RUSS PREVENTIVE COMPOSITIONS CONTAINING DIAMIDOCARBOXYLIC ACID

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This invention relates to rust preventive oleaginous compositions. More particularly the invention relates to the use of certain nitrogenous corrosion or rust inhibitors in compositions containing predominantly an oleaginous vehicle, and which compositions may become contaminated with water or steam.

The prevention of rust formation is particularly important in the protection of metal surfaces, particularly ferrous surfaces, where such surfaces are to be lubricated in the presence of contaminating moisture. Moisture may enter lubricating systems of land and marine turbine engines, for example, by leakage through steam glands and through water-cooled heat exchangers or simply by condensation from the atmosphere. The presence of rust is injurious because it causes excessive wear of gears and bearing surfaces, and may also clog the hydraulic governor system, which last result may lead to dangerous operating speeds. Furthermore, the presence of rust has been shown to increase the rate of oxidative breakdown of the lubricant. The prevention of rusting is also essential in the moving parts of hydraulic systems generally, such as hydraulic haling machinery, presses, etc. Other important applications of rust preventive compounds are in preservative oils, slushing oils, flushing oils, etc.

A great many materials have been proposed for the prevention of rust formation of metal surfaces, however, relatively few have been applicable in practice for the protection of lubricant systems because most are deleterious to the lubricant, the lubricant system or are disadvantageous in some other way. It has been proposed to add various carboxylic acid amidies to hydrocarbon oils either for rust prevention or in order to improve the film-strength and adhesion to metals. U. S. Patent No. 2,462,358 incorporates an acetocetyl amide having an acyl residue which is of a higher fatty acid or naphthenic acid, such as CnH2n+CONHCH2CHnHCOCH2CHnCOH, for the latter purpose. And U. S. Patent No. 2,403,293 discloses the incorporation of oleic monamide of ethylene diamine or of polyethylene polyamines, purportedly a rustproofing composition. It is claimed in U. S. Patents No. 2,490,744 of December 6, 1949, and No. 2,540,600 of February 6, 1951, that the alkyl succinic anhydride amine reaction product confers rust proofing properties to lubricating oils.

According to the present invention, it has now been found that the corrosive effect of lubricating oils and greases (oleaginous vehicle) upon bearing surfaces, gears and other metallic parts in the presence of water may be prevented by the incorporation in said oleaginous vehicle of a small amount of a class of compounds which are diamidocarboxylic acids and their salts, in which a high molecular weight ofphoric acid residue is bound to an amide nitrogen, substituted also by a carboxyalkyl group and by a carboxyalkyl group. Such compounds, when used in small amounts in lubricating compositions, it has been determined on a scientific basis, effectively prevent the rusting of metal surfaces; particularly those of ferrous metals, upon exposure to water or steam.

These additives moreover prevent rusting without influencing the lubricant action disadvantageously.

The rust prevention composition of this invention consists of major amounts of an oleaginous vehicle and a minor amount of the class of compounds diamidocarboxylic acids and their salts having the empirical formula

\[
R_1-N-(CH_2)_m-CN
\]

where \( R_1 \) represents an aliphatic carboxylic acid residue of C2-C4, or alkyl phosphoryl, alkyl phosphonil, alkyl sulfonyl, alkyl sulfruyl, wherein the alkyl radical has this same number of carbon atoms; where \( n \) and \( m \) represent the integers 1 or 2; where \( R_2 \) and \( R_3 \) respectively represent alkyl or aryl groups or \( H \); and \( X \) represents \( H \) or groups capable of forming salts with the carboxylic acid group, such as ammonium or substituted ammonium groups, e.g. organic amines, and metals, etc.

The higher molecular weight acid in the amide group can be any of the higher fatty acids, either saturated or oleifonic unsaturated, of this chain length, such as from caprylic acid through behenic in the saturated series. Many of these higher saturated and unsaturated fatty acids occur as glycerides in fats and oils in nature or as esters of monohydric alcohols in waxes. But higher molecular weight aliphatic acids within this general class which do not occur naturally, such as the mixed carboxylic acids in oxidized liquid or solid hydrocarbons, can be used. It will be understood that mixed acids can be used of any of these sources, i.e., mixed higher fatty acids, or the synthetic mixed aliphatic acids from hydrocarbon oxidation, or mixtures of each, etc.

The diamidocarboxylic acids and their salts of the present invention can be prepared in a number of ways, e.g., as outlined in Equations A, B, or C below.

