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UNITED STATES PATENT OFFICE

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METHOD FOR INHIBITING CORROSION OF FERROUS METAL

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7 Claims. (Cl. 117—134)

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The present invention relates to the prevention of rusting of metal surfaces, and more particularly, to compositions containing certain rust-preventives, adaptable to inhibit rusting of metals, particularly ferrous metals, as for example, the surfaces of machine parts, piston rings, light arms, gears, the inside of steel drums, and the like, upon exposure to humid atmospheres or other atmospheres corrosive to metals.

Generally speaking, the rust-inhibitors employed by the present invention comprise esters, such as obtained by esterification of tertiary alkylol amines with organic acids, preferably the fatty acids. As rust inhibitors these esters may be employed per se, in mixtures of such esters, or as additives to suitable solvent vehicles therefor to provide compositions adapted for treating metals to inhibit rusting thereof when exposed to corrosive atmospheres or other similar conditions corrosive to metal. The solvent vehicles to which the rust-inhibitors are added to provide rust-preventive compositions, in accordance with the present invention, may comprise oils, particularly of the relatively non-volatile type, such as a hydrocarbon lubricating oil, greases, petrolatums, other hydrocarbon or non-hydrocarbon substances, and the like. Generally, such rust-preventive compositions comprise a minor proportion of rust inhibitor and a major proportion of solvent vehicle. Accordingly, when the rust inhibitors of the present invention are employed as additives to lubricating vehicles, such as lubricating oils, the rust-preventive composition may be employed to serve a dual capacity; that is, the lubrication of and prevention of rust-formation on the interior parts of internal combustion engines or other mechanisms.

In my practice of the present invention, the rust inhibitors are provided by esterifying tertiary alkylol amines with organic acids, particularly those acids containing at least about four to about thirty carbon atoms, and more preferably, about eight to about twenty carbon atoms. Accordingly, I prefer to employ organic acids in the range of stearic, oleic, lauric, and the like for esterification with tertiary alkylol amines to provide the rust inhibitors of the present invention, as the presence of such long-chain hydrocarbon radicals in the ester provides for more effective solubility characteristics of the ester in commonly employed vehicles, such as mineral oils, and the like, in providing rust-preventive compositions. With further reference to the organic acids which may be employed, the present invention preferably embodies the use of fatty

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acids which are substantially uniform in chain structure and chain length, such as the higher fatty acids generally obtained by hydrolysis of oils and fats, as use of such acids generally provides a more uniform product when esterified with tertiary alkylol amines, as compared to carboxylic products resulting from acid oxidation of paraffin hydrocarbons.

In providing the rust inhibitors of the present invention by esterification of organic acids with tertiary alkylol amines, the amines employed are tertiary substituted amines having at least one of the substituents, attached to the nitrogen, represented by an alkylol group. Thus, particularly suitable amines of this type include tertiary amines containing from one to three alkylol groups. The reaction illustrating the esterification of organic acids with tertiary alkylol amines providing esters found particularly effective as rust inhibitors for metals is typified by the following equation directed specifically to preparation of B(N-diethyl) aminoethyl stearate, one of the preferred embodiments of the rust inhibitors of the present invention:

$$(C_2H_5)_2NCH_2CH_2OH + C_{17}H_{35}COOH \longrightarrow$$

diethylaminoethanol — stearic acid

$$(C_2H_5)_2NCH_2CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35} + H_2O$$

B(N-diethyl)aminoethyl stearate

diethylaminoethanol stearic acid B(N-diethyl)-aminoethyl stearate.

In a similar manner, other particularly effective rust inhibitors may be prepared, as for example, esters of stearic acid and triethanolamine having the formulas:

$$(C_{17}H_{35}-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2)_2N-C_2H_4OH$$

and

$$(C_{17}H_{35}-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2)_3N$$

and esters of oleic acid having the formulas:

$$C_{17}H_{33}-\overset{\overset{O}{\|}}{C}-O-CH_2CH_2N(C_4H_9)_2$$

and

$$C_{17}H_{33}-\overset{\overset{O}{|}}{C}-O-CH_2CH_2N(CH_3)_2$$

The tertiary alkylol amines, such as hereinbefore referred to as suitable for use in providing the rust inhibitors of the present invention, when employed per se or in mixtures thereof, have

relatively little, if any, effectiveness in prevention of rusting of metal surfaces, whereas, the esters provided by reacting organic acids with the tertiary alkylol amines exhibit excellent effectiveness in preventing rusting of metals. Furthermore, the esters exhibiting the rust-preventive properties, when employed in suitable solvent vehicles therefor, such as mineral oils, and the like, provide rust-preventive compositions that have excellent stability due to the compatible solubility characteristics of the esters.

