

1

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**METHOD FOR DISPERSING SODIUM NITRITE  
IN GREASE COMPOSITIONS**

Arnold J. Morway, Clark, and Carroll L. Knapp, Jr.,  
Cranford, N.J., assignors to Esso Research and En-  
gineering Company, a corporation of Delaware  
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This invention relates to a method for dispersing sodium nitrite in lubricating grease compositions.

The use of sodium nitrite as a rust preventive has long been recognized and it has been proposed to add sodium nitrite to lubricating greases in order to inhibit rusting of metal surfaces. This rusting can be caused by water or moisture which may become absorbed or entrained in the grease during use or actually rejected by water repellent greases, thus directly contacting metal surfaces. While a number of methods have been previously proposed for incorporating sodium nitrite into lubricating grease, these prior methods have had various disadvantages. One such prior method involved mixing an aqueous solution of sodium nitrite into the lubricating grease and then heating to evaporate the water to thereby obtain a homogeneous dispersion of the nitrite in the grease. However, if the grease contains a soap or salt of a metal other than sodium, particularly divalent metals, then metathesis occurs at the high temperature necessary for the evaporation of water and due to the presence of the water. The result is that metal of the soap or salt thickener is exchanged by sodium, thereby changing the characteristics of the original grease. This has been found particularly objectionable in the manufacture of alkaline earth metal greases, e.g. calcium soap grease, since the structural stability of the grease is down-graded by metathesis with the sodium nitrite. Another disadvantage of this method is that sodium nitrite crystallizes out of the aqueous solution in the form of rather large particles or crystals. These particles give the grease a grainy texture, as well as increasing its wearing tendency due to the abrasive nature of the sodium nitrite particles.

Another prior method of dispersing sodium nitrite in grease is disclosed in U.S. Patent No. 2,738,329. Here, the grease with sodium nitrite present, is heated to form a hot, fluid composition, i.e. heated to a temperature above the melting point of the grease. It was found that upon cooling of the composition, that the dropping point of the grease was very materially increased and other changes effected, even by the addition of small amounts of sodium nitrite. Apparently, some form of complex was formed between the grease thickener and the sodium nitrite. However, this method is not applicable where the aim is only to increase the rust resistance of the grease, but not to alter any of its other properties.

Another prior method involves the simple addition of powdered sodium nitrite into a finished grease composition with stirring. However, this method, even though the resulting composition is homogenized, results in a grainy grease and increases its wearing tendency and frequently causes noisy bearing operation.

In the method of the present invention, sodium nitrite can be added to a grease without affecting any of the other properties of the grease except inhibiting rusting caused

2

by entrained water. Furthermore, a smooth, homogeneous, non-grainy product is obtained. In this novel method, commercial granular sodium nitrite is dried and micronized, i.e. ground to below 40 micron particle size, followed by dispersion in mineral oil to form a concentrate, which concentrate is then added to a finished grease composition at temperatures no higher than 150° F. Specifically, sodium nitrite is micronized to a particle size of 5 to 40, preferably 3 to 15 microns. During this grinding or micronizing process, the heat of grinding evaporates water and results in a very dry sodium nitrite having a water content less than about 0.1 wt. percent. Sodium nitrite is very hygroscopic and tends to rapidly pick up water upon exposure to air with the resulting formation of hard granular particles or aggregates. Therefore, in this process, 0.5 to 1.5, preferably 0.85 to 1.15 parts by weight of dry, freshly micronized sodium nitrite is added per one part by weight of oil, e.g. lubricating oil. The oil insulates the nitrite from subsequently picking up water which would result in hygroscopic caking. And at the same time provides a convenient way of introducing sodium nitrite into lubricating grease, since the concentrate dispersion is readily dispersed in the grease composition with a minimum of mixing. It has been further found that by the addition of a small amount of a finely divided silica to the oil dispersion of the sodium nitrite, the stability of the sodium nitrite oil dispersion is further increased. With these stabilized dispersions there is substantially no settling or caking of the sodium nitrite from the oil, even after long periods of storage.

