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2,856,299

WATER-DISPLACING AGENT

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This invention relates to water displacing agents which will preferentially adsorb on a metallic surface displacing any residual moisture. Particularly, the invention relates to water displacing agents which may be added to rust preventive compositions to enhance their rust preventive properties.

It is usual to protect metal parts from corrosion by applying a temporary rust preventive between manufacturing steps and prior to storage or packaging. The parts to be protected are often coated with an undesirable film of water. The water film may come from cooling or cutting fluids, rinsing baths, or from condensation of water vapor from the atmosphere. This water film must be removed in order for the rust preventive to be effective. A common method of removing this film is to pass the metal parts through a heated drying oven prior to the application of the rust preventive. This process is both slow and expensive. A more efficient and desirable method is to embody into the rust preventive compound a material which will preferentially adsorb onto the metallic surface thereby displacing any residual moisture and permitting a continuous rust preventive coating. The condensation products of alkylene oxides and fatty acid-polyamine compounds have been found to be excellent additives for this purpose and are the subject of this invention.

The alkylene oxide condensates of the fatty acid-polyamines of this invention are formed by reacting an alkylene oxide with a fatty acid-polyamine compound which in turn has been formed by reacting a fatty acid and a polyamine.

It has been found that these materials, when blended in fluid type rust preventives in proportions ranging from about 0.1% to 10.0% by weight, materially increase the effectiveness of the rust preventive against rusting caused by the presence of residual moisture. It is preferred to use about 1.0% to 5.0% by weight of the additives of this invention.

The additive materials of this invention may be used with removable type fluid rust preventive compositions. Such rust preventive compositions contain a solvent or oil base material, a rust preventive agent, and frequently contain waxes which aid in forming a protective film. Additional additives may also be contained in the rust preventive composition such as anti-oxidants, metal deactivators, dyes, and other usual type additives.

The oleaginous base material or solvent may be volatile or non-volatile. Generally, a mineral oil product is used, such as "Stoddard Solvent"; naphthas, preferably naphthas having initial boiling points of about 180° F. to 310° F., and final boiling points of about 210° F. to 500° F.; gas oil; lubricating oil, preferably having a viscosity of about 35 to 1000 S. S. U. at 210° F.; and petrolatum. Vegetable or animal oils may be used, as well as synthetic oils, e. g., esters such as dibasic acid esters. Mixtures of any of the above solvent materials may also be used.

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Rust preventive agents which may be used include the C₁₂ to C₂₂ fatty acid partial esters of aliphatic polyhydric alcohols having about 3 to 12, preferably 3 to 8, carbon atoms. Examples of these partial esters are: sorbitan monooleate, glyceryl monooleate, pentaerythritol monooleate, the di-oleates of sorbitan, mannitan, pentaerythritol and related polyhydric alcohols, the corresponding partial stearic and palmitic acid esters of these alcohols, and partial esters of these alcohols made from mixtures of these fatty acids.

Another class of rust preventive compounds are the oil soluble sulfonate soaps, preferably of alkali or alkaline earth metals, such as calcium or sodium salts of mahogany sulfonic acids, said sulfonic acids having molecular weights of about 350 to 520 and preferably about 430 to 520.

Other rust preventives which may be used are oxidized wax esters, metal xanthates, metal phenolates, metal phenol sulfides, metal naphthenates, metal organo phosphates and thiophosphates, vegetable and animal fatty oils, etc. Wool grease (degras) is a particularly suitable additive when a residual coating which will adhere well to metal is desired.

Various mixtures of the above rust inhibitors may also be used. For example, metal sulfonate salts of the types mentioned are particularly desirable in combination with the partial esters of pentaerythritol in rust preventive coating compositions.

Various waxes may be used in the rust preventive composition for the purpose of forming a heavier film on the surface to be protected. The waxes may be crystalline or microcrystalline and may be derived from animal, vegetable or mineral origins or may be synthetic waxes. However, the most important of these waxes are the paraffin waxes derived from petroleum. These paraffin waxes may be either normal or iso-paraffin and preferably have melting points of about 100 to 200° F.

