United States Patent Office 2,976,179
Patented Mar. 21, 1961

2,976,179

RUST PREVENTIVES

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No Drawing. Filed Aug. 23, 1954, Ser. No. 451,686

1 Claim. (Cl. 117—127)

This invention relates to rust prevention and more particularly relates to a new class of chemical compounds which are useful as rust inhibitors, to rust preventive compositions containing such compounds and to methods for preventing the rusting of metals by applying such compositions to the metal surfaces. Still more particularly the novel rust inhibitors of this invention are the oil soluble salts of carboxylic acids and triethylene tetramine.

In the prior art numerous compounds have been suggested as inhibitors for preventing corrosion of ferrous metals. Among these compounds are the soaps or salts of organic amines and fatty acids, the amine portions of these compounds being derived from mono, di or tri alkyl, cyclo alkyl, or alkylated aromatic amines or their hydroxy derivatives. Although these amine compounds of the prior art may have provided adequate protection of metal surfaces in certain instances, it has been found that they do not provide effective protection over extended periods of time nor do they provide effective protection when the conditions of corrosion or rusting are severe.

A new class of compounds have now been found which are outstanding rust inhibitors and which are substantially superior to the aforementioned rust inhibitors of the prior art. The novel compounds of this invention are the oil soluble salts of carboxylic acids and triethylene tetramine. These new compounds may be used alone as rust preventives, if desired, but it is generally preferred to use them in rust preventive compositions containing a major proportion of an organic solvent in which the salts are soluble, such as a lubricating oil or a blend of a film forming material and a volatile organic solvent. When the rust inhibitors of this invention are so used they are preferably incorporated into the compositions in concentrations of about 0.01 to 30.0% by weight, based on the total composition, and more preferably about 1.0 to 10.0% by weight, based on the total composition.

In one specific application the rust inhibitors of this invention are dissolved in an oil medium. In this form they may be used to prevent the rusting of inaccessible systems, or to prevent the rusting of metal parts during processing or storage. Such compositions may also be advantageously employed in equipment which requires lubrication in addition to protection from corrosion such as circulating oil and hydraulic systems, bearings, instruments, internal combustion engines, etc. A particular advantage of the inhibitors of the invention is that in addition to being excellent rust preventives, the compounds are ashless and thus do not form metallic deposits in internal combustion engines. Also because the rust inhibitors of this invention are definite chemical compounds, the salts are more uniform than certain conventional inhibitors such as petroleum sulfonates, for example.

In another specific application, the rust inhibitors of this invention are incorporated into volatile solvent-type

rust preventive compositions. These compositions will generally also contain a conventional film-forming material such as a wax, resin, oil, petrolatum, etc. When such compositions are applied to metal surfaces the volatile solvent evaporates in a short time and leaves a thin film that inhibits rusting and corrosion of the metal. In this form the rust inhibitors are particularly useful for protecting various metal parts during semi-sheltered or indoor exposure to moist atmosphere. For example, finished machined parts, such as ball bearing assemblies, or component parts of semi-finished pieces may be protected during processing and/or storage prior to assembly. The rust preventing films supplied by the volatile solvent-type rust preventive compositions of this invention may be made extremely thin if desired and thus need not be removed between operations. A thicker coat of another rust preventive may be applied over this thin film if longer protection is required or the film-forming material of the first-mentioned composition may be modified to form a thicker and longer-lasting film containing the rust inhibitor of the present invention.

Triethylene tetramine which is employed to form the salts of this invention is a well-known chemical compound having the formula

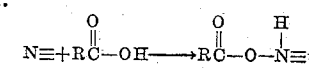
$$NH_2CH_2CH_2NHCH_2CH_2NHCH_2CH_2NH_2$$

This compound is reacted with 1 to 4 mols of a carboxylic acid to form the salts of this invention which are useful as rust inhibitors. In order to be effective rust inhibitors it is essential that the salt formed from the triethylene tetramine and the carboxylic acid be oil soluble as well as essentially water insoluble.

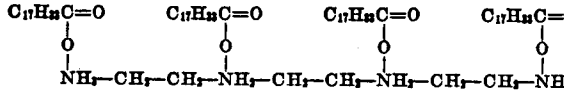
The triethylene tetramine salt is formed by the direct addition of the carboxylic acid to the triethylene tetramine. The reaction, which is immediate, is accomplished by simply mixing the two reactants together at or slightly above room temperature, preferably at a temperature in the range of about 70° to 100° F. When mixing the reactants together at room temperature, for example, the heat of reaction will cause the reaction mixture to rise to a temperature in the range of about 130° to 170° F. Care thus should be taken to prevent the temperature from rising much above about 200° F. in order to prevent water from being driven off from the reaction mixture as in such event an amide would be formed in the reaction rather than the salt of the present invention.

