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3,291,731

INCORPORATING SODIUM NITRITE INTO LUBRICANT COMPOSITIONS

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8 Claims. (Cl. 252—25)

This application is a continuation-in-part of application Serial No. 171,280 filed February 5, 1962, and abandoned after the filing of the present application.

The present invention relates to lubricant compositions containing sodium nitrite as a rust preventive. The invention also relates to imides formed by reaction of copolymers of maleic anhydride and styrene with amino compounds having a plurality of nitrogen atoms and at least one primary amino group.

It has been recognized for some time that sodium nitrite is an excellent rust preventive for lubricant compositions, and particularly for grease formulations. The rusting of metal surfaces that come into contact with greases can be caused by water or moisture that may have been entrained, or adsorbed, by the grease. The problem can also arise with water-repellent greases because the repelled water can remain in contact with the lubricated iron or steel surfaces.

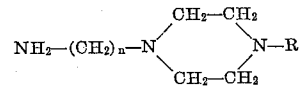
The incorporation of sodium nitrite into a grease is not a simple matter because of its tendency to form agglomerates. The agglomerates frequently result in noisy and rough operation of bearings. Also, in many cases the agglomerates can be felt as abrasive particles when a portion of the grease or lubricant is held between the fingers. Sufficient sodium nitrite to impart suitable rust prevention cannot be satisfactorily incorporated into a grease simply by adding powdered sodium nitrite to the grease or even by grinding the sodium nitrite into the grease.

If powdered sodium nitrite is simply added to a finished grease composition and stirred into it, a grainy grease results even though the grease is given a homogenizing treatment. A prior art method of incorporating sodium nitrite into a grease 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. 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. Even when increased wear is not too great, the large size crystals give noisy and objectionable anti-friction bearing operation.

It has now been found in accordance with the present invention that smooth, homogeneous, non-grainy grease products containing sodium nitrite can be obtained by employing a sodium nitrite carrier that is prepared by reacting a copolymer of styrene and maleic anhydride

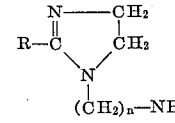
with an amino compound of from 2 to about 35 carbon atoms, said compound having from 2 to 5 nitrogen atoms, at least one of which is in the form of a primary amino group. Such amino compounds include alkylene polyamines, such as ethylene diamine, triethylene tetramine, tetraethylene pentamine, and propylene diamine. Other aliphatic polyamino compounds that may be used include 1,3-diamino propane, dimethyl amino propylamine, methyl propyl aminoamylamine, and N,N-di-(2-aminoethyl) ethylene diamine. They also include polyalkoxydiamines prepared by reaction of aliphatic amines such as ethyl amine, hexyl amine, etc., with alkylene oxides of from 2 to 8 carbon atoms, preferably propylene oxide and ethylene oxide. The polyalkoxydiamines thus prepared have repeating chains of alkylene oxide with terminal amino groups at each end of the alkylene oxide polymer chain.

Still other polyamino compounds that may be used include the N-aminoalkyl piperazines of the formula:



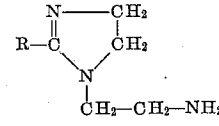
wherein n is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms. Specific examples include N-(2-aminoethyl) piperazine, N-(2-aminoisopropyl) piperazine, and N,N'-di-(2-aminoethyl) piperazine.

In addition to the polyamines and polyalkoxydiamines disclosed above, amino imidazolines may also be employed in preparing the imides. These will have the general structure:



In the above formula, n is about 2 to 6, preferably 2 to 3, and R is a C_6 to C_{22} hydrocarbon group, and preferably a C_{16} to C_{18} hydrocarbon group, either saturated or unsaturated, but preferably aliphatic.

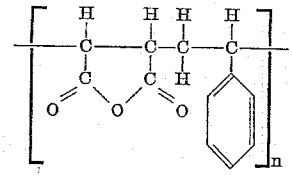
A specific example of an imidazoline fitting the above formula, which was used in the working examples of this invention, was a product sold by Nalco Chemical Company as Nalcamine G-39M. This was identified as 1-(2-aminoethyl)-2-n-alkenyl-2-imidazoline, having the formula:



R being heptadecenyl and heptadecadienyl chains in a 1:1 mole ratio.