Equation A

\[
\begin{align*}
R_1-COCl + NH_2CN & \rightarrow R_1-CN \\
& \text{where } R_1 = \text{an aliphatic carboxylic acid residue of C2-C4,}
\end{align*}
\]

Equation B

\[
\begin{align*}
R_1-COCl + NH_2CONH_2 & \rightarrow R_1-CN \\
& \text{where } R_1 = \text{an aliphatic carboxylic acid residue of C2-C4,}
\end{align*}
\]

Equation C

\[
\begin{align*}
R_1-CN + R_2R_3N & \rightarrow R_1-CN \\
& \text{where } R_1 = \text{an aliphatic carboxylic acid residue of C2-C4,}
\end{align*}
\]

The members of this class of compounds can be used alone in an oleaginous vehicle or solvent. The latter may be termed the lubricating oil or grease when the designation is thought of broadly. When used in an oleaginous vehicle, these compounds should be soluble, miscible or
dispersable in the vehicle. If the diamidocarboxylic acid or its salts are not soluble therein, at least in the concentration added, solubilizers may be added which bring this about; a suitable agent for this purpose is disclosed subsequently. The term “oleaginous vehicle” as used in the specification and claims includes mineral lubricating oils derived from the refinement of petroleum or any of the so-called non-mineral oils, such as animal, vegetable oils, fats, the synthetic polyesters of organic acids, polyisoxanes, polyalkylene glycols, polyolefins, also the rust-proof bases which may be used as the medium of application of rust preventive additive to the metal surface.

Some members of the lubricating oil base will be preferred for specific applications while other members will be preferred for either technical, industrial applications, where rust prevention is the objective. For it is obvious that the type of lubricating oil or grease for such surfaces as machine parts, piston rings, machine guns, light arms, gears, turbine engines, and the moving parts of hydraulic bailing machinery, or presses, metal drums, etc., will vary greatly.

Some members of this class of compounds, namely the diamidocarboxylic acid additives, will be preferred for specific industrial applications, while other members will be preferred for other technical or industrial applications where the aim is to prevent rust formation. As to the selection of the additive, the conditions of use of the finished lubricant and/or the type of oleaginous vehicle will dictate or influence the selection. It can be mentioned here that for use in turbine lubrication, the finished lubricant must permit ready separation of entrained water. It is essential for many reasons, which will not be elaborated upon, that water be easily separable from turbine lubricants by auxiliary oil purification equipment such as settling tanks, filters, blower presses, centrifuges, etc.

The amount of corrosion inhibitor incorporated in the finished lubricating composition may be very small, amounts of the order of 0.0125%–1%, based on the total finished oil lubricant, being sufficient to secure metallic corrosion prevention, more particularly where the surface is ferrous in nature. Greater amounts may be added as dictated by particular requirements and economic consideration.

The rust preventive effectiveness of liquid lubricant compositions may be demonstrated by a simple test developed by Jizman, et al., known as the “Static Water Drop Corrosion Test,” which is described in Industrial and Engineering Chemistry, volume 41, page 137 ff. (1949) and also set out in detail subsequently.

The following examples and test data will illustrate certain embodiments of this invention. But they are not to be construed as limiting the invention.

**EXAMPLE I**

(N-stearoyl)iminodiacetanitrile (36.1 grams) was dispersed in 170 milliliters of water at 65 to 70°C containing 4.4 grams of sodium hydroxide. The temperature of the reaction mixture was gradually raised to 100°C and maintained at this temperature for about 2 hours until substantially 0.1 mole of ammonia gas was evolved and swept out through the apparatus by a stream of nitrogen gas. The reaction mixture was then cooled to 20°C and neutralized with 6 N hydrochloric acid. The precipitate was formed, filtered and washed thoroughly with water. After drying, 40.0 grams of a light tan powder were obtained. This melted at 134 to 139°C and had a neutralization value of 389. The neutralization equivalent weight for (N-stearoyl) (N-carbamylmethyl) glycine is 398. Recrystallization from an isopropylacetate-methanol mixture yielded pure (N-stearoyl) (N-carbamylmethyl) glycine melting at 148 to 149°C.

The product described in the example was tested for its rust preventive properties by dissolving it in a solvent refined and filtered non-additive turbine grade lubricating mineral oil of 150 Saybolt Universal Seconds viscosity at 100°F. and subsequently testing these oil solutions by the “Static Water Drop Corrosion Test” described after Example II.

**EXAMPLE II**

31.7 grams of (N-lauroyl)iminodiacetanitrile was dispersed in 250 milliliters of water containing 4.4 grams of sodium hydroxide warmed to 60°C. The reaction mixture was stirred and heated at 95°C for two hours and twenty-five minutes until substantially 0.1 mole of evolved ammonia had been swept out of the reaction mixture by a stream of nitrogen gas. After cooling the reaction mixture to 35°C it was made acid to pH 2.0 with 6 N sulfuric acid. The precipitate which formed was filtered, washed with water and dried to a constant weight of 32.5 grams. On recrystallization from ethyl alcohol the purified (N-lauroyl) (N-carbamylmethyl) glycine melted at 148.5 to 149.5°C. It had a neutralization equivalent weight of 332. The theoretical neutralization equivalent weight of (N-lauroyl) (N-carbamylmethyl) glycine is 314.

