentrate means that the final grease product partially derived from the concentrate can include less than 0.1% by weight of water). It is an important advantage that the concentrates and grease compositions of the present invention can be substantially dehydrated without disturbing the dispersion of the corrosion inhibitor. Greases which require the incorporation of water to maintain the character of the grease cannot be used in instances, such as high temperature or vacuum service, where the water will evaporate or otherwise be removed from the grease composition. The greases of the present invention, which can be made water-free without destroying the improved nature of the grease have no such disadvantage. Of course, it is not necessary that these grease compositions be anhydrous. After the concentrate has cooled, the product optionally can be passed through an appropriately sized sieve or filter to remove trace amounts of large particles which may have formed. Except for these trace amounts, the corrosion inhibitor exists in the concentrate as solid particles less than 5 microns (and normally less than about 3 microns) in size.

The concentrate, once prepared, may be blended with additional oil and/or grease thickening agent and other conventional grease additives to give a grease composition according to the present invention. The resulting grease composition is effectively corrosion inhibited and less than 1% of the included solid corrosion inhibitor particles are greater than 5 microns in size (normally less than 1% of the included particles are greater than about 3 microns in size).

The invention having been described in detail, the following examples are provided to show specific embodiments of the compositions thereof. It will be understood the examples are given for illustration purposes only and not by way of limitation.

EXAMPLE 1

This example illustrates the preparation of a finely dispersed sodium nitrite concentrate composition of the present invention. The dispersant used was a cloudy type of overbased calcium sulfonate mixed with an oil carrier. The overbased sulfonate (including the carbonate) comprised about 40% by weight of the total mixture. The sulfonate was prepared from petroleum sources and contained about 20 to 40 carbon atoms per molecule and on the average, about 26 carbon atoms per molecule. The sulfonate-oil mixture had a base number of about 180. The major portion of the suspended calcium carbonate in this dispersant is in the form of platelets (i.e., cylinders) having a diameter within the range of about 700 A. to about 900 A. and a thickness in the range of about 70 A. to about 90 A.

The concentrate was prepared as follows. 7.20 pounds of mineral oil (1100 SUS viscosity at 100° F.) and 1.80 pounds of dispersant were charged to a pressure vessel equipped with a high speed mechanical mixer. The mixing motor was started and the temperature was increased to 170° F. by use of electric heaters. 3.00 pounds of sodium nitrite disolved in 2.00 pounds of hot water was added to the vessel. The vessel was then sealed and the temperature was increased to 337° F. The ingredients are thoroughly blended by the mechanical mixer. The pressure, which had built to 49 p.s.i.g. during heating and mixing was slowly vented to 5 p.s.i.g. while the temperature was maintained at 329–337° F. The vessel was repressured to 50 p.s.i.g. with air and the product was discharged into an open grease kettle preheated to 340° F. This step caused the water to be driven off as steam and in effect dehydrated the product, i.e., the product was substantially water-free (the grease composition made from this concentrate had less than 0.1% by weight of water). A sample of the dehydrated product was examined under an optical microscope with cross polarized illumination. The largest particle observed was 3 microns. The major portion of the particles were in the 1 to 3 micron range. The dehydrated product, or concentrate, was light brown in color and of a creamy consistency.

EXAMPLE 2

This example illustrates the production of a product having a higher concentration of sodium nitrite than the product of Example 1. Except for the concentration differences, the procedure followed was the same as in Ex-

ample 1. The following table gives the composition of the dehydrated products of Examples 1 and 2.

TABLE

Product	Percent by weight	
	Example 1	Example 2
Sodium nitrite	25	50
Cloudy overbased calcium sulfonate in oil carrier	15	15
Mineral oil	60	35

The dehydrated product of Example 2 was fluid. Under the optical microscope, the largest observed particle was 150 microns in trace amounts (less than about 1% of the total sodium nitrite). This dehydrated product was passed through a 200 mesh sieve to give a final concentrate with the largest observed particle being 80 microns. Except for trace amounts of particles (less than about 1% of the total sodium nitrite) in the 5 to 70 micron range, all the solid corrosion inhibitor in the fluid concentrate was less than 5 microns in size. The concentrates of Examples 1 and 2 were stable dispersions in that only a trace of oil separation was observed after storage for one month at room temperature.

EXAMPLE 3

In order to show the outstanding properties of the composition of this invention using an overbased dispersant in which the major portion of the solid particles have a maximum dimension greater than about 60 A. when in an oil carrier, a concentrate was prepared in a manner similar to that in Example 1, except that a clear type overbased calcium sulfonate was used as a dispersant. The clear sulfonate was a commercially available overbased calcium sulfonate (with about 300 total base number) in an oil carrier in which substantially all the solid particles had a maximum dimension of less than 60 A. The composition of the dehydrated product was:

	Percent by weight
Sodium nitrite	30
Commercially available clear overbased calcium sulfonate in oil carrier	15
Mineral oil	55

The sodium nitrite in this product was in the form of coarse grains of sodium nitrite (particle size about 50 to 150 microns). These particles separated from the oil after standing overnight.