Sodium nitrite in amounts of 0.5 to 3.0 wt. percent, preferably 1.5 to 2.0 wt. percent, based on the weight of the total composition, may be used in any of the common lubricating greases. Included are greases wherein lubricating oil is thickened with salts, soaps, soap-salt or mixed salt complexes, polymeric thickeners (e.g. polymers of C<sub>2</sub> to C<sub>4</sub> monoolefins of 10,000 to 200,000 molecular weight such as polyethylene), and inorganic thickeners (e.g. clay, carbon black, silica gel, etc.). However, the method is of particular value in cases where the grease is thickened with a metal soap other than sodium, and particularly where the metal is an alkaline earth metal such as calcium.

Generally, the greases will comprise either a synthetic or mineral lubricating oil thickened with about 3 to 35 wt. percent usually 3 to 20 wt. percent of a thickener. In the case of soap-salt and mixed-salt thickeners, the thickener is usually formed by co-neutralization in oil, by metal base, of various mixtures of high molecular weight fatty acids and/or intermediate molecular weight fatty acids with low molecular weight fatty acids.

The high molecular weight fatty acids useful for forming soap, soap-salt and mixed-salt thickeners include naturally-occurring or synthetic, substituted and unsubstituted, saturated and unsaturated, mixed or unmixed fatty acids having about 14 to 30, e.g. 16 to 22, carbon atoms per molecule. Examples of such acids include stearic, hydroxy stearic, such as 12-hydroxy stearic, di-hydroxy stearic, poly-hydroxy stearic and other saturated hydroxy fatty acids, arachidic, oleic, ricinoleic, hydrogenated fish oil, tallow acids, etc.

Intermediate molecular weight fatty acids include those aliphatic, saturated, unsubstituted, mono-carboxylic acids containing 7 to 12 carbon atoms per molecule, e.g., capric, lauric, caprylic, nonanoic acid, etc.

Suitable low molecular weight acids include  $C_2$  to  $C_4$  fatty acids. Acetic acid or its anhydride is preferred.

Metal bases which are frequently used to neutralize the above acids are the hydroxides, oxides or carbonates of alkali metals (e.g. lithium and sodium) or of alkaline earth metals (e.g. calcium, magnesium, strontium and barium).

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent based on the total weight of the composition) for example, oxidation inhibitors such as phenyl- $\alpha$ -naphthylamine; tackiness agents such as polyisobutylene; stabilizers such as aluminum hydroxy stearate; and the like.

The invention will be further understood by the following examples:

#### EXAMPLE I

A series of comparisons were made between prior methods and the method of the invention.

##### A. Addition of Dry Powdered Sodium Nitrite to Grease Composition

A calcium complex soap-salt grease composition was prepared having the following formulation:

|                                                              | Percent |
|--------------------------------------------------------------|---------|
| Glacial acetic acid.....                                     | 11.0    |
| Wecoline acids AAC (low mol. wgt. coconut fatty acids) ..... | 3.7     |
| Hydrofol acids Code 200 (12-hydroxy stearic acid) ..         | 1.8     |
| Hydrated lime.....                                           | 7.8     |
| Phenyl $\alpha$ -naphthylamine.....                          | 0.3     |
| Sodium nitrite.....                                          | 2.0     |
| Mineral lubricating oil (55 SUS at 210° F.).....             | 73.4    |

The lime, mineral oil and Hydrofol Acids Code 200 were added to a steam heated kettle and intimately mixed. A blend of the acetic and Wecoline AAC acids (a mixture of 28 wt. percent caprylic, 46 wt. percent capric and 26 wt. percent lauric acids) were then added slowly to the kettle while stirring. The mixture was dehydrated by heating to 325° F. while stirring. Next, the product was cooled to 200° F. by passing cool water through the kettle jacket. Phenyl  $\alpha$ -naphthylamine was added as an oxidation inhibitor and the grease was further cooled to 125° F. where commercial powdered sodium nitrite of about 200-400 micron particle size, was stirred into the grease composition until a seemingly homogeneous composition was obtained. The grease was homogenized in a Morehouse mill having a clearance of 0.003 inch.

