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SODIUM NITRATE STABILIZED WITH COLLOIDAL ASBESTOS

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ABSTRACT OF THE DISCLOSURE

Colloidal asbestos stabilizes finely divided sodium nitrite so that it can be dispersed in oil to form a concentrate which can be added as a rust inhibitor to lubricating grease.

This invention relates to oil dispersions of sodium nitrite containing colloidal asbestos as a stabilizer.

The use of sodium nitrite as a rust preventive in lubricating grease is known. 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. However, while a number of methods have been 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 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 downgraded 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, and when used in bearing lubrication, give a noisy operation.

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 up cooling of the composition, the dropping point of the grease was very material 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 si homogenized, results in a grainy grease and increases its wearing tendency and frequently causes noisy bearing operation.

Other methods have involved rather complicated procedures of chemically sub-dividing the sodium nitrite into fine particles by precipitation in the presence of protective materials which coat the finely-divided particles to prevent their later agglomeration, since without such a coating, the particles will cake upon storage. Prior methods of mechanically grinding the sodium nitrite to a small particle size, e.g., 35 microns or less, are taught in U.S. Patent 3,078,226. However, the sodium nitrite prepared in this manner has to be freshly used, or if stored, can be stabilized with Cab-O-Sil, which is a finely divided pyrogenic silicon dioxide, but which is relatively expensive.

In the method of the present invention, sodium nitrite can be prepared in large quantities and kept in storage for later use. It can be later added to a grease without affecting any of the other properties of the grease except inhibiting rusting caused by entrained water. Furthermore, a smooth, homogeneous, non-grainy grease product is obtained due to the fine particle size of the sodium nitrite. In this novel method, commercial granular sodium nitrite is dried and pulverized or micronized, e.g., ground to below 60 micron particle size, followed by dispersion in mineral oil using colloidal asbestos as a stabilizing agent, to form a concentrate. This concentrate is stable and can be stored for extended periods of time without caking or particle growth. The concentrate can be easily added to a finished grease composition, or can be added during the formation of the grease, but preferably after dehydration to avoid metathesis. The colloidal asbestos is much less expensive than the aforesaid Cab-O-Sil, and in addition has rust preventing properties of its own. Or alternatively, a dry mixture comprising a major amount of sodium nitrite and about 1 to 12 wt. percent colloidal asbestos, based on the weight of the total mixture, can be prepared by simply pulverizing the sodium nitrite in the presence of the asbestos to thereby give a free flowing stable mixture, which can later be added to oil or grease.

Specifically, sodium nitrite is pulverized, as by ball milling, to an average particle size of 5 to 60, preferably 5 to 40 microns. During this grinding, the heat of grinding will usually evaporate water so as to result in a very dry sodium nitrite having a low water content (usually less than about 0.1 wt. percent water). Colloidal asbestos can be present during the pulverizing step as it appears to help dry out the sodium nitrite by taking up water. 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 aggregate. Therefore, it is usually best to use freshly ground sodium nitrite, which along with colloidal asbestos, is added to the oil, e.g. lubricating oil. The resulting concentrate will generally comprise: oil, about 10 to 60 wt. percent sodium nitrite, and about 1 to 12 wt. percent (based on the weight of said nitrite) of colloidal asbestos. Preferred concentrates will comprise oil, about 30 to 60 wt. percent sodium nitrite, and about 2 to 8 wt. percent, based on the amount of nitrite, of colloidal asbestos.

The use of natural asbestos as an ingredient of lubricating compositions is quite old in the art and a number of various grease formulations are taught in the book "Lubricating Grease" by C. J. Boner, 2nd edition, pages 687 et seq. These prior greases utilized natural asbestos or asbestos floats, both of which are relatively long fibered asbestos. However, this fibered asbestos was always used in conjunction with other thickening agents such as soaps, since the long fibered asbestos will not form a thickened homogeneous grease gel by itself, but rather relies upon other ingredients to form the grease or gel-like structure. The asbestos of the present invention differs from the aforesaid long fibered conventional asbestos in that the asbestos particles are in a very small colloidal size, having a large surface area, and can be dispersed in the oil to form a gel by itself, and without settling out from the oil. This colloidal asbestos is chrysotile having the chemi-