EXAMPLE 4

The sodium nitrite concentrates of Examples 1, 2 and 3 were incorporated into a standard lithium soap based grease (containing no corrosion inhibitors) and the resulting greases were tested according to the Dirt Count Test (FED–STD–791–3005). In brief, the Dirt Count Test involves observation of a portion of the composition under an optical microscope to determine the size range of the solid particles in the composition. The greases made from the compositions of this invention (Examples 1 and 2) passed the Dirt Count Test, whereas the grease derived from the clear type overbased sulfonate (Example 3) failed the test, indicting that this grease contained solid particles greater than 125 microns in size.

This series of tests indicate that the compositions of the present invention allow one to control the size of solid corrosion inhibitor particles in grease compositions.

EXAMPLE 5

The grease compositions that were prepared in Example 3) failed the test, indicating that this grease contained 1 and 2 were tested for rust resistance. A sample of the lithium based grease, with no sodium nitrite, was also tested. The compositions of the various greases and test results are as follows:

TABLE

	Percent by weight		
Lithium based grease	94.0	98.5	100.0
Example:			
1 product	6.0		
2 product		1.5	
Total sodium nitrite content	1.5	0.75	0.0
Total water content	<0.1	<0.1	<0.1
ASTM D, 1743 Rust Test	Pass	Pass	Fail

These results show that not only is the sodium nitrite maintained within an acceptable particle size range in the compositions of the present invention, but also the sodium nitrite contained therein is an effective corrosion inhibitor at relatively low concentration.

EXAMPLE 6

This example shows the preparation of a concentrate composition of this invention using a dispersant comprising a combination of carboxylates overbased with calcium carbonate. The dispersant was prepared as follows:

A reaction vessel equipped with a high speed mixer was charged with 16.1 lbs. of mineral oil having a viscosity of 1100 SUS at 100° F. and 3.35 lbs. of hydrated lime. The mixer was activated and 1.79 lbs. of glacial acetic acid was added at a continuous rate over a 27 minute period of time. The temperature was then increased to 176° F. by the use of electric heaters. 1.77 lbs. of the glyceride of 12-hydroxy stearic acid was added and the reaction vessel was closed. The temperature was again raised to 292° F. Carbon dioxide was added so that the pressure increased to 79 p.s.i. during a one-hour period. The temperature increased to 319° F. during the carbonation period. The product was forced by pressure into an open grease kettle which had been preheated to 340° F. After this dispersant was cooled, an additional 2.0 lbs. of mineral oil and 0.1 lbs. of oxidation inhibitor were added to give a composition which had the appearance of a grease. The composition had an ASTM worked 60 stroke penetration of 301 and an approximate total solids content of 26.8% by weight. All the solid particles had a maximum dimension of 3 microns or less with the major portion of these particles having a maximum dimension larger than 100 A.

A sodium nitrite concentrate (approximately 50% by weight) was made as follows. A reaction vessel, equipped with a high speed mixer was charged with 1.05 lbs. of mineral oil and 2.45 lbs. of the previously made dispersant. The mixture was heated to 190° F. and 3.5 lbs. of sodium nitrite in 2.5 lbs. of hot water was added. The reaction vessel was closed and the temperature was increased to 335° F. and the pressure increased to 48 p.s.i. in a period of one hour. The gas was slowly vented over a period of one hour while the temperature was maintained at 335° F. to 347° F. The product was discharged to an open grease kettle and maintained for 1 hour at 345° F. This treatment substantially dehydrated the product. The product upon cooling had a fluid grease-like consistency and showed no oil separation on standing for 6 weeks at room temperature. Examination under an optical microscope showed that substantially all of the sodium nitrite particles were under 3 microns in size with the largest particle observed being 100 microns and present in trace amounts.

The concentrate was blended with a lithium soap based grease composition in a proportion so that the final grease product had a sodium nitrite concentration of 1.0% by weight.

EXAMPLE 7

This example shows that an effectively corrosion inhibited grease composition can be made directly from the combination of high and low molecular weight carboxylates overbased with oil-insoluble carbonates without first preparing a corrosion inhibitor concentrate as in Ex-

ample 6. The procedure followed was similar to that used in Example 6 for the preparation of the overbased dispersant except that immediately after the addition of the glyceride of 12-hydroxy stearic acid, a 50% by weight aqueous solution of sodium nitrite was added in an amount such that the final grease composition contains 1% by weight of sodium nitrite. All the calcium carbonate particles in this grease had a maximum dimension less than 3 microns in size with the major portion having a maximum dimension larger than 100 A. Substantially all the sodium nitrite particles were below 3 microns in size with only a trace amount as large as 100 microns.