The carboxylic acids employed in this invention may be aliphatic or cycloaliphatic and preferably contain 6 to 24 carbon atoms per molecule. Such acids may contain straight or branched chains and may be saturated or unsaturated and may contain one, two or more carboxyl groups. Particularly suitable acids which may be employed in the formation of the salts of the present invention are lauric palmitic, stearic, oleic, linoleic, ricinoleic, eleomargic, erucic, behenic, arachidic, lignoceric, and other fatty acids also the naphthenic acids, as well as carboxylic acids derived by the oxidation of petroleum products or of aldehydes produced from olefins, carbon monoxide and hydrogen, and from olefins, carbon monoxide and water. Acids derived from naturally occurring products such as tall oil, castor oil, soybean oil, linseed oil, olive oil, tung oil, rapeseed oil, menhaden oil and the like, may also conveniently be employed. The preferred carboxylic acids are the fatty acids containing 6 to 24 carbon atoms per molecule, oleic acid being particularly preferred.

The reaction between a fatty acid, for example, and the triethylene tetramine may be represented by the following equation:



where N≡ represents any one of the four trivalent nitrogen atoms in triethylene tetramine and RCOOH represents a fatty acid. It will be seen that the acid is added directly to the amine and that no water is split out. Since triethylene tetramine has four nitrogen atoms it is possible to add one, two, three or four mols of acid to one mol of triethylene tetramine. Thus, to form a particular desired compound, the appropriate stoichiometric quantity of acid is reacted with triethylene tetramine. This may be illustrated by the salts of oleic acid and triethylene tetramine. By reacting one mol of oleic acid with one mol of triethylene tetramine, triethylene tetramine monooleate is formed; by reacting two mols of oleic acid with one mol of triethylene tetramine, triethylene tetramine dioleate is formed; by reacting 3 mols of oleic acid with 1 mol of triethylene tetramine, triethylene tetramine trioleate is formed; and by reacting four mols of oleic acid with one mol of triethylene tetramine, triethylene tetramine tetraoleate is formed. It is probable that when one, two or three mols of acid are reacted with one mol of triethylene tetramine that a mixture of isomers is formed. The trioleate and especially the tetraoleate are preferred compounds of this invention. The tetraoleate, for example, may be represented by the following structural formula:



As has been stated previously it is preferred to incorporate the rust inhibitors of this invention into rust preventive compositions containing a major proportion of an organic solvent. There are several reasons for this. First it is advisable from an economic standpoint to use a relatively inexpensive film-forming material such as an oil, wax, resin, etc. as the major proportion of the protective film, and secondly, a great many different compositions having a wide variety of film-forming properties may be prepared by properly selecting the organic solvent and/or film-forming material used in the composition. It will be understood, however, that if desired the salts of this invention may be employed alone as a rust preventive material.

A wide variety of organic solvents may be employed in the rust preventive compositions of the present invention. In one respect these organic solvents may be classified into two general categories, namely (1) the low boiling solvents which are used in the volatile solvent type compositions and (2) the relatively high boiling solvents which are used in the oil-type compositions, such as the lubricating oil compositions.

The relatively high boiling solvents which are utilized for formulating oil-type rust preventive compositions and especially those which may be used partially or wholly for lubrication are preferably lubricating oil base stocks having an S.S.U. viscosity at 210° F. in the range of about 25 to 500 seconds, preferably in the range of about 35 to 200 seconds. These lubricating oil base stocks may be straight mineral lubricating oils or distillates derived from paraffinic, naphthenic, asphaltic or mixed base crudes, or if desired, various blended oils may be employed as well as residuals, particularly those from which asphaltic constituents have been removed. These mineral oils may be refined by conventional methods using acid, alkali, and/or clay or other agents such as aluminum chloride, or they may be extracted oils produced, for example, by solvent extraction with solvents of the type of phenol, sulfur dioxide, furfural, dichloroethyl ether, nitrobenzene, crotonaldehyde, etc.

Hydrogenated oils or white oils may also be employed as well as synthetic oils prepared, for example, by the polymerization of olefins or by the reaction of oxides of carbon with hydrogen or by the hydrogenation of coal or its products. Other synthetic oils which may be employed include esters, complex esters, alkyl silicates, carbonates, mercaptals, formals and the like. In certain instances cracking coil tar fractions and coal tar or shale oil distillates may also be used. Also, for special applications, animal, vegetable or fish oils, or their hydrogenated or voltolized products, may be employed, either alone or in admixture with other oils.

