

[54] METHOD FOR PRODUCING CORROSION
INHIBITING COMPOSITIONS

[75] Inventor: Manley Kjonaas, Hammond, Ind.

[73] Assignee: Atlantic Richfield Company, New
York, N.Y.

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Primary Examiner—H. Sneed

Attorney, Agent, or Firm—Frank J. Uxa

[57] ABSTRACT

Methods for producing corrosion inhibited compositions comprising lubricating oil, at least one cloudy type overbased alkali metal and/or alkaline earth metal dispersant and at least one water-soluble salt effective as a corrosion inhibitor are disclosed. These compositions can be combined with additional oil and conventional grease thickeners to form corrosion inhibited greases in which substantially all solid corrosion inhibitor particles are less than 5 microns in size.

21 Claims, No Drawings

METHOD FOR PRODUCING CORROSION INHIBITING COMPOSITIONS

This application is a continuation-in-part of application, Ser. No. 82,800, filed Oct. 21, 1970.

This invention relates to methods for producing grease compositions which have improved corrosion inhibiting properties. More particularly, it relates to methods for producing 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. No. 3,098,849); the reaction product of an imidazoline and a fatty acid (U.S. Pat. No. 3,291,494); and calcium mahogany sulfonates (U.S. Pat. No. 2,820,009). However, none of these dispersants are able to produce a completely acceptable solid particle size range in lubricants. U.S. Pat. No. 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. No. 2,820,009) tends to limit the utility of the composition. When the grease compositions of U.S. Pat. No. 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, an object of the present invention is to provide a process for the manufacture of 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 corrosion inhibitor concentrate comprising lubricating oil, at least one cloudy type overbased alkali or alkaline earth metal dispersant comprising at least one carboxylate and at least one oil-insoluble carbonate, and a corrosion inhibiting amount of water-soluble salt can be produced by an improved process comprising (1) contacting a mixture comprising the lubricating oil, carboxylate and at least one alkali or alkaline earth metal hydroxide with carbon dioxide to react with at least a major portion of the hydroxide and form solid carbonate particles the major portion of which have a maximum di-

mension of at least 60A., preferably at least about 100A., and substantially all of which particles have a maximum dimension less than about 3 microns, (2) contacting the carbonate-containing mixture with a water-soluble salt to form a substantially uniform composition in the presence of sufficient water to solubilize the water soluble salt, and (3) substantially dehydrating the composition to form a corrosion inhibitor concentrate wherein substantially all the particles of the water-soluble salt have a maximum dimension of less than 5 microns.

In the above embodiment, the present invention involves an improved method for producing a corrosion inhibitor concentrate, for example, for use in greases, which typically comprises (1) a lubricating oil in an amount from about 30 percent to about 95 percent 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 percent to about 30 percent, preferably from about 0.5 percent to about 20 percent, by weight of the total composition which dispersant comprises (a) at least one carboxylate and (b) solid particles of at least one oil-insoluble carbonate which is the reaction product of a hydroxide and carbon dioxide; 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 preferably being within the range of from about 0.5 percent to about 65 percent, more preferably about 20 to about 65 percent, by weight of the total composition.

The above embodiment of the invention can be used to produce a corrosion inhibitor concentrate which can be added to a base grease composition and/or additional lubricating oil 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.

These base grease compositions may contain materials conventionally used to thicken lubricating oils to grease consistency. Illustrative of these well known 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, preferably containing from about 12 to about 24 carbon atoms per molecule. Other well known grease thickeners, such as soaps of low molecular weight fatty acids, may also be used in these base grease compositions. In many instances, the dispersant in the corrosion inhibitor concentrate may act to at least aid in thickening the lubricating oil to grease consistency. Preferably, the total amount of grease thickener is from about 5 percent to about 25 percent by weight of the final grease product.

The concentrates in which the water-soluble salt is between about 20 percent and about 65 percent 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.