In general, the compositions of the invention are rust preventive compositions comprising a major amount of an oleaginous base, a minor amount, usually about .5 to 30%, preferably about 3% to 15% by weight, of a rust preventive agent, and about .1 to 10%, preferably 1 to 5% by weight of a water displacing agent. Waxes in amounts of about 1 to 40%, preferably 1 to 15% by weight, based on the total composition, may also be added where a heavier residual coating is desired.

Compositions of the invention embodying the use of partial esters as the rust inhibiting agent, will contain by weight, about 0.5 to 15 parts, preferably about 3 to 10 parts esters; about 0.1 to 10 parts, preferably about 1 to 5 parts, of the water displacing agent of the invention; and about 75 to 99 parts, preferably about 85 to 96 parts of an organic solvent or oleaginous base material. The oleaginous base material may be a straight lubricating oil, preferably a mineral lubricating oil, or a volatile hydrocarbon solvent, such as naphtha. Mixtures, in any proportions, of lubricating oil and naphtha may also be used. Waxes, preferably paraffin waxes, may be added in amounts of about 1 to 40, preferably 1 to 15 weight % and most preferably in amounts of about 2 to 8% by weight, based on the total composition.

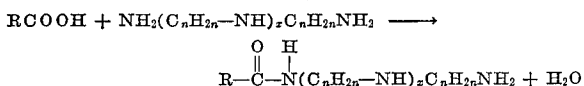
Compositions of the invention embodying the use of oil soluble petroleum sulfonates as the rust inhibiting agent will consist by weight, of about .5 to 15, preferably 2 to 8 parts of the oil-soluble alkali or alkaline earth metal sulfonate; about .1 to 10, preferably about 1 to 5 parts of a water displacing agent of the invention; and about 75 to 99 parts, preferably about 87 to 97 parts of a solvent. The solvent may be a lubricating oil or a volatile solvent such as naphtha, or mixtures thereof. To this composition may be added about 2 to 25, preferably

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about 2 to 10 weight percent, based on the total composition, of degreas. Wax may also be added in amounts of about 1 to 40 weight percent preferably about 1 to 15 weight percent, and most preferably about 2 to 8 weight percent, based on the total composition.

The rust inhibiting composition may also contain several different rust preventive agents. For example, an oil soluble metal sulfonate and a partial ester might both be used in the same composition.

The fatty acid-polyamine compound is prepared by reacting about equi-molar portions of the polyamine and fatty acid by well known methods. Although not known with certainty, the main reaction is believed to be a condensation reaction as follows;

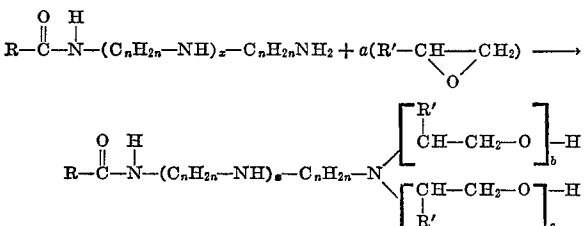


wherein, R is an aliphatic hydrocarbon radical which may be saturated or unsaturated, constituting the non-carboxylic portion of a fatty acid of about 10 to 22 carbon atoms and which may also contain substituents, such as hydroxy, halogen, or others, for hydrogen on one or more of the carbon atoms; n is an integer of about 1 to 4 and preferably about 2 to 3; and x is a whole number of about 0 to 3 and preferably is 0 to 1. The above equation is believed to define the main reaction and the reaction products, however, other reactions may take place. Temperatures maintained within the range of 110° C. to 250° C. for about 1.5 to 6 hours are suitable for this reaction and temperatures maintained within the range of 120° C. to 160° C. for about 2 to 4 hours are preferred. The water formed during the reaction can be removed from the reaction mixture by evaporation or distillation. In the case where the water is removed by distillation a water entraining agent such as xylene, toluene, benzene, naphtha and others, may be used.