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cal formulation $Mg_6(OH)_8Si_3O_{10}$. The usual mode of occurrence of chrysotile is a "cross-fiber" configuration in which filaments of chrysotile (i.e. bundles of fibers) are closely packed together and set at right angles to the walls or cracks and fissures that extend through the host rock of the ore body. However, in 1959, an unusual deposit of chrysotile asbestos, with properties and a mode of occurrence different from the previously known cross-fiber material, was discovered in central California. The ore of the new deposit, instead of occurring in veins, occurs in randomly-oriented, matte-like flakes and agglomerates of visible asbestos filaments, which in turn are made up of many thousands of extremely small tubular fibers. The lengths of these small fibers vary from a few millimicrons to thousands of millimicrons, generally 2,000 to 30,000 millimicrons, while the diameters of the fibers vary much less and are usually in the range of 1 to 800, e.g., 10 to 400, millimicrons. A typical colloidal asbestos that was used in the working examples of the invention had the following characteristics:

Properties of colloidal asbestos fibers

Brightness (GE)	74–76.
Refractive index	1.55.
Dispersion in water	Fully/pH range 4–6.
Surface area	47–50 sq. meters/gram.
Oil absorption	14–16 cc./10 grams of fibers.
Water retention	42 grams/20 grams of fibers.
Dry bulk density	2–2.5 lbs./cu. ft.
Fiber dimension:	
O.D.	25.0 millimicrons.
I.D.	6.0 millimicrons.
Length	2,500–25,000 millimicrons.

Sodium nitrite in amounts of 0.5 to 3.0 wt. percent, preferably 1.5 to 2.5 wt. percent, based on the weight of the total composition, may be used in any of the common lubricating greases. Usually about 1 to 12 wt. percent, based on the weight of sodium nitrite, of colloidal asbestos will be used to stabilize the nitrite in the grease. Included are greases wherein lubricating oil is thickened with salts, soaps, soap-salt or mixed salt complexes, polymeric thickeners (e.g. polymers of C_2 to C_4 monoolefins of 10,000 to 200,000 Staudinger molecular weight such as polyethylene) and inorganic thickeners (e.g. clay, carbon black, silica gel, etc.). However, the method of the invention 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 a major amount of either a synthetic or mineral lubricating oil, thickened with about 3 to 49 wt. percent, usually 20 to 45 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, or 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, dihydroxy stearic, polyhydroxy 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, monocarboxylic 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 wt. 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 following examples further describe the invention wherein all parts are parts by weight.

Example I

Part A.—Two parts of the previously described colloidal asbestos and 49 parts of a coarse commercial sodium nitrite were milled together in a ball mill for 16 hours until the sodium nitrite was reduced to an average particle size of about 35 microns. The milled mixture of asbestos and sodium nitrite was then removed from the ball mill, and mixed with 49 parts of a mineral lubricating oil having a viscosity of 55 SUS at 210° F.

Part B.—A sample of the mixture of Part A was stored at room temperature in a closed container for three months. At the end of this time, there was no settling of the sodium nitrite or asbestos from this oil.

Part C.—A sample of the dry mixture of 49 parts of sodium nitrite and 2 parts asbestos taken from the ball mill after 16 hours in Part A, without oil, was kept in a closed container to keep out moisture and stayed dry and showed no tendency to cake after storage for 24 months. It remained free flowing.

Part D.—In comparison, a sample of the same sodium nitrite pulverized to the same particle size in the ball mill, but without asbestos present, caked on standing overnight even though kept in a closed container.

Parts A and B illustrate that the colloidal asbestos will stabilize oil dispersions of sodium nitrite against separation. Parts C and D show that the asbestos acts to prevent caking of sodium nitrite.

Example II

Part A.—A lubricating grease was prepared as follows: A grease kettle was charged with 55.6 parts of mineral lubricating oil having a viscosity of 55 SUS at 210° F., and 10 parts of tallow fatty acid having a saponification number of 192 and a Wijs iodine number of 54. Then 13.4 parts of hydrated lime were added to the kettle, while mixing until smooth and homogeneous. Then, glacial acetic acid was slowly added to the kettle while maintaining the temperature of the kettle contents below about 200° F. External heating was then applied to the kettle and the contents were heated to about 325° F. to dehydrate the reaction product. One part of phenyl-alpha-naphthylamine was added as an antioxidant, following which the product was rapidly cooled from 325° F. to 100° F. by circulating cooling water through the kettle jacket. Then, 2 wt. % of sodium nitrite pulverized to an average micron size of 30, which had been standing 20 days in storage after pulverizing, was added to the grease product. The grease was then homogenized by passing through a Charlotte mill having a clearance opening of about .002". The resulting grease product was grainy due to the presence of hard, large sodium nitrite particles caused by reagglomeration of the pulverized sodium nitrite.