The rust inhibitors of the present invention may be employed as such for prevention of rusting of metals, in which case the rust inhibitors may be applied in any suitable manner, as a coating on the surface of the metal to be protected. However, for purposes such as economy and ease of application, it is preferred to employ the rust inhibitors as additives to suitable vehicles therefor, including oils, such as hydrocarbon lubricating oils, other hydrocarbon or nonhydrocarbon substance, petrolatum, and the like. Generally, such compositions comprise a minor proportion of the rust inhibiting ingredients, or mixtures thereof, and a major proportion of solvent vehicle for the rust inhibitor. Such compositions when employed for rust prevention of metals may be applied to the metal surface in any suitable manner to provide a coating thereon and effectively inhibit the rusting of the metal. Furthermore, when the rust inhibitors of the present invention are employed in lubricating oils, such as for lubricating the interior parts of internal combustion engines, the presence of the rust inhibitor imparts effective rust-preventive characteristics to the lubricating oil whereby rust-formation is inhibited on metal parts of the system that normally corrode when lubricants that do not contain the rust inhibitors are employed.

In order to further illustrate the invention, the following compositions are set forth showing particularly effective rust-preventive compositions of the type embodied herein:

Comp. No.	1	2	3	4	5	6	7	8	9	10	11	12
	Percentage by Weight											
Mid-Cont. 1120 grade Avia. Oil	98.0	85	95.0	98.0	96.0	98.0	96.0	98.0	96.0	98.0	96.0	98.0
B(N-diethyl) amino ethyl stearate	2.0		5.0									
B(N-ethanol) amino (di ethyl oleate)				2.0	4.0							
B(N-diethyl) amino ethyl oleate	15					2.0	4.0					
Triethanolamine trioleate								2.0	4.0			
B(N-di-n-butyl) amino ethyl oleate										2.0	4.0	
B(N-diethanol) amino ethyl oleate												2.0

In preparing the rust-preventive compositions of the present invention, i. e., compositions comprising the rust inhibitors and a suitable solvent vehicle therefor, the preferred procedure is to add, or otherwise incorporate, the rust inhibitor to the solvent vehicle and establish a homogeneous solution. In order to facilitate dissolution of the rust inhibitor in the vehicle, it is preferable to agitate the mixture, employing means for agitation such as stirring and/or heating of the mixture when necessary. When heating is employed to facilitate dissolution, the maximum temperatures employed should be lower than the temperatures at which the mixture, components thereof, or the final homogeneous composition may be deleteriously effected, such as by chemical decomposition.

As hereinbefore stated, B(N-diethyl) amino ethyl stearate has been found to be a particularly effective rust preventive in accordance with the present invention. Accordingly, for purposes of illustrating a procedure for preparation of the rust inhibitors of the present invention the following example is set forth directed to preparation of B(N-diethyl) amino ethyl stearate:

119 grams of diethylethanolamine is mixed with 284.5 grams of stearic acid and to the mixture, a slight amount of concentrated sulfuric acid, i. e., about 1 to 4 drops is added to facilitate the esterification reaction. The mixture of the amine and acid is refluxed while stirring. During the refluxing, the temperature of the reacting mixture decreases from about 145° C. to about 125° C. which is believed to be due to accumulation of water which is also a product of the esterification reaction. The water is distilled off slowly using a short distilling column and the temperature of the reacting mass is allowed to reach about 225° C. at which temperature the reaction is substantially complete providing B(N-diethyl) amino ethyl stearate. The reaction which takes place in the aforesaid procedure for preparing B(N-diethyl) amino ethyl stearate is as follows:

$$(C_2H_5)_2NCH_2CH_2OH + C_{17}H_{35}-COOH \longrightarrow H_2O + (C_2H_5)_2NCH_2CH_2-O-\overset{\overset{O}{\|}}{C}-C_{17}H_{35}$$

In the preparation of the esters contemplated by the present invention, such as are obtained by reacting organic acids with tertiary alkylol amines, the ratio of amounts of reactants generally employed for the esterification reaction to provide true esters therefrom is substantially one mole of the organic acid, such as stearic, oleic, and the like, for each alkylol group of the amine that is to be esterified. However, in my practice of the invention, I prefer to employ a slight excess of the amine whereby more complete utilization of the acid is effected thereby providing for more efficient and complete esterification. The use of an excess of amine in the reaction does not appear to have any deleterious effect in rust-preventive properties of the ester produced, as the excess amine is removed during the distillation employed to remove water formed during the reaction.

