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RUST PREVENTIVE PREPARED FROM SODIUM NITRITE AND THE REACTION PRODUCT OF FATTY ACID AND IMIDAZOLINE

Arnold J. Morway, Clark, N.J., assignor to Esso Research and Engineering Company, a corporation of Delaware

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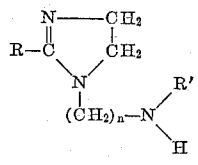
3 Claims. (Cl. 252—18)

This invention relates to rust preventives, their manufacture, and compositions containing said rust preventives. More particularly, the invention relates to a rust preventive additive prepared by dispersing sodium nitrite in the reaction product of an imidazoline and a fatty acid. This rust preventive additive can then be incorporated into lubricants, e.g. lubricating grease, in order to prevent corrosion of the lubricated parts. Or, the rust preventive additive can be added to oils or solvents to form rust preventive compositions for coating metal surfaces.

Sodium nitrite has been recognized as an excellent rust preventive. It has been added to various oils and lubricants to inhibit rusting of metal surfaces by water contamination. For example, it has been added to water repellant grease, since otherwise the repelled water can cause rust of lubricated iron or steel surfaces. More recently, in U.S. Patent No. 2,971,911, it was disclosed that certain oil-soluble amino imidazolines and sodium nitrite, when added to greases containing soaps of substantially saturated hydroxy fatty materials, will result in improved rust prevention since the imidazoline increases the effectiveness of the nitrite. In this patent, it was taught that the sodium nitrite is added to the grease in the form of an aqueous solution. However, if the grease is later heated to evaporate the water and disperse the sodium nitrite in the grease to thereby form a dry grease, the volatilization of the aqueous solution of sodium nitrite in oil, in large scale manufacture of grease, will usually result in agglomerates of sodium nitrite. These agglomerates frequently result in noisy and rough operation of bearings, e.g. roller bearings, and in fact can generally be felt in the grease as abrasive particles.

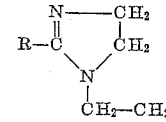
The present invention has as one of its features, an improved method of incorporating an amino imidazoline and nitrite into a grease. More particularly, it has been found that if the amino imidazoline is first reacted with fatty acid in the presence of water, that a soft creamy mayonnaise type gel forms. Then the sodium nitrite can be dispersed in the aqueous gel. The resulting dispersion can then preferably be dried out by heating, while mixing in the presence of a small amount of mineral oil. This will form a grease-like solid stable dispersion of extremely small particle size sodium nitrite. Small quantities of this dispersion can be added to various greases to thereby give excellent rust protection, while the sodium nitrite is in a particle size so that it cannot be seen or felt, and will not cause noise in bearing operation. The above-mentioned dispersion can also be used to form film type rust preventives for direct metal coating, etc.

The amino imidazolines useful in the present invention include those having the general structure:



In the above formula, n is about 2 to 6, preferably 2 to 3; R is a C_6 to C_{22}, preferably a C_{16} to C_{18}, hydrocarbon group, either saturated or unsaturated, but preferably aliphatic; while R′ is either hydrogen or a C_1 to C_{18} alkyl group. Preferably the number of carbon atoms in R is small, R′ is hydrogen and n is a small integer, e.g. 2, in order that the effectiveness of the imidazoline is as great as possible per pound of material. In other words, the effectiveness of the imidazoline in the present invention apparently depends on the ring structure and the terminal amino group, while the number of carbon atoms in the branches merely dilute the effectiveness of the material per pound of imidazoline.

A specific example of imidazoline of the above formula, which was used in the working examples of the invention, was a commercial 1-(2 amino ethyl-2-n-alkenyl-2-imidazoline) having the formula:



wherein R represents heptadecenyl and heptadecadienyl chains in a mol ratio of about 1:1, respectively. This product is sold by Nalco Chemical Company as Nalcamine G-39M.