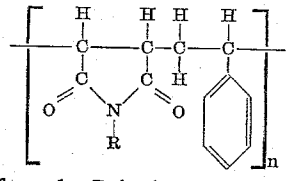
The preparation of copolymers of styrene and maleic anhydride is accomplished by conventional polymerization techniques. For example, copolymers of styrene and maleic anhydride may be obtained by heating substantially equimolar quantities of the reactants at temperatures within the range of about 120° to about 300° F. in the presence of about 0.1 to about 5 wt. percent of a peroxide catalyst such as benzoyl peroxide or di-tert. butyl peroxide. Reaction time will vary from about a few minutes to several hours, depending on the temperature and the mode of addition of the peroxide catalyst. The copolymerization can be carried out in the presence of a solvent if desired. Suitable solvents are toluene,

xylene, and dioxane. The formula for the copolymer may be represented as follows:



In the above formula, n will be a number between 2 and 15, preferably a number between about 3 and 8. The molecular weights of such copolymers are from about 400 to about 3000.

To prepare the imide derivative of the copolymer of styrene and maleic anhydride, the polyamine and the copolymer are reacted under conditions which will drive off one mole of water for each nitrogen atom taking place in the reaction. The resulting imide may be represented by the formula:



In the above formula, R is the residue of the particular amino compound that has been used in forming the imide.

In many instances it is desirable to add water to catalyze the reaction. In such cases the anhydride will first be converted to the dicarboxylic acid, so that during the reaction there will be two moles of water driven off for each nitrogen atom taking place in the reaction. Although in general the imides will be formed by reaction of one amino group for each anhydride group present, proportions greater or less than this may also be employed, e.g. from about 0.5 to 2 amino groups per anhydride group. Some of the acyl groups may also be reacted with other suitable compounds such as alcohols, glycols, alkylene oxides, and the like. Thus, for example, from 1 to 20% of the total number of acyl groups may be so reacted.

For use as a sodium nitrite carrier in accordance with the present invention, the imide is preferably used in combination with sodium nitrite in the proportion of from 0.5 to 5, and preferably from about 0.8 to 2 parts by weight, of the imide per part of sodium nitrite. Conveniently, the combination of sodium nitrite and imide can be made in the form of a concentrate containing from 2 to about 70, and preferably from about 5 to about 60 wt. percent of the combination in a suitable base oil. Then a sufficient amount of the concentrate can be added to a conventional grease to incorporate from 0.1 to about 10 and preferably from about 0.5 to 5 wt. percent of the rust inhibiting nongrainy combination into said grease.

Generally, it is desirable to incorporate about 0.1 to 3 wt. percent, or more usually about 0.3 to about 2 wt. percent of sodium nitrite, based on the total composition weight, into a grease for satisfactory rust prevention. The combined concentrate of sodium nitrite and imide is conveniently added to the grease in the desired amount simply by stirring and then milling the grease in a conventional manner.

It is convenient and usually preferable to prepare the combination of sodium nitrite and imide in situ when preparing a concentrate. For example, a homogeneous dispersion may be prepared by mixing a styrene-maleic anhydride copolymer with the amine that is to be used in forming the imide. Then an aqueous solution of sodium nitrite containing from 10 to 70 wt. percent, and preferably from about 10 to 50 wt. percent, of sodium nitrite is added to the slurry. The slurry is then stirred and heated and heating is continued to drive off the water at a convenient dehydration temperature, which is

preferably in the range of 250 to 350° F. The resulting product can then be milled or homogenized, if desired.

The combination of sodium nitrite and imide prepared in accordance with this invention may be added to any type of grease composition. Included are greases thickened with salts, soaps, soap-salt complexes or mixed salt complexes, polymeric thickeners (e.g. polymers of C_2 to C_4 mono-olefins of 10,000 to 200,000 molecular weight such as polyisobutylene or polyethylene), and inorganic thickeners (e.g. clay, carbon black, silica gel, etc.).

Generally, the greases will comprise either a synthetic oil or a 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-salt, soap, and mixed-salt thickeners include naturally occurring or synthetic, substituted or unsubstituted, saturated or unsaturated, mixed or unmixed fatty acids having about 14 to 30, or more usually 16 to 22, carbon atoms per molecule. Examples of such acids include stearic, hydroxy fatty acids, 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 that are frequently used to neutralize the above acids are the hydroxides, oxides or carbonates of alkaline earth metals (e.g. calcium, magnesium, strontium and barium).