Although the procedure set forth hereinbefore relates to preparation of B(N-diethyl) amino ethyl stearate, it will be appreciated by those skilled in the art that the procedure, subject to modifications and variations, may be employed generally in preparing the rust inhibitors of the present invention, i. e., the esters such as provided by esterification of tertiary alkylol amines with organic acids, particularly fatty acids. Furthermore, and although I have set forth a specific method suitable for preparing rust inhibitors embodied in the present invention, I do not intend to limit my invention to rust inhibitors prepared by the method set forth, as

my invention embodies the use, as rust inhibitors, of such esters prepared by methods other than hereinbefore set forth. Thus, for example, in preparing the esters embodied herein by reaction of organic acids with tertiary alkylol amines, it may be found necessary, particularly depending upon the reaction product it is desired to obtain, to vary conditions including temperature and proportions of reactants, and other variables in the foregoing method of preparation relating to B(N-diethyl) amino ethyl stearate.

In providing rust-preventive compositions comprising rust inhibitors and a suitable solvent vehicle therefor, such compositions generally comprise a minor proportion of rust inhibitor and a major proportion of vehicle. Hence, in general, the rust inhibitor content of such compositions need not exceed about 20% by weight, and for most purposes, amounts considerably lower than 20%, such as about 2% to 5% by weight, and as low as 0.5% by weight are generally employed. As will be readily appreciated by those skilled in the art, the properties of the rust inhibitor compositions depend upon factors such as conditions under which the compositions are to be employed, and upon the particular type and composition of the vehicle with which it is to be associated. Accordingly, the proportions of rust inhibitors to vehicle shown in the examples set forth herein are not to be considered as critical or limitative, as, under different conditions of contemplated use and differences in vehicles employed, other proportions of rust inhibitors may be employed with equally satisfactory results. Hence, as will be further appreciated by those skilled in the art, an important factor that should be taken into consideration in preparing the rust-preventive compositions is solubility characteristics of a particular rust inhibitor in a proposed vehicle therefor as the relative solubilities of the rust inhibitors have considerable bearing on the proportions employed in preparing homogeneous rust-preventive solutions.

Although the exact nature of the reasons underlying the high degree of rust-prevention provided by the compositions of the present invention is not fully known, such phenomena obviously occur as will be appreciated by reference to the examples set forth hereinafter showing the excellent results obtained when compositions of the present invention are subjected to metal corrosion tests. Furthermore, the compositions provided by my invention have a strong wetting action upon and adherence to, metal surfaces. Current usage of rust-preventive compositions of the type embodied herein requires that they adhere tenaciously to metal surfaces in a substantially unbroken film under quite adverse conditions, as for example, when the metal to be protected against rusting is subjected to high temperatures and humidities over extended periods of time. The compositions provided by my invention have the desired properties of adhering tenaciously to metal surfaces and protect the surface under adverse conditions as will be appreciated from the tests set forth hereinafter illustrating certain embodiments of the present invention:

Example I

Employing as a vehicle conventional 1120 Grade Aviation Oil derived from Mid-Continent crude, various compositions were prepared by adding from about 3% to 5% by weight of B(N-diethyl) amino ethyl stearate to the vehicle. Each of the compositions were found to be effective in preventing rusting of steel surfaces to which they were applied, as will appear from the following described corrosion test under high humidity:

In the stated humidity corrosion test which is more fully described in "Army-Navy Aeronautical Specification Compound; Corrosive Preventive, Aircraft Engine, AN-VV-C-576B—April 28, 1945," two freshly-sand blasted steel panels are coated on all surfaces with the test composition, drained for four hours in an atmosphere maintained at a relative humidity not exceeding 50% and a temperature of 25° C., plus or minus 3° C., and then subjected to a circulating atmosphere of 95–100% relative humidity at a temperature of 120° F. for 150 hours. At the end of the test period, the panels are removed from the humidity cabinet, cleaned with naphtha, and examined. The presence of any corrosion on the panel, except within ⅛ inch from any edge thereof, evidences failure of the composition.

The rust-preventive compositions prepared as set forth in Example I were subjected to the above-described humidity corrosion test and passed the requirements thereof in that the test panels, after being coated with the composition and exposed as described, showed no evidence of corrosion.