The grease products of Examples 6 and 7 were tested for both corrosion inhibiting properties and particle size. The results of these tests are as follows:

Grease product	Example 6	Example 7
Total sodium nitrite content, wt. percent	1.0	1.0
Total water content, wt. percent	<0.1	<0.1
ASTM D-1743 Rust Test	Pass	Pass
FED-STD-291-3005 (Dirt Count Test)	Pass	Pass

Examples 1 to 5 show that the compositions of the present invention form stable dispersions which have excellent corrosion properties as well as being able to meet the Dirt Count Test. These examples also indicate that grease compositions which do not include the cloudy type overbased dispersants do not have the outstanding properties of the compositions of the present invention.

Examples 6 and 7 indicate that a combination of both high and low molecular weight carboxylate overbased with oil insoluble carbonate can be used solely as a dispersant for corrosion inhibitor or as both a dispersant and grease thickener. In either case, the final grease compositions is effectively corrosion inhibited with finely dispersed solid particles of corrosion inhibitor.

The compositions of the present invention can be substantially dehydrated without disrupting the stability of the dispersion. As has been noted previously, this property is advantageous in greases which are to be used in severe applications, for example, at high temperatures and under vacuum.

While in the foregoing disclosure certain examples have been set forth which illustrate details specifying modes of applying this invention, it should be understood that such details may be varied considerably by one skilled in the art without departing from the spirit of this invention.

What is claimed is:

1. A grease composition comprising: (1) a major amount of a lubricating oil thickened to grease consistency; (2) at least one cloudy type overbased alkaline earth metal dispersant and being present in an amount from about 0.01% to about 15% by weight of the total grease composition, said dispersant comprising (a) at least one salt of an organic acid selected from the group consisting of sulfonic acids, carboxylic acids and mixtures thereof, and (b) solid particles of at least one oil-insoluble alkaline earth metal carbonate, said dispersant containing particles, the major portion of which have a maximum dimension greater than about 60 A. when said dispersant is in an oil carrier; and (3) at least one water-soluble salt in a corrosion inhibiting amount selected from the group consisting of alkali metal nitrites, alkali metal chromates, and mixtures thereof and having a particle size less than 5 microns.

2. The composition of claim **1**, wherein said organic acid is a sulfonic acid having about 12 to about 200 carbon atoms per molecule.

3. The composition of claim **2**, wherein said dispersant includes particles the major portion of which have a maximum dimension greater than about 100 A. when said dispersant is in an oil carrier and less than about 3 microns when said dispersant is in said grease composition.

4. The composition of claim **3**, wherein said dispersant is calcium sulfonate overbased with calcium carbonate.

5. The composition of claim **4**, wherein the major portion of the calcium carbonate particles are within the range of from about 300 A. to about 1200 A. in size when said dispersant is in an oil carrier.

6. The composition of claim **5**, wherein the major portion of the calcium carbonate particles are within the range of from about 700 A. to about 900 A. in size when said dispersant is in an oil carrier.

7. The composition of claim **6**, wherein said water-soluble salt is sodium nitrite present in an amount from about 0.1% to 5.0% by weight of the total grease composition.

8. The composition of claim **7**, wherein said composition is substantially dehydrated.

9. The composition of claim **1**, wherein said organic acid is a carboxylic acid having between about 12 and about 200 carbon atoms per molecule.

10. The composition of claim **1**, wherein said cloudy type overbased dispersant comprises (1) at least one high molecular weight carboxylate having between about 12 to about 200 carbon atoms per molecule and a low molecular weight carboxylate having between 1 to about 12 carbon atoms per molecule.

11. The composition of claim **10**, wherein said cloudy type overbased dispersant comprises (1) at least one high molecular weight carboxylate having between about 12 to about 24 carbon atoms per molecule and at least one low molecular weight carboxylate having between about 2 to about 4 carbon atoms per molecule, wherein the ratio of said low molecular weight carboxylate to said high molecular weight carboxylate is between about 1 to about 15, said dispersant including particles the major portion of which have a maximum dimension greater than about 100 A. when said dispersant is in an oil carrier and less than about 3 microns when said dispersant is in said grease composition.

12. The composition of claim **11**, wherein the mol ratio of said low molecular weight carboxylate to said high molecular weight carboxylate is between about 3 and about 7, and said high molecular weight carboxylate and low molecular weight carboxylate are calcium salts, said oil-insoluble carbonate is calcium carbonate.