In another embodiment, the present invention involves a method for producing a grease composition comprising a major amount of lubricating oil, at least one cloudy type overbased alkali or alkaline earth metal dispersant comprising a combination of at least two carboxylates and at least one oil insoluble carbonate in an amount effective to thicken the lubricating oil to grease consistency and at least one water-soluble salt in a corrosion inhibiting amount which comprises (1) contacting a mixture comprising lubricating oil, the carboxylate combination and at least one alkali or alkaline earth metal hydroxide with carbon dioxide to react with at least a major portion of the hydroxide and form solid carbonate particles the major portion of which have a maximum dimension of at least 60A., preferably at least about 100A., and substantially all of the particles having a maximum dimension less than about 3 microns, (2) contacting the carbonate-containing mixture with the water-soluble salt to form a substantially uniform composition in the presence of sufficient water to solubilize the water-soluble salt, and (3) substantially dehydrating the composition to form a grease composition wherein substantially all the particles of the water soluble salt have a maximum dimension of less than 5 microns.

This embodiment of the present invention may be used to produce grease compositions typically comprising: (1) a major amount of a lubricating oil; (2) at least one cloudy type overbased alkali and/or alkaline earth metal dispersant in an amount from about 0.01 percent to about 15 percent by weight of the total composition and being effective to thicken the lubricating oil to grease consistency, the dispersant comprising (a) a combination of at least one low molecular weight carboxylate containing from 1 to about 12 carbon atoms per molecule and at least one high molecular weight carboxylate containing from about 12 to about 200 carbon atoms per molecule, the mole ratio of said low molecular weight carboxylate to said high molecular weight carboxylate being in the range from about 1 to about 15 and (3) at least one water-soluble salt in a corrosion inhibiting amount. Although additional grease thickener materials may be added to these grease compositions, it is preferred that the dispersant described above act alone to thicken the lubricating oil to grease consistency.

The method by which the corrosion inhibitor concentrates may be produced is illustrated as follows. A mixture of lubricating oil, carboxylate(s) and hydroxide is formed at slightly elevated temperature, e.g., about 100°F. to about 200°F., to allow efficient blending. The carboxylate(s) can be formed in situ by the reaction of carboxylic acids with hydroxide. In any event, once the mixture is formed, carbon dioxide is contacted with the mixture to react with at least a major amount of the hydroxide and form solid particles of oil insoluble carbonate of proper size. During the contacting with carbon dioxide, the temperature of the mixture is preferably in the range from about 200°F. to about 400°F., more preferably from about 250°F. to about 400°F. Preferably, the mixture is maintained at super atmospheric pressure, e.g., from about 20 psig. to about 200 psig., or more, to promote more efficient contacting with the carbon dioxide and to allow retention of at least a major amount of the water formed by the reaction be-

tween the hydroxide and carbon dioxide. Carbon dioxide may be added to the mixture in any form, e.g., gas, liquid or solid. However, in order to efficiently control the rate of reaction with the hydroxide it is preferred that gaseous carbon dioxide be used in the contacting step. The contacting conditions are maintained for a period of time, preferably from about 10 minutes to about 24 hour or more, and more preferably from about ½ hour to about 10 hours, to allow the carbon dioxide to react with at least a major amount, preferably at least about 80 percent and more preferably at least about 95 percent of the hydroxide present in the mixture at the beginning of the contacting. It has been found that this contacting provides a mixture containing solid particles of oil-insoluble carbonate the major portion of which have a maximum dimension of at least 60A., preferably at least about 100A., and substantially all of the solid particles in the mixture have a maximum dimension less than about 3 microns. After the carbonate-containing mixture is formed, the water-soluble salt(s) preferably in the form of an aqueous solution, may be added to form a substantially uniform composition in the presence of sufficient water to solubilize the water-soluble salt. This water may be derived from any source, for example, from an extraneous source and/or from the reaction of carbon dioxide and hydroxide. This water may be added to the carbonate-containing mixture separately from the water-soluble salt and/or may be added to this mixture as an aqueous solution of the water-soluble salt. In any event, sufficient water to solubilize the water-soluble salt is present in the substantially uniform composition formed. Thus, the water-soluble salt-containing composition, while being mechanically or otherwise stirred, may be heated to about 220°F. to about 400°F., preferably from about 300°F. to about 400°F., under sufficient pressure to prevent release of a substantial amount of water, preferably from about 20 psig. to about 200 psig. or more, and maintained at these conditions for a period of time, preferably from about 5 minutes to about 5 hours or more, more preferably from about 10 minutes to about 2 hours to allow the corrosion inhibitor to become substantially completely dispersed. Although it is preferred to contact the mixture with carbon dioxide before contact with the water-soluble corrosion inhibitor, the corrosion inhibitor can be added before such carbon dioxide contacting provided that sufficient water is present during the contacting with carbon dioxide to substantially solubilize the corrosion inhibitor. 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 percent by weight of water).