Various other additives may also be incorporated in conventional amounts into the grease formulations. These include antioxidants such as phenyl-alpha-naphthylamine, tackiness agents such as polyisobutylene, stabilizers such as aluminum hydroxy stearate, and the like.

This invention can be best understood by reference to the following specific examples. In these examples the base oil was an unextracted low cold test oil having a viscosity of 510 SSU at 100° F. and an API gravity of 22 at 60° F. The styrene-maleic anhydride copolymer consisted of eight repeating units of the styrene maleic anhydride shown structurally above; i.e., n was equal to 8. The copolymer was known as SMA 1000A resin manufactured by Texas Butadiene and Chemical Corporation. It had a molecular weight of approximately 1600 and was a light powder melting in the range of 165 to 180° C. and had an acid number of 500 mg. of KOH per gram.

EXAMPLE 1

One hundred grams of diethylene triamine and 15 grams of the SMA 1000A copolymer were added to 100 grams of the base oil along with 10 grams of water, which was employed for catalyzing the reaction. The mixture was heated at 300–350° F. until no more water was driven off.

EXAMPLE 2

Twenty-one and six-tenths (21.6) wt. percent of Nalcamine G–39, 11.7 wt. percent of the SMA 1000A copolymer, 33.3 wt. percent of the base oil and 33.4 wt. percent sodium nitrite were mixed together in a Hobart mixer. The percentage of sodium nitrite is given on a dry basis although a 50 wt. percent aqueous solution was actually used. The reaction mixture was heated to 300° F. to drive off all of the water and the water of reaction. The reaction product was allowed to cool and was then

milled in a Morehouse mill. The product was an excellent, homogeneous, smooth product having a semifluid consistency.

EXAMPLE 3

Twenty-one and six tenths (21.6) wt. percent of the product of Example 1, 11.7 wt. percent of the SMA 1000A copolymer, 33.3 wt. percent of the base oil and 33.4 wt. percent (dry basis) of sodium nitrite as a 50 wt. percent aqueous solution were mixed together in a Hobart mixer. The reaction mixture was heated to 300° F. to drive off all of the water. The product, while cooling, was milled in a Morehouse mill, yielding an excellent, smooth, homogeneous, greaselike material.

EXAMPLE 4

A base grease is prepared from 19% glacial acetic acid, 10% tallow fatty acids, 14% of hydrated lime, 1% of phenyl-alpha-naphthyl amine, and 56% of a refined oil of 500 SSU viscosity at 100° F. To this grease is then added 2 wt. percent of a concentrate containing sodium nitrite and the imide formed by reacting tetraethylene pentamine with a styrene-maleic anhydride copolymer having a molecular weight of about 850, 1 mole of tetraethylene pentamine being used for each acid anhydride group in the copolymer. The concentrate is made up of 50 wt. percent of a mineral base oil, 30 wt. percent of the imide and 20 wt. percent of sodium nitrite.

EXAMPLE 5

One wt. percent of the product of Example 2 and 1 wt. percent of the product of Example 3 were added to separate 99% portions of a base grease prepared as described in Example 4. The product in each case was stirred into the base grease and the grease was then milled. The two resulting greases were examined under a microscope and were found to contain no particles larger than 5 microns in diameter. These greases were compared with the base grease in a rust test, using the CRC Technique L–41 described in ASTM–D–1743–60T. This test was carried out by lubricating three separate bearings with the three greases to be tested, running the bearings under a light load and storing them for two weeks at 77° F. and 100% relative humidity. The three bearings were then examined after 14 days. The results of the test were summarized in Table I below:

Table I.—Rust test

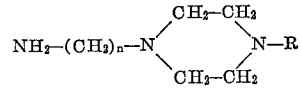
Product:	Rust on Bearing and Cup after 14 days
Base grease (no inhibitor)	Badly rusted; large black spots on cone and cup.
99% above grease+1% Example 2 product	Like original, no rust spots.
99% above grease+1% Example 3 product	Like original, no rust spots.

Although the invention has been described in the foregoing specification with a certain degree of particularity, it will be understood that modifications and variations thereof can be employed without departing from the spirit of the invention or from its scope as defined in the appended claims.