In addition to the rust inhibitors of the present invention which may be added to the oil base stocks described above, other agents may also be used such as dyes, pour depressors, heat thickened fatty oils, sulfurized fatty oils, organo-metallic compounds, metallic or other soaps, sludge dispersers, antioxidants, thickeners, viscosity index improvers, other corrosion inhibitors, oiliness agents, resins, olefin polymers, voltolized fatty oils or fats, voltolized mineral oils, and/or voltolized waxes and colloidal solids such as graphite or zinc oxide, etc. The particular selection of these agents and the oil base stock will be apparent to those skilled in the art.

The low boiling organic solvents employed in the volatile solvent-type compositions preferably have a boiling range between about 150 to 650° F. Examples of these volatile solvents include petroleum solvent naphthas, kerosene, mineral spirits, light spindle oil, petroleum ethers, mineral seal oil, petroleum derived octane, isooctane, dodecane, toluene, benzene, hexane, heptane, cycloparaffins, e.g. cyclohexane, methyl cyclohexane, etc. and the like.

When the compounds of this invention are employed in volatile solvent-type rust preventive compositions it is preferred to also include in these compositions certain conventional film-forming materials such as rosin, petroleum or coal-tar resins, natural or petroleum waxes, degras, petrolatum, asphalt, heavy mineral oils, etc. or combinations of these. Preferred compositions contain about 2 to 70%, and more preferably about 5 to 25% by weight, based on the total composition, of such film-forming materials. These conventional film-forming materials are well known in the art. The petroleum resins, for example, which are obtained by propane precipitation of Pennsylvania or Mid-Continent base oils are adhesive and tacky in nature and adhere exceedingly well to metal surfaces when applied thereto in volatile solvents. The method of recovering these petroleum resins from crude oils is described in the prior art, such as in U.S. Patents 2,143,872, 2,143,882, etc. and involves the dilution of mineral oil residues with propane, or similar light hydrocarbon, which dissolves the paraffinic constituents and separates the resinous materials. These resins have a viscosity generally of 1,000 to 4,000 seconds S.S.U. at 210° F. or higher. The petroleum waxes generally have a melting point in the range of about 110° to 210° F. and are obtained by dewaxing lubricating oil stocks. The utilization of these particular film-forming materials disclosed above in the rust preventive compositions of the present invention will be apparent to those skilled in the art.

After the evaporation of the volatile solvent, the film or coating remaining should contain at least about 0.01% by weight of the rust inhibitor of the present invention. However, if desired the film may contain up to 100% by weight of the rust inhibitors of this invention.

In addition to the rust inhibitors of the present invention, the volatile organic solvent and the conventional film-forming materials, the volatile solvent-type rust preventive compositions of this invention may also include additional ingredients as will be evident to those skilled in the art. Thus other corrosion inhibitors such as sodium phosphite, sodium nitrite, sodium benzoate, sorbitan monooleate, lecithin, etc. as well as dyes, oxidation inhibitors and the like may be incorporated into the volatile solvent-type rust preventive compositions of this invention in minor proportions without departing from the spirit thereof.

Besides being employed in compositions having primary utility as rust preventive compositions, it will be understood that the rust inhibitors of the present invention may be added to various other products such as gasolines, kerosenes, fuel oils, diesel fuels, lubricating oils, transformer oils, flushing oils, greases, etc., in order to inhibit rusting of metal surfaces which contact such products during their use.

The following examples of the present invention are presented in order to set forth the invention in greater detail as well as to show the superiority of the novel compounds of this invention over certain prior art compounds, although it will be understood that it is not intended that the invention be limited in any way by these examples.

EXAMPLE 1.—OIL-TYPE RUST PREVENTIVE COMPOSITIONS

The following oil-type rust preventive compositions were prepared. Each composition consisted of 3% by weight of the stated inhibitor and 97% by weight of a naphthenic-type mineral oil having an SSU viscosity at 210° F. of 40 seconds.

Part I.—Compositions containing rust inhibitors of the present invention

Composition A.—This composition contained triethylene tetramine monooleate as a rust inhibitor. The monooleate was prepared by adding 146.2 grams (one mol) of triethylene tetramine to 282.5 grams (one mol) of oleic acid at 77° F. with constant stirring. The reaction was immediate and the temperature rose to 143° F. The product was a light yellow fluid.

Composition B.—This composition contained triethylene tetramine dioleate as a rust inhibitor. The dioleate was prepared by adding one mol of triethylene tetramine to two mols of oleic acid at 77° F. with constant stirring. Reaction was immediate and the temperature rose to 164° F. The resulting product was a light yellow paste.