Alternately, a grease composition can be made directly from a mixture comprising lubricating oil; a carboxylate combination, particularly the combination of low molecular weight carboxylate and high molecular weight carboxylate, noted previously, and hydroxide. The carboxylate combination can be formed in situ by the reaction of two or more carboxylic acids with hydroxide. Once the mixture is formed, it is contacted with carbon dioxide, added preferably as a gas, to react with at least a major portion of the hydroxide and form

solid particles of oil insoluble carbonate of proper size. The conditions at which carbon dioxide is contacted with the mixture are similar to the conditions for carbon dioxide contacting in the manufacture of the corrosion inhibitor concentrates noted previously.

The carbonate-containing mixture is contacted with a corrosion inhibiting amount of water-soluble salt, preferably in the form of an aqueous solution, in the presence of sufficient water to substantially solubilize the salt. This contacting with the water-soluble salt takes place at elevated temperatures, e.g., from about 220°F. to about 400°F., preferably from about 300°F. to about 400°F., under sufficient pressure to prevent release of a substantial amount of water, preferably from about 20 psig. to about 200 psig. or more for a period of time, preferably from about 5 minutes to about 5 hours or more, more preferably from about 10 minutes to about 2 hours, to allow the corrosion inhibitor to become substantially completely dispersed. The corrosion inhibitor containing composition is substantially dehydrated, for example, by exposure to the atmosphere, to form a grease composition.

It is an important advantage of the present invention that the concentrates and grease compositions produced thereby 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 produced by the present invention, which can be made substantially 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. Controlled amounts of water may be added back to the products produced by the present invention to obtain the desired composition. After the substantially dehydrated product has cooled, the product optionally can be passed through an appropriately size 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 product, i.e., corrosion inhibitor concentrate or grease composition as solid particles less than 5 microns (and normally less than about 3 microns) in size. The corrosion inhibitor concentrate, once prepared, may be blended with additional oil and/or grease thickening agent and other conventional grease additives to give grease composition.

The compositions produced by the present invention are effectively corrosion inhibited and less than 1 percent of the included solid corrosion inhibitor particles are greater than 5 microns in size (normally less than 1 percent of the included particles are greater than about 3 microns in size).

It is preferred that the water-soluble corrosion inhibitor be present in the final grease composition in an amount from about 0.1 percent to about 5.0 percent, most preferably between about 0.1 percent and about 2.0 percent, by weight of the total composition. The final grease compositions produced by the present invention has corrosion inhibiting properties without detrimentally affecting any of the lubricating qualities of the greases. It is, of course, understood that more than one overbased dispersant and/or corrosion inhibitor can be used in producing a single grease and the pro-

duction of 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.

The oils used in the methods 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 2,000 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 1,100 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 of the compositions produced by the present invention comprise: (1) alkali and alkaline earth metal carboxylates and mixtures thereof; and (2) solid particles of at least one oil-insoluble alkali and alkaline earth metal carbonates which are the reaction products of alkali and alkaline earth metal hydroxides and carbon dioxide. The carboxylates include those derived from acids containing from 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 carboxylates may be derived from carboxylic acids of the aliphatic type which contain elements in the aliphatic radical other than carbon and hydrogen; examples of such acids are the carbamic acids, ricinoleic acids, chloro-stearic acids, mono-, and dihydroxy stearic acids, nitro-lauric acids, etc. In addition to the aliphatic carboxylic acids, it is intended to employ carboxylates derived from the cyclic types of acids, 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 petroleum naphthenic acids, cetyl cyclohexane carboxylic acids, di-lauryl deca-hydronaphthalene carboxylic acids dioctyl cyclo-pentane carboxylic acids, etc.