13. The composition of claim **11**, wherein said high molecular weight carboxylate is selected from the group consisting of monohydroxy aliphatic carboxylates and dihydroxy aliphatic carboxylates and said low molecular weight carboxylate is acetate.

14. The composition of claim **13**, wherein said water-soluble salt is sodium nitrite.

15. The composition of claim **14**, wherein said composition is substantially dehydrated.

16. A composition of matter for use as a corrosion inhibitor concentrate in the preparation of a grease composition comprising: (1) a lubricating oil in an amount from about 30% to about 95% by weight of the total composition; (2) at least one cloudy type overbased alkaline earth metal dispersant, said dispersant being present in an amount from about 0.5% to about 30% by weight of the total composition, said dispersant comprising (a) at least one salt of an organic acid selected from the group consisting of sulfonic acids, carboxylic acids and mixtures thereof, and (b) solid particles of at least one oil-insoluble alkaline earth metal carbonate, said dispersant containing particles the major portion of which have a maximum dimension greater than about 60 A. when said dispersant is in an oil carrier; and (3) at least one water-soluble salt selected from the group consisting of alkali metal nitrites, alkali metal chromates, and mixtures thereof and having a particle size less than 5 microns and being present in an amount such that when the total composition is added to said grease composition, said grease composition will have a corrosion inhibiting amount of said water-soluble salt, said amount of water-soluble salt being within the range of about 0.5% to about 65% by weight of the total composition.

17. The composition of claim **16**, wherein said organic acid is a sulfonic acid having about 12 to about 200 carbon atoms per molecule.

18. The composition of claim **17**, wherein said dispersant includes particles the major portion of which have a maximum dimension greater than about 100 A. when said dispersant is in an oil carrier and less than about 3 microns when said dispersant is in said grease composition.

19. The composition of claim **18**, wherein said amount of water-soluble salt is within the range of about 20% to about 65% by weight of the total composition.

20. The composition of claim **18**, wherein said dispersant is calcium sulfonate overbased with calcium carbonate.

21. The composition of claim **20**, wherein the major portion of the calcium carbonate particles are within the range of from about 300 A. to about 1200 A in size when said dispersant is in an oil carrier.

22. The composition of claim **20**, wherein the major portion of the calcium carbonate particles are within the range of from about 700 A. to about 900 A. in size when said dispersant is in an oil carrier.

23. The composition of claim **22**, wherein said water-soluble salt is sodium nitrite.

24. The composition of claim **23**, wherein said composition is substantially dehydrated.

25. The composition of claim **16**, wherein said organic acid is a carboxylic acid having between about 12 and about 200 carbon atoms per molecule.

26. The composition of claim **16**, wherein said cloudy type overbased dispersant comprises at least one high molecular weight carboxylate having between about 12 to about 200 carbon atoms per molecule and at least one low molecular weight carboxylate having between 1 to about 12 carbon atoms per molecule.

27. The composition of claim **26**, wherein said cloudy type overbased dispersant comprises at least one high molecular weight carboxylate having between about 12 to about 24 carbon atoms per molecule and at least one low molecular weight carboxylate having between 2 to about 4 carbon atoms per molecule, wherein the mol ratio of said low molecular weight carboxylate to high molecular weight carboxylate is between about 1 to about 15, said dispersant including particles the major portion of which have a maximum dimension greater than about 100 A. when said dispersant is in an oil carrier and less than about 3 microns when said dispersant is in a grease composition.

28. The composition of claim **27**, wherein the mol ratio of said low molecular weight carboxylate to said high molecular weight carboxylate is between about 3 to about 7.

29. The composition of claim **27**, wherein said high molecular weight carboxylate and said low molecular weight carboxylate are calcium salts and said oil-insoluble carbonate is calcium carbonate.

30. The composition of claim **29**, wherein said high molecular weight carboxylate is selected from the group consisting of monohydroxy aliphatic carboxylates and dihydroxy aliphatic carboxylates and said low molecular weight carboxylate is acetate.

31. The composition of claim **30**, wherein said water-soluble salt is sodium nitrite.

32. The composition of claim **31**, wherein said composition is substantially dehydrated.

References Cited

UNITED STATES PATENTS

2,820,009	1/1958	Smith et al.	252—18
3,065,176	11/1962	Blake et al.	252—18
2,956,018	10/1960	Carlyle et al.	252—18

FOREIGN PATENTS

778,468	7/1957	Great Britain	252—18

PATRICK P. GARVIN, Primary Examiner

I. VAUGHN, Assistant Examiner

U.S. Cl. X.R.

252—17, 25, 389