Operable polyamines include those containing primary amine groups such as ethylene diamine, propylene diamine, butylene diamine, etc., and also include polyamines which may contain both primary and secondary amine groups such as diethylene triamine, triethylene tetramine, tetraethylene pentamine, dipropylene triamine, tripropylene pentamine, and the like.

Operable fatty acids are those having about 10 to 22 carbon atoms, preferably about 12 to 18 carbon atoms and which may be saturated or unsaturated, and which may be substituted for hydrogen on one or more of the carbon atoms. Examples of such acids include stearic, hydroxy stearic, such as 12-hydroxy stearic, di-hydroxy stearic, poly-hydroxy stearic, capric, lauric, myristic, palmitic, oleic, linoleic, linolinic, ricinoleic, erucic, behenic and others.

When the fatty acid-polyamine compound has been formed, it is further reacted with from about 1 to 10 moles, preferably 2 to 5 moles, of an alkylene oxide by methods well known in the art. The primary reaction is believed to be as follows:



wherein, R is an aliphatic hydrocarbon radical, which may be saturated or unsaturated, constituting the non-carboxylic portion of a fatty acid of about 10 to 22 carbon atoms and which also may contain substituents for hydrogen on one or more of the carbon atoms; n is an integer of about 1 to 4, preferably 2 to 3; x is a whole number of 0 to 3, preferably 0 to 1; R' is a radical selected

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from the group consisting of hydrogen and alkyl radicals containing about 1 to 3 carbon atoms, a is an integer of about 1 to 10, preferably about 2 to 5; b and c are integers of about 0 to 10 each, preferably 0 to 5, provided however, that the sum of $b+c$ must equal a .

The above equation is believed to represent the main reaction that takes place. However, other reactions may take place in which alkylene oxide groups may attach onto the intermediate nitrogen atoms (i. e., the nitrogen atoms in the group $-\text{C}-\text{N}-\text{C}-$).

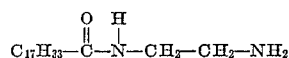
The reaction should be carried out at a temperature within the range from about 25° C. to 200° C., preferably 100° C. to 150° C. and at pressures from about 1 to 10 atmospheres, preferably 2 to 6 atmospheres for about 1 to 24 hours, preferably 2 to 5 hours. A trace of water or an aqueous solution of alkali or alkaline earth hydroxides may be used as a catalyst. The reaction product may be used without further purification.

Operable alkylene oxides include ethylene oxide, propylene oxide, butylene oxide and the like.

The invention will be more clearly explained by reference to the following examples.

EXAMPLE I

One mole (282 grams) of oleic acid and 1 mole (60 grams) of ethylene diamine and 680 grams of xylene (a water entraining agent) were added to a flask equipped with a stirrer, thermometer and a reflux condenser having a water trap. The mixture was stirred at room temperature for about one-half hour to form the ammonium salt. The reaction mixture was then heated to about 140-150° C. and refluxed at this temperature for about two and a half hours during which time one mole (18 cc.) of water was collected in the water trap. The remaining mixture was then distilled under a vacuum of 10 mm. mercury over a period of about one hour to remove the xylene. The resulting fatty acid-polyamine product, which was a dark, viscous liquid, was believed to be chiefly an amido-amine having the formula:



This product was then placed in a stainless steel pressure bomb and a trace (about 0.5 cc.) of a 2 normal sodium hydroxide solution was added. This was then heated to 110° C. under a pressure of 4 atmospheres. Three moles of ethylene oxide were slowly bubbled into the bomb over a time of about 40 minutes while the temperature of the contents was maintained at 100-120° C. by external cooling. After the 3 moles of ethylene oxide were added, the temperature of the bomb was held at about 110° C. for 3 more hours to complete the reaction.