The present invention also involves production of compositions in which the high molecular weight carboxylates, i.e., about C₁₂ to about C₂₀₀, preferably about C₁₂ to about C₂₄, are used in combination 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 mole 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. This combination of carboxylates overbased with solid particles of oil insoluble carbonate, not only has been found to be an effective dispersant for the corrosion inhibitor, but can also be used as a grease thickener. Therefore, this dispersant can perform a dual function in the corrosion inhibitor concentration and grease compositions produced by the present invention. The overbased carboxylate combination can, however, function solely as a dispersant for water-soluble salts, such as when used to produce corrosion inhibitor concentrates with other conventional grease thickeners being added to at least aid in achieving the proper consistency of the final grease product.

The present invention involves the use of dispersants which include particles the major portion of which have a maximum dimension greater than the about 60A., and preferably greater than about 100A., 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 30,000A. (3 microns). With certain of these dispersants the entire dispersant (and not just the carbonate) is oil insoluble. In these instances, the total dispersant should have the particle sizes noted herein. (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.)

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 nitrates, carbonates, bicarbonates, sulphites, borates, chlorates, perchlorates, hypochlorites, silicates, phosphates, salicylates, citrates, tartrates, lactates, tartrates, oxyates, phthalates, acetates, iodates, sebacates, arsenites, chromates, molybdates and tungstates, and amine nitrites, phosphates, and iodates. Of course, mixtures of more than one water-soluble corrosion inhibitor can be used in the methods of the present invention. Because of their inexpensive cost and superior corrosion inhibition properties, the alkali metal nitrates and chromates, and mixtures thereof and in, particular, sodium nitrite, are preferred.

The water-soluble corrosion inhibitors are preferably used in the methods of the present invention in the form of aqueous solutions. Solubility characteristics and, therefore, optimum solution concentrations may vary from inhibitor to inhibitor. The aqueous solutions used in the present invention preferably contain at least about 1 percent, more preferably at least about 5 percent, by weight of water-soluble corrosion inhibitor. In any event, when the water-soluble corrosion inhibitor is contacted with the carbonate-containing composition, sufficient water to substantially solubilize the corrosion inhibitor is to be present.

Additional components, such as oxidation inhibitors, detergents and other grease additives well known in the art, may be added to the grease compositions produced by the present invention. 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 shows the preparation of a concentrate composition of this invention using a dispersant comprising a combination of carboxylates and solid particles of 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 1,100 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 psi. during a one-hour period. The temperature increased to 319°F. during the carbonation period. The produce 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 percent 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 100A.

A sodium nitrate concentrate (approximately 50 percent 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 psi. 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 percent by weight.

EXAMPLE 2

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 Example 1. The procedure followed was similar to that used in Example 1 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 percent 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 100A. 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 1 and 2 were tested for both corrosion inhibiting properties and particle size. The results of these tests are as follows:

GREASE PRODUCT	Example 1	Example 2
Total Sodium Nitrite Content, Wt. %	1.0	1.0
Total Water Content, Wt. %	<0.1	<0.1
ASTM D-1743 RUST TEST	Pass	Pass
FED-STD 291-3005 (DIRT COUNT TEST)	Pass	Pass

Examples 1 and 2 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 composition is effectively corrosion inhibited with finely dispersed solid particles of corrosion inhibitor.

The compositions prepared by 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.