The fatty acids, which are reacted with the amino imidazoline, include C_2 to C_{36}, prefrably C_2 to C_{18}, and most preferably C_2 to C_4 acid, either saturated or unsaturated, straight chain or branched chain. Those fatty acids of low molecular weight are preferred because they allow a greater proportion of active ingredient and form more stable dispersions. One molar amount of the imidazoline will be reacted with one to two molar amounts of the fatty acid to form the salt reaction product. At least one of the H or R′ of the imidazoline is split off by reaction with the fatty acid, although both the H and R′ may be split off if desired.

The rust preventive additive of the invention will comprise a mixture of (1) the salt reaction product of the amino imidazoline and a fatty acid, and (2) sodium nitrite. This additive, in turn, may be dispersed in oil or water for ease of handling to thereby form concentrates for subsequent mixing into other compositions. Usually, said rust preventive additive will comprise about 0.1 to 10.0 parts by weight of sodium nitrite per one part by weight of the imidazoline-fatty acid reaction product. A preferred rust preventive additive will comprise 0.5 to 2.0 parts of sodium nitrite per one part of the imidazoline-fatty acid reaction product. About 10 to 90 wt. percent of this rust preventive additive can be dispersed in 90 to 10 wt. percent water or oil to form additive concentrates.

The preceding rust preventive additive, or its additive concentrate, can be added to other oleaginous compositions to form final compositions containing about 0.1 to 5.0 wt. percent, preferably 0.5 to 2.0 wt. percent, of the rust preventive additive, said weight percent being based on the weight of the final rust inhibited oleaginous composition. The final oleaginous compositions can be rust preventive compositions containing a volative solvent or a mineral oil base material, such as film type rust preventives or slushing oils, or they can be fluid lubricating oil compositions such as crankcase oils, or they can be lubricating greases, etc.

If the rust preventive additive of the invention is to be used in a film type rust preventive, then the oleaginous base material or solvent may be volatile or non-volatile. Such oleaginous base materials will include Stoddard Solvent, naphthas, gas oil, lubricating oil, petrolatum, etc. Various waxes, e.g. 2 to 10 wt. percent, can be used in the rust preventive composition for the purpose of forming a heavier film on the surface to be protected. The waxes can be crystalline or microcrystalline, synthetic or natural. The most common of these waxes are the

paraffin waxes derived from petroleum. These paraffin waxes can be either normal or isoparaffin. Additional additives can also be contained in the final film type rust preventive composition such as anti-oxidants, metal deactivators, dyes, etc.

The rust preventive additive of the invention can also be incorporated into greases thickened with various thickeners such as: metal salts of C_2 to C_{30} fatty acids, polymeric thickeners (e.g., polymers of C_2 to C_4 monoolefins of 10,000 to 200,000 mol. wt. such as polyethylene), inorganic thickners, (e.g., clay, carbon black, silica gel), etc.

The fatty acid salt thickeners are formed by the neutralization of a fatty acid with a metal base. The fatty acid can be a high molecular weight fatty acid, an intermediate molecular weight fatty acid, or a low molecular weight fatty acid. The metal base will generally be an alkali or alkaline earth metal base. Frequently, mixed metal salts of different molecular weight fatty acids are used. For example, a mixed-salt thickener can contain alkaline earth metal (frequently calcium) salts of 4 to 30 molar proportions of a low molecular weight fatty acid (e.g. acetic acid) per molar proportion of higher fatty acid, e.g. oleic acid or capric acid. These mixed-salt thickeners are generally prepared by coneutralizing the various acids involved with metal base, e.g. lime, in situ in the lubricating oil. The lubricant can then be used as is, if a "cold set" lubricant is desired, or it can be heated to temperatures of about 225° to 550° F. to dehydrate the lubricant. Either solid greases can be formed in the preceding manner, or fluid or semi-fluids can be prepared, depending upon the amount of lubricating oil used.