The product was a dark, viscous liquid which was used without further purification.

EXAMPLE II

This was similar to Example I except diethylene triamine was used in place of the ethylene diamine. The reaction product was a condensate of 3 moles of ethylene oxide with the reaction product prepared by reacting equi-molar amounts of oleic acid and diethylene triamine. The effectiveness of these materials as water displacing agents was determined in the following manner.

Water displacing test procedure

Two inch by three inch sandblasted panels of mild steel are dipped in water to deposit a water film over the panel. The wetted panel is then submerged in the test blend for 15 seconds without agitation. The panel is then stored in a humidity cabinet in an upright position for 1 hour at a temperature of 77° F. and at a relative humidity of 100%. At the end of this time, the panel is rinsed in heptane and examined for rust and discoloration.

The following examples illustrate the rust preventive

effectiveness of compositions utilizing the water displacing agents of the present invention.

EXAMPLE III

The water displacing agents of Examples I and II were added to a base which was a rust preventive composition. Said base consisted of 3.75% by weight of a mineral oil with a viscosity of about 100 S. S. U. at 100° F. and 3.75 weight percent of sodium soap of a petroleum sulfonic acid having an average molecular weight of 450; 7.5 weight percent of neutral degreas; and 85 weight percent of a hydrocarbon solvent naphtha having a flash point of 105° F. and a mid-boiling point of 338° F. and a final boiling point of about 397° F. The following data was obtained in the water displacing test mentioned above.

TABLE I

Test No.	Composition	Amount of Rust
0	Base	Moderate Rust.
1	Base+1% A ¹	Trace Stain, No Rust.
2	Base+2% A	No Stain or Rust.
3	Base+4% A	Do.
4	Base+1% B ²	Trace Stain, No Rust.
5	Base+2% B	No Rust or Stain.
6	Base+4% B	Do.

¹ A is the reaction product of Example I, which is a condensate of 3 moles of ethylene oxide and 1 mole of a fatty acid-polyamine compound prepared by reacting 1 mole of oleic acid and 1 mole of ethylene diamine.

² B is the reaction product of Example II which is a condensate of 3 moles of ethylene oxide and 1 mole of a fatty acid-polyamine compound prepared by reacting 1 mole of oleic acid and 1 mole of diethylene triamine.

EXAMPLE IV

Various other compositions were prepared which embodied water displacing agents of the invention. Water displacing tests were also run on these compositions, and the results are listed in Table II below:

TABLE II.—WATER DISPLACING AGENT

Composition, Weight Percent	1	2	3	4	5	6	7	8	9
Sorbitan Monooleate	5.0	5.0	5.0						
Glyceryl Monooleate				5.0	5.0	5.0			
135/137 EMP (English Melting Point) Refined Paraffin Wax	5.0	5.0	5.0	5.0	5.0	5.0	4.0	4.0	4.0
Hydrocarbon Oil ¹	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0	10.0
Naphtha ²	80.0	77.0	77.0	80.0	77.0	77.0	80.0	77.0	77.0
Additive A (Reaction Product of Example I)		3.0			3.0			3.0	
Additive B (Reaction Product of Example II)			3.0			3.0			3.0
Barium Sulfonate ³							6.0	6.0	6.0
Blend Appearance	Clear	Clear	Clear	Clear	Hazy	Hazy	Clear	Clear	Clear
Water Displacement	Moderate	Trace	No	Moderate	No	No	Moderate	No	No
Amount Rust	Rust	Stain	Stain	Rust	Stain	Stain	Rust	Stain	Stain

¹ Hydrocarbon mineral lubricating oil having an A. P. I. gravity of 40.3 degrees, flash point of 270° F., and a viscosity of 51.9 S. S. U. at 100° F.

² Hydrocarbon solvent naphtha having a flash point of 105° F., a mid-boiling point of 338° F. and a final boiling point of about 397° F.