The embodiments of the invention in which an exclusive property or privilege is claimed are defined as follows:

1. A method for producing a corrosion inhibitor concentrate comprising lubricating oil, at least one cloudy type overbased alkali or alkaline earth metal dispersant comprising at least one carboxylate and at least one oil-insoluble carbonate, and a corrosion inhibiting amount of a water soluble salt which comprises:

1. contacting a mixture comprising said lubricating oil, said carboxylate and at least one hydroxide selected from the group consisting of alkali metal hydroxide, alkaline earth metal hydroxides and mixtures thereof, with carbon dioxide to react with at least a major portion of said hydroxide and form solid carbonate particles the major portion of which have a maximum dimension of at least 60A, and substantially all of the particles in said carbonate-containing mixture have a maximum dimension less than about 3 microns;
2. contacting said carbonate-containing mixture with said water-soluble salt to form a substantially uniform composition in the presence of sufficient water to solubilize the water soluble salt; and
3. substantially dehydrating the composition to form said corrosion inhibitor concentrate wherein sub-

stantially all of the particles of said water soluble salt have a maximum dimension of less than 5 microns.

2. The method of claim 1 wherein the contacting of step (1) occurs at a temperature in the range from about 200°F. to about 400°F. and at a pressure in the range from about 20 psig. to about 200 psig, and the contacting of step (2) occurs at a temperature in the range from about 200°F. to about 400°F. and at a pressure to prevent release of a substantial amount of water from said carbonate-containing mixture, said pressure being in the range from about 20 psig. to about 200 psig.

3. The method of claim 2 wherein at least one carboxylate contains from about 12 to about 200 carbon atoms per molecule and said carboxylate and said carbonate are of a metal selected from the group consisting of alkaline earth metal and mixtures thereof.

4. The method of claim 3 wherein step (2) comprises contacting said carbonate-containing mixture with an aqueous solution of said water-soluble salt, said aqueous solution containing at least about 1 percent by weight of said water soluble salt.

5. The method of claim 4 wherein said water-soluble salt is selected from the group consisting of alkali metal nitrates, alkali metal chromates and mixtures thereof, said aqueous solution contains at least about 5 percent by weight of said water-soluble salt, and said carboxylate and said carbonate are calcium carboxylate and calcium carbonate.

6. The method of claim 5 wherein the contacting of step (1) occurs at a temperature in the range from about 250°F. to about 400°F. for a period of time from about 10 minutes to about 24 hours and the contacting of step (2) occurs at a temperature in the range from about 300°F. to about 400°F. for a period of time from about 10 minutes to about 2 hours.

7. The method of claim 6 wherein said corrosion inhibitor concentrate comprises from about 30 percent to about 95 percent by weight of said lubricating oil, from about 0.5 percent to about 30 percent by weight of said dispersant and from about 0.5 percent to about 65 percent by weight of said water-soluble salt.

8. The method of claim 7 wherein said carboxylate is a combination of at least one low molecular weight carboxylate containing from 1 to about 12 carbon atoms per molecule at least one high molecular weight carboxylate containing from about 12 to about 200 carbon atoms per molecule, the mole ratio of said low molecular weight carboxylate to said high molecular weight carboxylate being from about 1 to about 15.

9. A method for producing a grease composition comprising a major amount of lubricating oil, at least one cloudy type overbased alkali or alkaline earth metal dispersant comprising a combination of at least two carboxylates and at least one oil insoluble carbonate in an amount effective to thicken said lubricating oil to grease consistency and at least one water-soluble salt in a corrosion inhibiting amount which comprises:

1. contacting a mixture comprising said lubricating oil, carboxylate combination and at least one hydroxide selected from the group consisting of alkali metal hydroxides, alkaline earth metal hydroxides and mixtures thereof to react with at least a major portion of said hydroxide and form solid carbonate particles the major portion of which have a maxi-

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imum dimension of at least 60A, and substantially all of the particles in said carbonate-containing mixture have a maximum dimension less than about 3 microns;

2. contacting said carbonate-containing mixture with said water-soluble salt to form a substantially uniform composition in the presence of sufficient water to solubilize said water-soluble salt; and
3. substantially dehydrating said composition to form a grease composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

10. The method of claim 9 wherein the contacting of step (1) occurs at a temperature in the range from about 200°F. to about 400°F. and at a pressure in the range from about 20 psig. to about 200 psig. and the contacting of step (2) occurs at a temperature in the range from about 220°F. to about 400°F. and at a pressure to prevent release of a substantial amount of water from said carbonate-containing mixture, said pressure being in the range from about 20 psig. to about 200 psig.