##### B. Addition of Aqueous Solution of Sodium Nitrite to Grease Composition

A grease was prepared having the same formulation as grease A and following the same general procedure, except that after the temperature was raised to 325° F., a 50 wt. percent aqueous solution of sodium nitrite was added through an inlet at the bottom of the kettle. Heating was then continued for about 30 minutes at this temperature of 325° F. while stirring, in order to dehydrate the product. The grease was then cooled to 200° F. where the phenyl  $\alpha$ -naphthylamine was added and then the grease was cooled to room temperature. The grease was homogenized in a Morehouse mill having a clearance of 0.003 inch.

##### C. Method of the Invention for Adding Sodium Nitrite to Grease Composition

A 50 wt. percent dispersion of sodium nitrite in a mineral lubricating oil of 55 SUS viscosity at 210° F. was prepared by simple mixing of a dry micronized sodium nitrite into the oil. The sodium nitrite had a particle size within the range of 5 to 40 microns, averaging about 15 microns, and a water content of less than 0.1%. A grease was prepared having the same formulation as A above and following the same general procedure, except that after the addition of phenyl  $\alpha$ -naphthylamine, the grease was cooled to 125° F. at which point the dispersion of so-

dium nitrite was added to the grease composition and stirred in. The grease was then passed through a Morehouse mill having a clearance opening of 0.003 inch.

The compositions A, B, and C prepared above were submitted to the usual grease tests and were also tested for corrosion by the Bearing Protection Test, described in paragraph 45.4 of military specification MIL-G-3278A for aircraft and instrument grease.

The properties of compositions A, B, and C are summarized in the following table:

TABLE I

| Properties of Greases                                                             | Example I |                    |                     |
|-----------------------------------------------------------------------------------|-----------|--------------------|---------------------|
|                                                                                   | A         | B                  | C                   |
| 15 Appearance.....                                                                | Grainy..  | Smooth.....        | Smooth.             |
| Dropping Point, ° F.....                                                          | 500+..... | 500+.....          | 500+.               |
| Penetrations, 77° F., mm./10:                                                     |           |                    |                     |
| Unworked.....                                                                     | 285.....  | 335.....           | 260.                |
| Worked 60 Strokes.....                                                            | 300.....  | 350.....           | 278.                |
| Worked 10,000 Strokes.....                                                        | 340.....  | 400+.....          | 324.                |
| Wheel Bearing Test (1 Hr., 220° F., tilted).                                      | Pass..... | Pass.....          | Pass.               |
| Timken Test—45 lbs. Load.                                                         | Fail..... | Pass (Broad Scar). | Pass (Narrow Scar). |
| 14 Day Corrosion Test (MIL-G-3278A).                                              | Pass..... | Pass.....          | Pass.               |
| 25 4-Ball Wear Test: Scar Diameter, mm. (1,800 r.p.m.—10 Kg. load—1 hour—75° C.). | 0.72..... | 0.35.....          | 0.22.               |

While all three compositions of the table had acceptable rust preventing properties, there were substantial differences in other properties. The method of the invention (I-C) resulted in a smooth, non-grainy grease having very low wear. On the other hand, the addition of powdered sodium nitrite to the grease composition (Example I-A) resulted in a softer grease and a grainy product which gave high wear. The addition of the aqueous solution (Example I-B) and the subsequent evaporation of the water from the composition had a pronounced effect upon the structural stability of the grease as seen by its penetrations. This change is attributable to the fact that a portion of the calcium in the complex thickener was replaced by sodium, since metathesis can readily occur due to the water phase present and the high temperatures involved. It is to be also noted that the wear scar diameter was considerably higher than that obtained by the method of the invention.