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

Intermediate molecular weight fatty acids used in preparing metal salts, include those fatty acids containing 7 to 12 carbon atoms per molecule, e.g., capric, lauric, caprylic, nonanoic, etc.

Suitable low molecular weight acids include C_2 to C_6 fatty acids. Acetic acid or its anhydride is preferred.

Various other additives may also be added to the lubricating composition (e.g. 0.1 to 10.0 weight percent each, based on the total weight of the composition). Specific examples of these additives include oxidation inhibitors such as phenyl-alpha-naphthylamine, tackiness agents such as polyisobutylene, stabilizers such as aluminum hydroxy stearate, etc.

The rust preventive additive is preferably prepared as follows:

The imidazoline is dispersed in water, preferably using as little water as necessary in order to completely disperse the imidazoline. Next, the fatty acid is slowly added to the aqueous solution of the imidazoline while stirring. The lower fatty acids containing less than six carbon atoms per molecule are water soluble and can be readily added with no problem. The higher fatty acids, e.g. those containing above six carbon atoms, are water insoluble and are slowly added in flake or granular form. Upon the addition of all the fatty acid to the imidazoline, a soft creamy gel will usually result, into which is stirred granular sodium nitrite. If desired, the sodium nitrite can also be added as an aqueous solution in any concentration, although it is desirable to use the minimum amount of water required. Upon the addition of the sodium nitrite, the composition is then preferably heated to temperatures ranging from about 275° to 335° F. in order to evaporate all the water which may be present and to thereby form a dehydrated gel. If an oil concentrate is desired, then mineral or other inert oil can be stirred into the dehydrated gel, preferably while the gel is still hot. After the addition of mineral oil, the resulting product can be homogenized, if desired, and will constitute a rust inhibitor additive concentrate.

Certain variations in the above procedure can be utilized if desired. For example, it is not always essential to evaporate the water from the mixture of imidazoline-fatty acid-sodium nitrite, depending upon the final end use of the concentrate. If the water containing mixture is added to a batch of hot grease, or during the formation of a grease which is to be subsequently heated, then the water evaporation can take place during the grease-forming step rather than taking place directly in the formation of the additive.

The invention will be further understood by reference to the following examples, which include a preferred embodiment of the invention, and wherein all parts are by weight.

EXAMPLE I

30.5 parts of 1-(2 amino ethyl-2-n-alkenyl-2-imidazoline), Nalcamine G–39M, was dissolved in 30.5 parts of water. While stirring, 8.5 parts of glacial acetic acid was slowly added (a molar amount equal to twice the molar amount of said imidazoline). A mayonnaise type gel resulted, into which was stirred 30.5 parts of granular sodium nitrite. The composition was then heated while stirring to a temperature ranging from about 250° to 300° F. until all the water had volatilized to thereby form a dehydrated gel. 30.5 parts of mineral lubricating oil of 55 SUS viscosity at 210° was then slowly added and thoroughly mixed into the dehydrated gel. After all the mineral oil was added, the resulting product was then homogenized by passing through a Morehouse mill having 0.003" clearance. The resulting product was a smooth soft grease-like material having an ASTM unworked penetration at 77° F. of about 300 mm./10.

EXAMPLE II

A product was prepared according to the method of Example I except that different proportions of ingredients were used. A softer, more fluid gel resulted due to the use of a lesser amount of acetic acid.

EXAMPLE III

31.8 parts of imidazoline was mixed with 31.8 parts of water and 4.6 parts of glacial acetic acid to form a gel. 31.8 parts of granular sodium nitrite was added and dispersed into the gel. A slight degree of heating was applied to obtain a smooth homogeneous composition. The resulting product was a stable emulsion showing no phase separation when stored in a sealed container. However, the water-containing product was somewhat unstable when stored in an open container because of surface crystallization of sodium nitrite because of water evaporation.