³ Barium soap of a sulfonic acid having a molecular weight of about 440. It is a concentrate of 45% soap by weight in a mineral oil having a viscosity of about 100 S. S. U. at 100° F.

As can be seen from the above tables, the additives of this invention were very effective in preventing rust caused by residual moisture on a metallic surface.

EXAMPLE V

A further test was run to determine the effect of the compounds of the invention on the life of a rust preventive. Several of the compositions of Example III were subjected to the humidity test. The humidity tests were run in the humidity cabinet described in the Military Specification JAN-H-792, which is recognized standard humidity test. The test panels were sandblasted, rinsed in boiling naphtha and boiling methanol, and cooled to room temperature in a desiccator. The panels were dipped for 2 minutes in the rust preventive composition, withdrawn and hung for 25 hours at room temperature prior to being placed in the cabinet.

TABLE IV.—HUMIDITY CABINET LIFE

Composition, Weight Percent	JAN-H-792 Humidity Cabinet Life, hrs., Average of 2 runs
Base ¹	480
Base+1% A ²	648+
Base+1% B ³	576

¹ The base is the exact same base material used in Example III which was 3.75% sodium sulfonate, 7.5% degreas, 85% solvent, and 3.75% by weight of a mineral oil having a viscosity of about 100 S. S. U. at 100° F.

² A is the reaction product of Example I.

³ B is the reaction product of Example II.

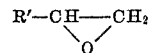
As seen from the above table, the addition to the rust preventive composition of 1% of the water displacing agents prepared in Examples I and II improved the resistance to rusting.

What is claimed is:

1. A rust inhibiting composition comprising a major proportion of an oleaginous solvent, a rust preventive proportion of a rust preventive, and a water displacing proportion of a water displacing agent, said water displacing agent being the condensation product of (1) the fatty acid-polyamine reaction product of substantially equi-molar portions of a fatty acid containing about 10 to 22 carbon atoms and a polyamine having the formula:



wherein, n is an integer of about 1 to 4 and x is an integer of about 0 to 3, and (2) about 1 to 10 moles of an alkylene oxide having the formula:



wherein R' is a member selected from the group consisting

of hydrogen and alkyl radicals containing from about 1 to 3 carbon atoms.

2. A rust inhibiting composition according to claim 1 wherein said water displacing agent is present in amounts of about 0.1 to 10% by weight of the total composition.

3. A rust inhibiting composition according to claim 1 wherein said water displacing agent is present in amounts of about 1.0 to 5.0% by weight of the total composition.

4. A rust inhibiting composition according to claim 1 in which said water displacing agent is the condensation product of (a) 3 moles of ethylene oxide and (b) 1 mole of the fatty acid-polyamine reaction product of equal moles of oleic acid and ethylene diamine.

5. A rust inhibiting composition according to claim 1 in which said water displacing agent is the reaction product of 3 moles of ethylene oxide and 1 mole of the

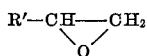
condensation product prepared by reacting 1 mole of oleic acid and 1 mole of diethylene triamine.

6. A rust inhibiting composition according to claim 1 which contains about 1 to 40 weight percent of a wax.

7. A liquid rust preventive composition comprising about 75 to 99 parts of an oleaginous base, about 0.5 to 15 parts of a partial ester of a fatty acid having about 12 to 22 carbon atoms per molecule and an aliphatic polyhydric alcohol having about 3 to 12 carbon atoms per molecule, and about .1 to 10% of a water displacing agent, said water displacing agent being the condensation product of (1) the fatty acid-polyamine reaction product of substantially equi-molar portions of a fatty acid containing about 10 to 22 carbon atoms and a polyamine having the formula:



wherein n is an integer of about 1 to 4 and x is an integer of about 0 to 3, and (2) about 1 to 10 moles of an alkylene oxide having the formula:

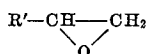


wherein R' is a member selected from the group consisting of hydrogen and alkyl radicals containing about 1 to 3 carbon atoms.