It has been further found that by the addition of a small colloidal amount of silicon dioxide ( $SiO_2$ ) to the oil dispersion of the sodium nitrite, the nitrite-oil dispersion is stabilized with the result that no settling occurs even upon prolonged storage. Thus, while the silica is not essential since the settled out sodium nitrite can be put back into an even dispersion, still it is obviously more advantageous to provide a dispersion which will not separate. The material utilized for the purpose is a very finely divided silica ( $SiO_2$ ) having a particle size less than 1 micron and preferably less than 0.1 micron. One source of such finely divided silica is by the condensation of the smoke or fumes obtained by burning ethyl silicate. Another method of preparing such colloidal silica is by heating silica gel above its critical temperature while at a pressure above its critical pressure, followed by suddenly releasing the pressure. As a result, the silica gel literally explodes and very fine particle sizes are obtained.

A specific silica that was used in the examples of the invention is available under the trade-name Cab-O-Sil and has been described in Industrial and Engineering Chemistry, vol. 51, No. 3, 1959. This commercial material is 99.0 to 99.7% silica having an average particle size of 15 to 20 millimicrons (i.e. 0.015 to 0.020 micron).

Usually about 0.5 to 4.0, preferably 0.5 to 2.0 wt. percent of the colloidal silica, based on the weight of sodium nitrite, is sufficient to stabilize oil dispersions of the sodium nitrite.

The invention will be further understood by the following examples:

### EXAMPLE II

A. Freshly pulverized dry sodium nitrite having particles within the range of 5 to 40 microns and averaging about 15 microns, was dispersed in 50 wt. percent of a mineral lubricating oil having a viscosity of 55 SUS at 210° F. The oil composition was then milled in a Morehouse mill having a clearance of 0.003".

B. A composition was prepared using 50 wt. percent of the sodium nitrite described above, 49 wt. percent of the mineral lubricating oil described above and 1 wt. percent of Cab-O-Sil (a finely divided silica sold by Godfrey L. Cabot Inc.)

The two sodium nitrite dispersions were then stored and their storage stability determined. Results obtained are summarized in Table II which follows:

TABLE II

| Properties                                 | Example II                                         |                                                                     |
|--------------------------------------------|----------------------------------------------------|---------------------------------------------------------------------|
|                                            | A                                                  | B                                                                   |
| Consistency (fresh).....                   | Semi-fluid.....                                    | Soft solid structure which readily fluidizes on disturbing surface. |
| Appearance After:<br>10 Days' Storage..... | Sodium nitrite settling out, clear oil on surface. | No sign of settling, no clear oil on surface.                       |
| 30 Days' Storage.....                      | Caked on bottom of container.                      | Do.                                                                 |
| 150 Days' Storage.....                     | do.....                                            | Slight oil separation on top; no tendency to cake.                  |

As seen by the above table, a very small amount of the silica prevented separation of the sodium nitrite from the oil dispersion. The advantage of this is that it permits the formation of high concentrates of the sodium nitrite in oil, which concentrates may be stored over long periods of time and used as required without the necessity of stirring the concentrate before use and with the assurance that a homogeneous concentrate is at hand.

### EXAMPLE III

To show that the addition of the Cab-O-Sil had no adverse effect upon a finished grease composition, two greases were prepared in the manner of preparation of the greases described in Example I. The compositions of these greases and their properties are summarized in Table III which follows:

TABLE III

| Formulations, Percent Wgt.                                        | Greases          |                  |
|-------------------------------------------------------------------|------------------|------------------|
| Glacial Acetic Acid.....                                          | 10.00.....       | 10.00.           |
| Weccline A.A.C. Acids.....                                        | 3.34.....        | 3.34.            |
| Hydrofol Acids Code 200.....                                      | 1.67.....        | 1.67.            |
| Hydrated Lime.....                                                | 6.77.....        | 6.77.            |
| Phenyl $\alpha$ -Naphthylamine.....                               | 1.00.....        | 1.00.            |
| Mineral Lubricating Oil (55 SUS at 210° F.).....                  | 73.22.....       | 73.22.           |
| Sodium Nitrite Dispersion <sup>1</sup> .....                      | 4.00.....        | 4.00.            |
| Sodium Nitrite Dispersion <sup>2</sup> .....                      | 4.00.....        | 4.00.            |
| Properties:                                                       |                  |                  |
| Appearance.....                                                   | Smooth, uniform. | Smooth, uniform. |
| Dropping Point, ° F.....                                          | 500+.....        | 500+.            |
| Penetrations, 77° F., mm/10—                                      |                  |                  |
| Unworked.....                                                     | 280.....         | 278.             |
| Worked 60 Strokes.....                                            | 325.....         | 322.             |
| Worked 10,000 Strokes.....                                        | 340.....         | 341.             |
| Lubricating Life <sup>3</sup> (@250° F., 10,000 r.p.m.).....      | 2,000+ hours.    | 2,000+ hours.    |
| Water Solubility (Boiling Water).....                             | Insoluble.....   | Insoluble.       |
| 14 Day Corrosion Test (Bearing Protection Test, MIL-G-3278A)..... | Pass.....        | Pass.            |

<sup>1</sup> 50 wt. percent sodium nitrite and 50 wt. percent mineral lubricating oil of 55 SUS at 210° F.

<sup>2</sup> 50 wt. percent sodium nitrite, 49 wt. percent mineral lubricating oil and 1 wt. percent Cab-O-Sil.

<sup>3</sup> ABEC-NLGI Spindle Test.

As seen by the above table, no adverse effects were incurred by the addition of the silica in the grease composition.

What is claimed is:

1. A method for dispersing sodium nitrite in a lubricating grease composition which comprises:
  - (a) dry grinding sodium nitrite to form a micronized sodium nitrite having an average particle size within the range of 5 to 40 microns and a water content of less than 0.1 wt. percent,
  - (b) dispersing the micronized sodium nitrite in oil to form an oil dispersion wherein the weight ratio of said micronized sodium nitrite to said oil in said oil dispersion is from 0.5:1 to 1.5:1, and
  - (c) mixing said oil dispersion into said grease composition at a temperature of less than 150° F.
2. A method as defined in claim 1 wherein said oil dispersion also contains from 0.5 to 4.0 wt. percent of silica as a stabilizing agent, said silica having a particle size less than 1 micron, and said wt. percent of silica being based on the weight of said sodium nitrite.
3. A method as defined in claim 1 wherein said lubricating grease composition is a calcium grease.
4. A method for dispersing sodium nitrite in a lubricating grease composition wherein said lubricating grease composition comprises a mineral oil thickened to a grease consistency with a mixture of calcium salts of C<sub>2</sub> to C<sub>30</sub> fatty acids, which comprises:
  - (a) dry grinding sodium nitrite to form a micronized sodium nitrite having an average particle size within the range of 5 to 40 microns and a water content of less than 0.1 wt. percent,
  - (b) dispersing 0.5 to 1.5 parts by weight of said micronized sodium nitrite in one part by weight of oil to form an oil dispersion, and
  - (c) mixing said oil dispersion into said lubricating grease composition at a temperature of less than 150° F., the amount of said dispersion being sufficient to provide from 0.5 to 3.0 wt. percent of sodium nitrite in said lubricating grease composition.
5. A method as defined in claim 4 wherein said oil dispersion also contains silica having a particle size of less than 0.1 micron, said silica being present in an amount of from 0.5 to 4.0 wt. percent based on the weight of said sodium nitrite.
6. A method as defined in claim 4 wherein the amount of said oil dispersion mixed with said lubricating grease composition is sufficient to provide from 1.5 to 2.0 wt. percent of sodium nitrite in said grease.
7. A composition of matter consisting essentially of:
  - (a) 0.5 to 1.5 parts by weight of sodium nitrite having a particle size within the range of 5 to 40 microns and a water content of less than 0.1 wt. percent,
  - (b) one part by weight of lubricating oil, and
  - (c) about 0.5 to 4.0 wt. percent of silica having a particle size less than one micron, the weight percent of silica being based on the weight of said sodium nitrite.

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