11. The method of claim 10 wherein said carboxylate combination comprises at least one low molecular weight carboxylate containing from 1 to about 12 carbon atoms per molecule and at least one molecular weight carboxylate containing from about 12 to about 200 carbon atoms per molecule, the mole ratio of said low molecular weight carboxylate to said high molecular weight carboxylate being in the range from about 1 to about 15 and said carboxylate combination and said carbonate are of a metal selected from the group consisting of alkaline earth metal and mixtures thereof.

12. The method of claim 11 wherein step (2) comprises contacting said carbonate containing mixture with an aqueous solution of said water-soluble salt, said aqueous solution containing at least about 1 percent by weight of said water-soluble salt.

13. The method of claim 12 wherein said water-soluble salt is selected from the group consisting of alkali metal nitrites alkali metal chromates and mixtures thereof and said aqueous solution contains at least about 5 percent by weight of said water-soluble salts.

14. The method of claim 13 wherein the contacting of step (1) occurs at a temperature in the range from about 250°F. to about 400°F. for a period of time from about 10 minutes to about 24 hours and the contacting of step (2) occurs at a temperature in the range from about 300°F. to about 400°F. for a period of time from about 10 minutes to about 2 hours.

15. The method of claim 14 wherein said grease composition comprises a major amount of lubricating oil, from about 0.1 percent to about 15 percent by weight of said dispersant, and from about 0.1 percent to about

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5.0 percent by weight of said water-soluble salt.

16. The method of claim 9 wherein said low molecular weight carboxylate contains from 2 to 4 carbon atoms per molecule and said high molecular weight carboxylate contains from about 12 to about 24 carbon atoms per molecule and the mole ratio of said low molecular weight carboxylate to said high molecular weight carboxylate is between about 3 to about 7.

17. In a method for producing a corrosion inhibited grease comprising a major amount of lubricating oil thickened to grease consistency and a water-soluble salt in a corrosion inhibiting amount, the improvement which comprises contacting lubricating oil with the corrosion inhibitor concentrate of claim 1 to form a lubricating oil composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

18. In a method for producing a corrosion inhibited grease comprising a major amount of lubricating oil thickened to grease consistency and a water-soluble salt in a corrosion inhibiting amount, the improvement which comprises contacting lubricating oil with the corrosion inhibitor concentrate of claim 2 to form a lubricating oil composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

19. In a method for producing a corrosion inhibited grease comprising a major amount of lubricating oil thickened to grease consistency and a water-soluble salt in a corrosion inhibiting amount, the improvement which comprises contacting lubricating oil with the corrosion inhibitor concentrate of claim 4 to form a lubricating oil composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

20. In a method for producing a corrosion inhibited grease comprising a major amount of lubricating oil thickened to grease consistency and a water-soluble salt in a corrosion inhibiting amount, the improvement which comprises contacting lubricating oil with the corrosion inhibitor concentrate of claim 6 to form a lubricating oil composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

21. In a method for producing a corrosion inhibited grease comprising a major amount of lubricating oil thickened to grease consistency and a water-soluble salt in a corrosion inhibiting amount, the improvement which comprises contacting lubricating oil with the corrosion inhibitor concentrate of claim 8 to form a lubricating oil composition wherein substantially all the particles of said water-soluble salt have a maximum dimension of less than 5 microns.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,850,823 Dated 11/26/74

Inventor(s) Manley Kjonaas

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 11, line 26; after the word "one"
insert ---high---.

Signed and sealed this 11th day of February 1975.

(SEAL)
Attest:

RUTH C. MASON
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents
and Trademarks

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