Part B.—A grease was prepared in the same manner as in Part A, but instead of using the two parts by weight of sodium nitrite per se, there was used instead a dispersion consisting of two parts by weight of the pulverized nitrite (average size of 30 microns) dispersed in two parts of the mineral lubricating oil. This dispersion, after two

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weeks' storage, had separated with the sodium nitrite settling out as a hard mass on the bottom of the container. This showed that even though protected by oil, the sodium nitrite agglomerates. With much difficulty, and with vigorous stirring, it was possible to redisperse the nitrite so it could be added to the grease.

Part C.—A grease was prepared in the same manner as shown in Part A, except there was used 2.0% of a mixture consisting of 49 parts of dry pulverized sodium nitrite stabilized with two parts of the aforesaid colloidal asbestos, which mixture had been in storage for two weeks in air-tight drums. The condition of the sodium nitrite was uncaked and it could be poured.

Part D.—A grease was prepared in the same manner as in Part A, except that 2% of the sodium nitrite-colloidal asbestos mixture was added in the form of the oil dispersion of Example I, Part A.

The compositions and properties of the greases of Example II are summarized in the following table:

TABLE

	Example II			
	A	B	C	D
Composition (Parts by Weight):				
Glacial acetic acid	18.0	18.0	18.0	18.0
Tallow fatty acid	10.0	10.0	10.0	10.0
Hydrated lime	13.4	13.4	13.4	13.4
Phenyl-alpha-naphthylamine	1.0	1.0	1.0	1.0
Sodium nitrite of 35 micron average size	2.0	2.0	1.92	1.92
Colloidal asbestos	0.0	0.0	0.08	0.08
Mineral lubricating oil of 55 SUS at 210° F	55.6	55.6	55.6	55.6
Properties:				
Appearance	Grainy	Smooth	Smooth	Smooth
ASTM Cone Penetration, 77° F.:				
Unworked	320	325	325	320
Worked 60 Strokes	320	325	325	325
Worked 10,000 Strokes	329	329	322	322
Timken E.P. Test (lbs. load carried)	40	45	45	45
CRC–L–41 (14 Day Corrosion)	Pass	Pass	Pass	Pass
Bearing Noise	Noisy	No Noise	No Noise	No Noise

The CRC–L–41 Test was carried out by coating chemically clean Timken bearings (cup and bearing) with a thin coating of the grease and subjecting the bearings to turning at 600 r.p.m. under a load to spread the grease in a thin layer. The cup and bearing assembly were then dipped in water and stored for 14 days in a closed glass jar containing a small amount of water so as to maintain a humid atmosphere. After that, the bearing was then examined for rust.

The Bearing Noise Test was carried out in a soundproof room, measuring the noise level obtained during operation of a Timken roller bearing.

While the compositions containing sodium nitrite gave no rust in the CRC–L–41 Test, a similar grease containing no sodium nitrite agent results in bad rusting of the bearing.

As seen in the table, in greases A to D, the sodium nitrite imparted rust inhibition to the greases as indicated by the 14-day Corrosion Test. However, grease A was grainy and resulted in bearing noise, thus indicating that the sodium nitrite was in large particle sizes. Grease B gave good results, but the sodium nitrite had separated from the oil and was very difficult to redisperse. Greases C and D, representing the invention, formed smooth homogeneous greases and gave no noise in the Bearing Noise Test, while at the same time there was no difficulty with the sodium nitrite separating as in the case of grease B.

What is claimed is:

1. A lubricating grease comprising a major amount of lubricating oil thickened to a grease consistency with about 3 to 49 wt. percent of metal salt of fatty acid wherein said metal is selected from the group consisting of alkali and alkaline earth metals, as grease thickener, and containing 0.5 to 3.0 wt. percent of sodium nitrite having an average particle size less than about 60 microns, and as a stabilizing agent for said nitrite, about 1 to 12 wt. percent, based on the weight of said sodium nitrite, of a finely divided colloidal asbestos having particle outer diameters of about 1 to 80 millimicrons and particle lengths of about 2,000 to 25,000 millimicrons.

2. A grease according to claim **1**, wherein said oil is a major amount of mineral lubricating oil, said thickener is about 20 to 45 wt. percent of calcium mixed salts of acetic and higher fatty acid, the amount of sodium nitrite is about 1.5 to 2.5 wt. percent based on the weight of the total grease composition, and said asbestos has a particle outer diameter of about 10 to 40.0 millimicrons.

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