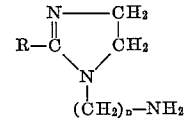
What is claimed is:

1. A lubricant composition comprising a major proportion of a lubricating oil, a thickening amount of a grease thickener, and from 0.1 to 10 wt. percent of a dispersion of sodium nitrite in an imide formed by reaction of a copolymer of styrene and maleic anhydride of from 400 to 3000 molecular weight with an amino compound having from 2 to about 35 carbon atoms and from 2 to 5 nitrogen atoms, at least one of which is in a primary amino group, there being from about 0.5 to 5 parts by weight of the imide per part of sodium nitrite, said amino compound being selected from the group consisting of

alkylene polyamines, N-aminoalkyl piperazines of the formula:



wherein n is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms, polyalkoxydiamines prepared by the reaction of aliphatic amines with alkylene oxides of from 2 to 8 carbon atoms, and amino imidazolines having the formula:



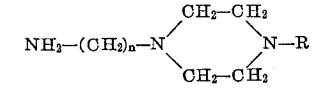
wherein n is about 2 to 6, and R is a C_6 to C_{22} hydrocarbon group.

2. A lubricant composition as defined by claim 1 wherein said amino compound is diethylene triamine.

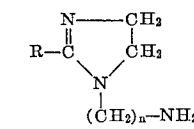
3. A lubricant composition as defined by claim 1 wherein said amino compound is tetraethylene pentamine.

4. A lubricant composition as defined by claim 1 wherein said amino compound is 1-(2-aminoethyl)-2-n-alkenyl-2-imidazoline, said alkenyl being heptadecenyl and heptadecadienyl in about equimolar proportions.

5. A concentrate adapted for addition to a lubricating grease to incorporate sodium nitrite therein, which comprises a mineral lubricating oil base and from 2 to about 70 wt. percent of a dispersion of sodium nitrite in an imide formed by reaction of a copolymer of styrene and maleic anhydride of from 400 to 3000 molecular weight with an amino compound having from 2 to 35 carbon atoms and from 2 to 5 nitrogen atoms, at least one of which is in a primary amino group, there being from about 0.5 to 5 parts by weight of the imide per part of sodium nitrite, said amino compound being selected from the group consisting of alkylene polyamines, N-aminoalkyl piperazines of the formula:



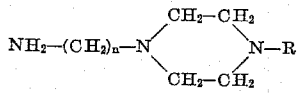
wherein n is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms, polyalkoxydiamines prepared by the reaction of aliphatic amines with alkylene oxides of from 2 to 8 carbon atoms, and amino imidazolines having the formula:



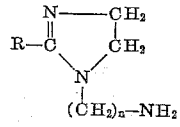
wherein n is about 2 to 6, and R is a C_6 to C_{22} hydrocarbon group.

6. A method of preparing an additive mixture adapted for addition to a lubricating grease to incorporate sodium nitrite therein which comprises mixing together a copolymer of styrene and maleic anhydride of from 400 to 3000 molecular weight and an amino compound having from 2 to about 35 carbon atoms and from 2 to 5 nitrogen atoms, at least one of which is in a primary amino group, the proportion of amino compound to copolymer being such as to react about 0.5 to 2 amino groups per acid anhydride group, adding to said mixture an aqueous solution containing from 10 to 70 wt. percent of sodium nitrite, and heating said mixture for a sufficient time and at a sufficient temperature to drive off the water of said solution and to form an imide between said amino group and said acid anhydride group, the amount of sodium nitrite being present being such as to provide from 0.5 to 5 parts

by weight of imide per part of sodium nitrite, said amino compound being selected from the group consisting of alkylene polyamines, N-aminoalkyl piperazines of the formula:

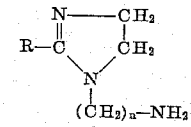


wherein n is a number 1 to 3, and R is hydrogen or an aminoalkyl radical containing 1 to 3 carbon atoms, polyalkoxydiamines prepared by the reaction of aliphatic amines with alkylene oxides of from 2 to 8 carbon atoms, and amino imidazolines having the formula:



wherein n is about 2 to 6, and R is a C_6 to C_{22} hydrocarbon group.

7. The imide obtained by the reaction of a copolymer of styrene and maleic anhydride of from 400 to 3000 molecular weight with an amino imidazoline having the general formula:



wherein n is a number of from 2 to 6 and R is a C_6 to C_{22} hydrocarbon group.

8. The imide as defined by claim 7 wherein the amino imidazoline is 1 - (2-aminoethyl)-2-n-alkenyl-2-imidazoline, said alkenyl being heptadecenyl and heptadecadienyl in about equimolar proportions.

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