The compositions of the products of Examples I to III in parts by weight of ingredients present in the product are summarized in Table I which follows:

Table I

Ingredients (parts by weight)	Examples		
	I	II	III
1-(2 amino ethyl-2-n-alkenyl-2-imidazoline)	30.5	37.7	31.8
Glacial acetic acid	8.5	5.3	4.6
Sodium nitrite	30.5	37.8	31.8
Mineral Lubricating Oil, 55 SUS at 210° F.	30.5	18.9	
Water	0.0	0.0	31.8
Properties: Appearance	Smooth soft solid grease.	Semi-fluid	Stable liquid emulsion.

A series of greases were next prepared using the products of Examples I to III as the rust preventive additives.

EXAMPLE IV

This lubricating grease was prepared as follows:

13.6 parts of hydrated lime, 10 parts of vegetable fatty acid and 58.4 parts of mineral lubricating oil were intimately mixed in a steam jacketed grease kettle. 19.0 parts of glacial acetic acid was slowly added to the mixture, while stirring. The heat of reaction raised the temperature to about 210° F. External heating was then initiated and the temperature of the reaction mass raised to 320° F., where it was held for about two hours to dehydrate the reaction mass. The resulting grease was rapidly cooled to about 200° F. by passing cold water through the kettle jacket. One part of phenyl-alpha-naphthylamine was then added as an oxidation inhibitor. The grease was then cooled to 150° F. where two parts of the product of Example I was added by simple mixing into the grease. The grease was then cooled to 100° F. where it was finished by first passing through a Charlotte mill having a 0.003" clearance and then passing through a Cornell homogenizer for deaeration before packaging.

The vegetable fatty acid used above was iso-oleic acid, which comprises chiefly elaidic acid, with minor amounts of oleic acid (9-octadecenoic acid), and other isomers of oleic acid, e.g. 12-octadecenoic acid, linoleic acid, etc.

EXAMPLE V

A grease was prepared in the same manner as that of Example IV except that the rust preventive additive product of Example II was used in place of the additive product of Example I, and said additive product of Example II was added to the dehydrated grease at 300° F. before cooling said grease.

EXAMPLE VI

A grease was prepared in the same manner as that of Example V. except that the rust preventive additive product of Example III was used.

The compositions of the greases prepared above, and their properties, are summarized in Table II which follows:

Table II

Formulation, (Parts by Weight)	Examples		
	IV	V	VI
Acetic anhydride	16.0	16.0	16.0
Vegetable fatty acid	10.0	10.0	10.0
Hydrated lime	13.6	13.6	13.6
Phenyla-naphthylamine	1.0	1.0	1.0
Product of Example I	2.0		
Product of Example II		2.0	
Product of Example III			2.0
Mineral Lubricating Oil, 55 SUS at 210° F.	58.4	58.4	58.4
Properties:			
Appearance	Excellent	Excellent	Excellent
Dropping Point, ° F	500+	500+	500+
Penetrations 77° F. mm./10:			
Unworked	300	300	300
Worked 60 strokes	320	310	310
Worked 10,000 strokes	320	325	340
14-day Corrosion Test CRC-L-41 Test	None	None	None
Bearing Noise	None	None	None
Lubrication Life [1] in Hours at 250° F. and 10,000 r.p.m.	2,000+	2,000+	2,000+

[1] ABEC—NLGI Spindle Test.

As seen by Table II, the grease containing the rust inhibitor concentrates of the invention, showed no rust in the CRC-L-41 test after 14 days, and showed no noise during operation of a bearing. Specifically, 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. The bearing was then examined for rust.

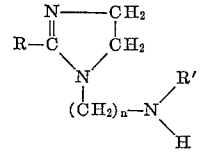
The Bearing Noise test was carried out in a soundproof room, measuring the noise level obtained during operation of a Timken roller bearing.

While the compositions of the invention gave no rust in the CRC-L-41 test, a similar grease containing no rust preventive agent results in bad rusting of the bearing.