Composition C.—This composition contained triethylene tetramine trioleate as a rust inhibitor. The trioleate was prepared by adding one mol of triethylene tetramine to three mols of oleic acid at 77° F. with constant stirring. Reaction was immediate and the temperature rose to 147° F. The product resembled a yellow grease.

Composition D.—This composition contained triethylene tetramine tetraoleate as a rust inhibitor. The tetraoleate was prepared by adding one mol of triethylene tetramine to four mols of oleic acid at 77° F. with constant stirring. Reaction was immediate and the temperature rose to 137° F. The product was orange and semi-fluid.

Part II.—Compositions containing other amine salts as rust inhibitors

These compositions contained 3% by weight of the following amine salts:

Composition	Amine Salt
E	Tertiary octylamine oleate.
F	Tri-ethanol amine oleate.
G	Tributylamine oleate.
H	Dibutylamine oleate.

Each of the above compositions was then evaluated in the fog cabinet developed by the Naval Research Laboratory. This cabinet is used to determine the rust-inhibiting properties of non-aqueous fluids, compositions and greases. It is described in Method 5312 of Federal Specification VV-L-791E. In this test distilled water is atomized in a chamber maintained at 95° F. Sand-blasted steel panels (2" x 4") were immersed in the test blends for one minute, removed and allowed to drain for two hours. They were then placed in the fog cabinet and examined periodically for signs of rust. This test is known to give results comparable to those of the JAN-H-792 humidity cabinet in one-sixth to one-ninth the time required for the latter test.

The following results were obtained in these tests:

TABLE I.—RESULTS OF FOG CABINET TESTS

Composition [1]	Amount of Rust After Fog Cabinet Exposure for [2]—				
	15 Min.	2 Hours	4 Hours	20 Hours	44 Hours
Base Oil ..... percent	100				
A ..... do	None		None	Trace	100
B ..... do	None		None	None	Trace
C ..... do	None		None	None	None
D ..... do	None		None	None	None
E ..... do	None	None	None	95	
F ..... do	None	None	10	100	
G ..... do	None		None	100	
H ..... do	None	None	None	90	

[1] Compositions A–H contain 3% by weight of rust inhibitor.
[2] Average of two tests.

It will be seen from the test results shown in Table I that the compounds of the present invention (Compositions A–D) were substantially superior to the other amine salts (Compositions E–H). More specifically it will be seen that all of the metal samples coated with the compositions containing these other amine salt rust inhibitors showed substantial rusting after a 20-hour period. On the other hand, the metal samples coated with the compositions containing the rust inhibitors of the present invention showed no substantial rusting and in fact the dioleate, trioleate and tetraoleate compounds showed no rusting at all. The test results at 44 hours indicate the outstanding rust inhibiting properties of the trioleate and tetraoleate compounds of the present invention as even under these severe test conditions the metal samples coated with the compositions containing these two compounds of the present invention showed no evidence of rusting.

EXAMPLE II.—VOLATILE SOLVENT TYPE RUST PREVENTIVE COMPOSITIONS

The following compositions were prepared and were evaluated for rust prevention:

Ingredient	Weight Percent		
	Composition I	Composition II	Composition III
Triethylene tetramine tetraoleate [1]			5.0
Heavy mineral oil [2]		10.0	10.0
Wax [3]	10.0	10.0	5.0
Volatile Solvent [4]	90.0	80.0	80.0
	100.0	100.0	100.0

[1] Prepared as described in Example I (Composition D).
[2] A heavy mineral oil having an SSU viscosity of 200 seconds at 210° F.
[3] A scale wax having an oil content of about 1% and a melting point of about 132° F. obtained by dewaxing a mineral oil distillate.
[4] A petroleum distillate having a boiling range of about 315 to 403° F.

These compositions were evaluated in the humidity cabinet described in Federal Specification JAN-H-792. This cabinet is the most widely used laboratory test for evaluating rust preventives. Sandblasted steel panels (2" x 4") were immersed in the blend of one minute, removed and allowed to dry for 24 hours at 77° F. They were then placed in the humidity cabinet and examined periodically for signs of rust.

The following results were obtained in these tests:

TABLE II.—RESULTS OF JAN-H-792 HUMIDITY CABINET LIFE

Composition:	Cabinet life, hours [1]
I	1
II	1
III	900+

[1] Average of two tests.

The above tests indicate that volatile solvent-type rust preventive compositions containing the compounds of this invention, and particularly the tetraoleate compound, exhibit outstanding rust prevention properties.

What is claimed is:

A method for inhibiting the rusting of a metal which comprises coating the surface of said metal with an oil type rust preventive composition containing as the essential rust inhibitor 0.01 to 30 weight percent of a salt selected from the group consisting of triethylene tetramine trioleate, and triethylene tetramine tetraoleate.

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