Example II

A composition was prepared comprising about 96% by weight of a conventional 1120 Grade Aviation Oil, derived from Mid-Continent crude, and the balance, about 4% by weight of B(N-diethyl) amino ethyloleate. This composition was subjected to test in the same manner as set forth in Example I and passed the high humidity corrosion test set forth therein.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will readily recognize that variations and modifications can be made. Such variations and modifications are to be considered to be within the purview of the specification and the scope of the appended claims.

I claim:

1. Method for inhibiting corrosion of a ferrous metal subjected to the rust-inducing effects of highly humid atmospheres which comprises coating the surface of said metal with a liquid hydrocarbon having dissolved therein a small amount, sufficient to substantially increase the rust-inhibiting characteristics of said liquid, of B(N-diethyl) aminoethylstearate obtained by esterifying diethylaminoethanol with stearic acid obtained by hydrolysis of a member of the group consisting of naturally-occurring fats and naturally-occurring fatty oils.

2. Method for inhibiting corrosion of a ferrous metal upon exposure to highly humid-rust inducing atmospheres which comprises coating the surface of said metal with a substantially non-corrosive liquid having dissolved therein a small amount, sufficient to substantially increase the rust-preventive characteristics of said liquid, of a tertiary alkyl alkylolamine containing an alkylol group esterified with a long chain fatty acid obtained by hydrolysis of a member of the group consisting of naturally-occurring fats and naturally-ocurring fatty oils.

3. Method, as defined in claim 2, wherein the non-corrosive liquid is a liquid hydrocarbon.

4. Method, as defined in claim 2, wherein the non-corrosive liquid is a mineral oil.

5. A method, as defined in claim 2, wherein the tertiary amine is a dialkylalkylolamine.

6. A method, as defined in claim 2, wherein the esterified alkylolamine is B(N-di-n-butyl) amino-ethyloleate.

7. A method, as defined in claim 2, wherein the esterified alkylolamine is B(N-diethyl) amino-ethyloleate.

JOHN W. BISHOP.

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Certificate of Correction

Patent No. 2,520,356 August 29, 1950

JOHN W. BISHOP

It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction as follows:

Column 2, lines 31 and 32, strike out "diethylaminoethanol stearic acid B(N-diethyl)-aminoethyl stearate"; lines 50 and 51, for

$$-\underset{\underset{O}{|}}{C}- \quad \text{read} \quad -\underset{\underset{O}{\|}}{C}-$$

column 3, line 22, for the word "substance" read *substances*; columns 3 and 4, for that portion of the table reading

Comp. No.	1	2	3	4	5	6	7	8	9	10	11	12
	Percentage by Weight											
Mid-Cont. 1120 grade Avia. Oil	98.0	85	95.0	98.0	96.0	98.0	96.0	98.0	96.0	98.0	96.0	98.0
B(N-diethyl) amino ethyl stearate	2.0	----	5.0	----	----	----	----	----	----	----	----	----
B(N-ethanol) amino (di ethyl oleate)	----	----	----	2.0	4.0	----	----	----	----	----	----	----
B(N-diethyl) amino ethyl oleate	15	----	----	----	----	2.0	4.0	----	----	----	----	----

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	Percentage by Weight											
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B(N-diethyl) amino ethyl stearate	2.0	----	5.0	----	----	----	----	----	----	----	----	----
B(N-ethanol) amino (di ethyl oleate)	----	----	----	2.0	4.0	----	----	----	----	----	----	----
B(N-diethyl) amino ethyl oleate	----	15	----	----	----	2.0	4.0	----	----	----	----	----

column 6, lines 63 and 64, for "humid-rust inducing" read *humid rust-inducing*; and that the said Letters Patent should be read as corrected above, so that the same may conform to the record of the case in the Patent Office.

Signed and sealed this 12th day of December, A. D. 1950.

[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.

Certificate of Correction

Patent No. 2,520,356 August 29, 1950

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B(N-diethyl) amino ethyl stearate	2.0	----	5.0	----	----	----	----	----	----	----	----	----
B(N-ethanol) amino (di ethyl oleate)	----	----	----	2.0	4.0	----	----	----	----	----	----	----
B(N-diethyl) amino ethyl oleate	15	----	----	----	----	2.0	4.0	----	----	----	----	----

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B(N-diethyl) amino ethyl stearate	2.0	----	5.0	----	----	----	----	----	----	----	----	----
B(N-ethanol) amino (di ethyl oleate)	----	----	----	2.0	4.0	----	----	----	----	----	----	----
B(N-diethyl) amino ethyl oleate	----	15	----	----	----	2.0	4.0	----	----	----	----	----

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[SEAL]

THOMAS F. MURPHY,
Assistant Commissioner of Patents.