EXAMPLE VII

A slushing oil composition was prepared consisting of 0.5 wt. percent of the product of Example I, 5.5 wt. percent paraffin wax and 94.0 wt. percent of a mineral lubricating oil of 55 SUS viscosity at 210° F. This composition was prepared by dispersing the product of Example I into the oil-wax blend at 150° F., followed by homogenizing to obtain a smooth composition. Steel panels were dipped into the composition and hung in a humidity cabinet operating at 120° F. and 98% humidity. No rusting had occurred after 45 days storage in said cabinet. Uncoated steel panels, or steel panels coated only with a blend of said mineral oil and said wax will show severe rusting under similar humidity cabinet conditions.

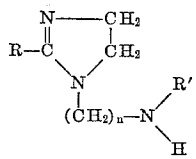
As a further illustration of the invention, Example I can be repeated but using in place of the 1-(2 amino ethyl-2-n-alkenyl-2-imidazoline), an imidazoline of the formula:



where R is an n-octyl group and R′ is an ethyl group.

What is claimed is:

1. A method of preparing a rust preventive additive concentrate containing finely divided sodium nitrite comprising reacting by simple mixing of a molar proportion of imidazoline with 1 to 2 molar proportions of a C_2 to C_{30} fatty acid in the presence of water to form a gel, dispersing sodium nitrite into said gel, heating said gel to volatilize the water present and thereby form a dehydrated gel, and then adding and mixing mineral lubricating oil and cooling the product to thereby form said concentrate as a stable dispersion of small particle size sodium nitrite in the reaction product of said imidazoline and said fatty acid, wherein the amount of sodium nitrite is about 0.1 to 10.0 parts by weight per part by weight of said reaction product, and said oil constitutes 10 to 90 wt. percent of said concentrate, wherein said imidazoline has the general formula

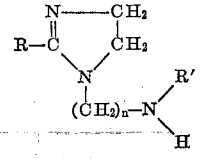


wherein n is an integer of about 2 to 6, R is a C_6 to C_{22} hydrocarbon group and R′ is selected from the group consisting of hydrogen and C_1 to C_{18} alkyl groups.

2. A method according to claim 1, wherein said imidazoline is 1-(2 amino ethyl-2-n-alkenyl-2-imidazoline), and said fatty acid is acetic acid.

3. A method of preparing a concentrate consisting essentially of a rust preventive additive in 10 to 90 wt. percent mineral oil, comprising mixing water, the imidazoline salt which is the reaction product formed by simple mixing of a molar proportion of imidazoline with 1 to 2

molar proportions of a C_2 to C_{30} fatty acid, and sodium nitrite wherein said sodium nitrite is dissolved in said water and the mixture is gelled by said imidazoline salt, and heating to dehydrate said mixture and then adding mineral oil to thereby form said concentrate, wherein the amount of sodium nitrite is about 0.1 to 10.0 parts by weight per part by weight of said reaction product, and wherein said imidazoline has the general formula:



wherein *n* is an integer of about 2 to 6, R is a C_6 to C_{22} hydrocarbon group and R′ is selected from the group consisting of hydrogen and C_1 to C_{18} alkyl group.

References Cited by the Examiner

UNITED STATES PATENTS

2,267,965	12/1941	Wilson	260—309.6
2,355,837	8/1944	Wilson	252—8.8
2,466,517	4/1949	Blair et al.	252—392
2,553,183	5/1951	Caron et al.	44—63
2,648,633	8/1953	Peterson et al.	252—28
2,735,815	2/1956	Morway	252—39
2,846,392	8/1958	Morway et al.	252—40.7 X
2,915,376	12/1959	Raifsnider	252—390
2,971,911	2/1961	Caruso	252—18 X
3,013,968	12/1961	Blake	252—18
3,089,848	5/1963	Morway	252—18

DANIEL E. WYMAN, *Primary Examiner.*

JOSEPH R. LIBERMAN, *Examiner.*