8. A liquid rust preventive composition comprising about 75 to 99 parts of an oleaginous base, about 0.5 to 15 parts of an oil soluble metal soap of a sulfonic acid, and about 0.1 to 10 parts of a water displacing agent, said water displacing agent being the condensation product of (1) the fatty acid-polyamine reaction product of substantially equi-molar portions of a fatty acid containing about 10 to 22 carbon atoms and a polyamine having the formula:



wherein, n is an integer of about 1 to 4 and x is an integer of about 0 to 3, and (2) about 1 to 10 moles of an alkylene oxide having the formula:



wherein, R' is a member selected from the group consisting of hydrogen and alkyl radicals containing from about 1 to 3 carbon atoms.

9. A composition according to claim 8 which contains about 2 to 25 weight percent degrass, based on the total composition.

10. A composition according to claim 8 which contains about 1 to 40 weight percent wax, based on the total composition.

11. A rust preventive composition which comprises (1) about 96 to 99 weight percent of a base material consisting of 3.75 weight percent of a sodium soap of a petroleum sulfonic acid having an average molecular weight of 450, 3.75 weight percent of a mineral oil having a viscosity of about 100 S. S. U. at 100° F., 7.5 weight percent of neutral degrass; 85 weight percent of a naphtha; and (2) about 1 to 4 weight percent of the condensation product of 3 moles of ethylene oxide and 1 mole of the reaction product of equal moles of oleic acid and ethylene diamine.

12. A rust preventive composition which comprises (1) 96 to 99 weight percent of a base material consisting of 3.75 weight percent of a sodium soap of a petroleum sulfonic acid having an average molecular weight of 450, 3.75 weight percent of a mineral oil having a viscosity of about 100 S. S. U. at 100° F., 7.5 weight percent of neutral degrass; 85 weight percent naphtha; and (2) about 1 to 4 weight percent of the reaction product of 3 moles of ethylene oxide and 1 mole of the condensation product of equal moles of oleic acid and diethylene triamine.

13. A rust preventive composition comprising by weight, 5.0% sorbitan monooleate, 5.0% paraffin wax, 10.0% hydrocarbon mineral lubricating oil, 77.0% hydrocarbon solvent naphtha, and 3% of the condensation product of 3 moles of ethylene oxide and 1 mole of the reaction product of equal moles of oleic acid and ethylene diamine.

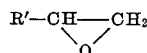
14. A rust preventive composition comprising by weight, 5.0% sorbitan monooleate, 5.0% paraffin wax, 10.0% hydrocarbon lubricating oil, 77.0% hydrocarbon solvent naphtha, and 3% of the condensation product of 3 moles of ethylene oxide and 1 mole of the reaction product prepared by reacting 1 mole of oleic acid and 1 mole of diethylene triamine.

15. A rust preventive composition comprising by weight 4.0% of a refined paraffin wax, 13.3% of a hydrocarbon mineral lubricating oil, 77.0% of naphtha, 2.7% of a barium soap of a sulfonic acid having a molecular weight of about 440, and 3.0% of the condensation product of 3 moles of ethylene oxide and 1 mole of the reaction product of equal moles of oleic acid and ethylene diamine.

16. An improved process for the temporary protection of metal parts from corrosion from residual moisture which comprises coating said metal parts with a rust preventive composition which contains a water displacing amount of a water displacing agent, said water displacing agent being the condensation product of (1) the fatty acid-polyamine reaction product of substantially equi-molar portions of a fatty acid containing about 10 to 22 carbon atoms and a polyamine having the formula:



wherein, n is an integer of about 1 to 4 and x is an integer of about 0 to 3, and (2) about 1 to 10 moles of an alkylene oxide having the formula:



wherein R' is a member selected from the group consisting of hydrogen and alkyl radicals containing from about 1 to 3 carbon atoms.

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