The respective products described in the example were tested for their rust preventive properties by dissolving each in a solvent-refined and filtered non-additive turbine-grade lubricating mineral oil of 150 Saybolt Universal Seconds viscosity at 100°F. and subsequently testing these oil solutions by the “Static Water Drop Corrosion Test” described above. Briefly, the test consists essentially of observing rusting at 14°F. in the presence of liquid water in the dipole of a triangular cold-rolled steel specimen immersed in the test oil. An effective rust preventive oil will prevent rusting for several days while straight mineral oils permit rusting to occur within 2 hours of test.

Solubilization of these diamidocarboxylic acids was effected by the addition of a solubilization agent which per se in oil solution had little, if any, rust preventive properties. The agent used was “Primene JMR,” a commercially available primary, aliphatic amine, which has a tertiary-alkylamine structure, the tertiary groups having from 18 to 24 carbon atoms. It is marketed by Rohm and Haas Company.

The results of these tests are given in Table I.

<table>
<thead>
<tr>
<th>Additive</th>
<th>Example No. (A)</th>
<th>WT. Per Cent Primene JMR</th>
<th>Primene JMR</th>
<th>“Static Water Drop Corrosion Test” Time to Rust (Hours)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(N-stearoyl)iminodiacetanitrile</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Less than 16.</td>
</tr>
<tr>
<td>(N-stearoyl)iminodiacetanitrile</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Less than 2.</td>
</tr>
<tr>
<td>(N-stearoyl)iminodiacetanitrile</td>
<td>None</td>
<td>None</td>
<td>None</td>
<td>Less than 2.</td>
</tr>
</tbody>
</table>

1 **Primene JMR** is a mixture of highly branched, aliphatic primary amines having the tertiary-alkylamine structure in which the primary amino nitrogen is directly attached to a tertiary carbon atom; it is composed principally of amines from eighteen to twenty-four carbon atoms and the predominant portion may be represented by the formula (N-lauroyl)-alkylamine. It contains about 8-10% non-amine material. It is a non-viscous liquid, colorless to straw colored, insoluble in water and does not disperse water to an appreciable extent. It exhibits solubility in hydrocarbon solvents and glycerol, diethylene glycol, and in other organic liquids previously referred to under the term “oleaginous vehicles”. Additional physical properties are:

**Physical Properties**

- **Molecular Weight**: Generally 250-350.
- **Refractive Index**: 58.5° C.
- **Refractive Index**: 100°C.
- **Refractive Index**: 1.495.
- **Refractive Index**: 5495°C. 564°C.
- **Refractive Index**: 278-340°C.

**Rust Preventive Effectiveness**

It is evident that the rust preventive effectiveness of...
lubricating oil solutions of the diamidocarboxylic acids is much improved over the base oil alone or with the solubilizer in it. It is also evident that the diamido-
carboxylic acids are qualitatively superior in rust pre-
ventive effectiveness than a typical high molecular weight
fatty acid such as stearic acid.

Having disclosed the nature of our invention and the
manner in which it may be practiced, what we claim and
desire to protect by Letters Patent are the following:

1. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
an oleaginous vehicle and a diamidocarboxylic acid
having the following empirical formula:

$$R_1\text{CONH}\left(CH_2\text{COOH}\right)$$

where $R_1$ represents an aliphatic carboxylic acid residue
of C$_n$-C$_m$, where $n$ and $m$ each represents integers 1-2,
and $X$ represents hydrogen and groups capable of forming
salts with the carboxylic acid group, said diamido-
carboxylic acid being present in said oleaginous composition
in minor amounts, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared to the check.

2. A rust-inhibited oil composition adapted for use in
the presence of water, in systems containing metal suscep-
tible of corrosion by said water, comprising a hydro-
carbon oil and a diamido carboxylic acid having the
following empirical formula:

$$R_1\text{CONH}\left(CH_2\text{COOH}\right)$$

where $R_1$ represents an aliphatic carboxylic acid residue
of C$_n$-C$_m$, where $n$ and $m$ each represents integers 1-2,
and $X$ represents hydrogen and groups capable of forming
salts with the carboxylic acid group, said diamido-
carboxylic acid being present in said oil composition in
minor amounts, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared to the check.

3. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
an oleaginous vehicle and a diamidocarboxylic acid hav-
ing the following empirical formula:

$$R_1\text{CONH}\left(CH_2\text{COOH}\right)$$

where $R_1$ represents an aliphatic carboxylic acid residue
of C$_n$-C$_m$, where $n$ and $m$ each represents integers 1-2,
and $X$ represents hydrogen and groups capable of forming
salts with the carboxylic acid group, said diamido-
carboxylic acid being present in said oleaginous composi-
tion in minor amounts, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared to the check, and alkyl primary amines having
18-24 carbon atoms in sufficient amount to solubilize
said diamidocarboxylic acid, in the oleaginous vehicle,
the said alkyl amines being soluble in the oleaginous
vehicle but insoluble in water.

4. A rust preventive oil composition adapted for use
in the presence of water, in systems containing metal sus-
ceptible of corrosion by said water, comprising a
hydrocarbon oil and a diamidocarboxylic acid having the
following empirical formula:

$$\left(CH_2\text{CONH}\right)$$

where $R_1$ represents an aliphatic carboxylic acid residue
of C$_n$-C$_m$, where $n$ and $m$ each represents integers 1-2,
and $X$ represents hydrogen and groups capable of forming
salts with the carboxylic acid group, said diamido-
carboxylic acid being present in said oil composition in
minor amounts, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared to the check, and alkyl primary amines having
18-24 carbon atoms in sufficient amount to solubilize said
diamidocarboxylic acid, in the hydrocarbon oil, the said
alkyl amines being soluble in hydrocarbon oil but insolu-
ble in water.

5. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
an oleaginous vehicle and a minor amount of (N-
stearoyl) (N-carbamylmethyl) glycine, as little as a frac-
tion of 1% to amounts greater than 1% but in sufficient
quantity to inhibit the corrosion of said metal to a great
degree when compared with the check.

6. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
an oleaginous vehicle and a minor amount of (N-
lauroyl) (N-carbamylmethyl) glycine, as little as a frac-
tion of 1% to amounts greater than 1% but in sufficient
quantity to inhibit the corrosion of said metal to a great
degree when compared with the check.

7. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
a mineral oil and a minor amount of (N-stearoyl) (N-
carbamylmethyl) glycine, as little as a fraction of 1% to
amounts greater than 1%, but in sufficient quantity to inhibit the corrosion of said metal to a great degree when
compared with the check.

8. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
a mineral oil, a minor amount of (N-lauroyl) (N-carbamylmethyl)
glycine, as little as a fraction of 1% to amounts greater than 1%, but in sufficient quantity to inhibit the corrosion of said metal to a great degree when
compared with the check.

9. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible of corrosion by said water, comprising
an oleaginous vehicle, a minor amount of (N-stearoyl)
(N-carbamylmethyl) glycine, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared with the check, and alkyl primary amines having
18-24 carbon atoms in sufficient amount to solubilize said
acyl (N-carbamylmethyl) glycine, in the oleaginous
vehicle, the said alkyl amines being soluble in the oleaginous
vehicle but insoluble in water.

10. A rust preventive oleaginous composition adapted
for use in the presence of water, in systems containing
metal susceptible to corrosion by said water, comprising
an oleaginous vehicle, a minor amount of (N-lauroyl)
(N-carbamylmethyl) glycine, as little as a fraction of 1% to
amounts greater than 1% but in sufficient quantity to inhibit corrosion of said metal to a great degree when
compared with the check, and alkyl primary amines having
18-24 carbon atoms in sufficient amount to solubilize said
acyl (N-carbamylmethyl) glycine, in the oleaginous
vehicle, the said alkyl amines being soluble in the oleaginous
vehicle but insoluble in water.
11. A rust preventive oil composition adapted for use in the presence of water, in systems containing metal susceptible to corrosion by said water, comprising a mineral oil, a minor amount of (N-stearoyl) (N-carbamylmethyl) glycine, as little as a fraction of 1% to amounts greater than 1% but in a sufficient quantity to inhibit corrosion of said metal to a great degree as compared with the check, and alkyl primary amines having 18–24 carbon atoms in sufficient amount to solubilize said acyl (N-carbamylmethyl) glycine, in the mineral oil, the said alkyl amines being soluble in the mineral oil but insoluble in water.

12. A rust preventive oil composition adapted for use in the presence of water, in systems containing metal susceptible to corrosion by said water, comprising a mineral oil, a minor amount of (N-lauroyl) (N-carbamylmethyl) glycine, as little as a fraction of 1% to amounts greater than 1% but in a sufficient quantity to inhibit corrosion of said metal to a great degree as compared with the check, and alkyl primary amines having 18–24 carbon atoms in sufficient amount to solubilize said acyl (N-carbamylmethyl) glycine, in the mineral oil, the said alkyl amines being soluble in the mineral oil but insoluble in water.

References Cited in the file of this patent

UNITED STATES PATENTS

2,462,358 Caldwell .......................... Feb. 22, 1949
2,568,876 White et al. ...................... Sept. 25, 1951