

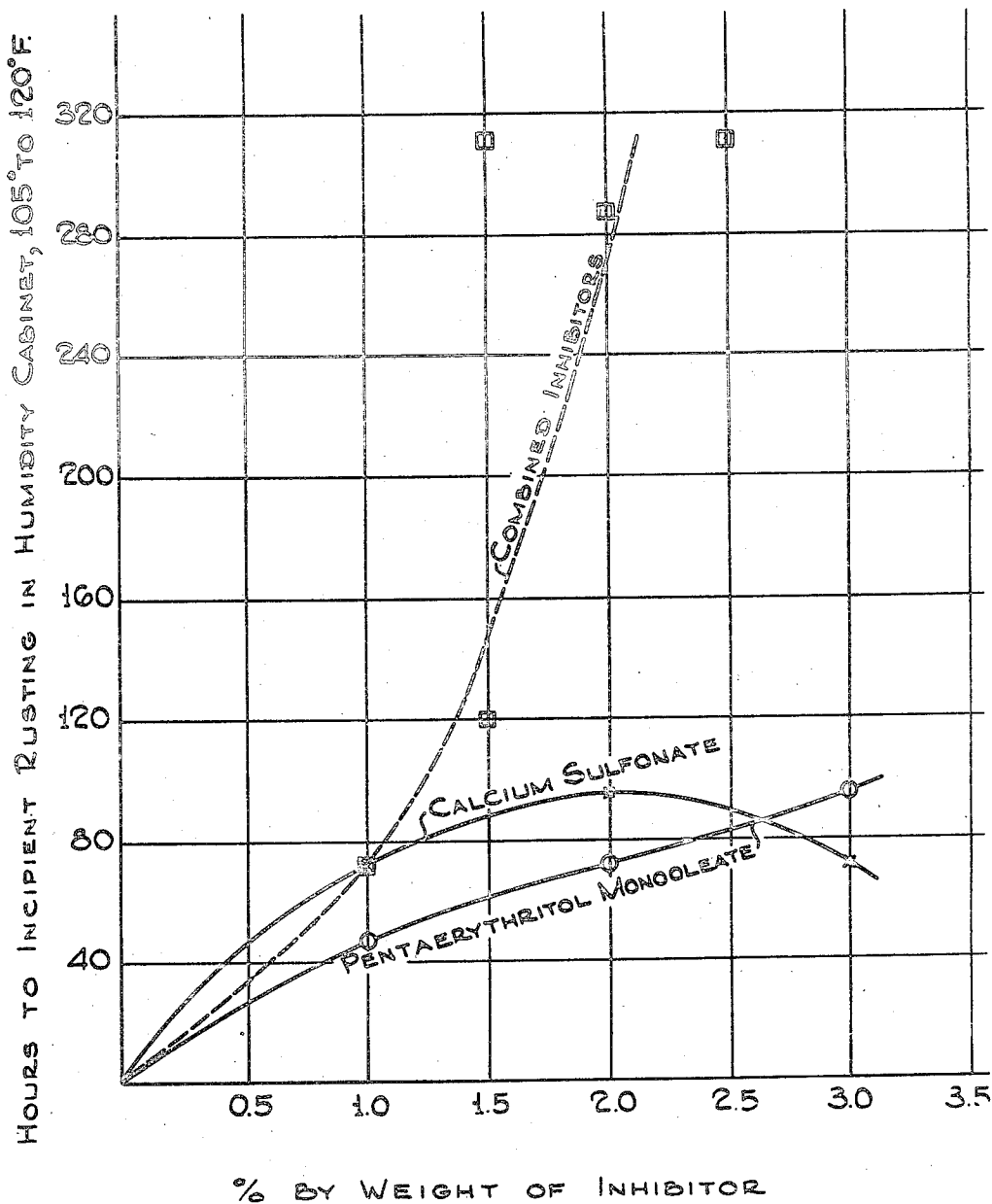
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RUST INHIBITING COMPOSITION

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RUST INHIBITING COMPOSITION

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This invention relates to rust inhibiting compositions, especially to compositions of matter for arresting, preventing and inhibiting the corrosion of metals, and more particularly, for the preservation of articles fabricated from iron, steel and other ferrous alloys. The present application is a continuation-in-part of accompanying application Serial Number 622,102, filed on October 12, 1945, which became abandoned on July 27, 1948.

The corrosion of a metal, particularly a ferrous metal, is a problem which has existed since the making of metallic articles and tools began. Many corrosion problems arise calling for special consideration, such, for instance, as the handling of large volumes of acid; however, by far the greatest corrosion problem is in connection with ferrous metals and their proclivity for corrosion when exposed to even normal atmospheric conditions. Active corrosion of metallic surfaces has been impeded, arrested, or prevented by coating the metallic surface with an inert, impervious film applied to the metallic surface by dipping, spraying, brushing or swabbing.

An object of the present invention is the formation of an oily, preferably non-drying composition of matter for arresting or inhibiting the rusting of ferrous metals. Another object is the preparation of a composition containing multifunctional agents of a corrosion preventive, anti-oxidant and dispersant character.

Still another object is the preparation of compositions of this type which may be used not only as protective coatings but which also may be employed if desired as internal combustion engine lubricants. Such lubricants combine the advantages of promoting general engine cleanliness during use and of inhibiting rusting and related corrosion caused by the presence of moisture and of acidic fuel residues during periods of non-use. When operating internal combustion engines in climates having high humidity it is not uncommon for rusting to begin in an engine within as short a period of time as one hour after the engine is shut down. The advantages of a lubricating oil composition having the property of preventing rusting under such conditions are obvious. For related reasons, compositions suitable for lubrication or for protective coating of firearms, ordnance equipment, industrial machinery, etc., can be prepared in accordance with the present invention. The above objects of the invention, as well as other objects, will be ap-

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parent to those skilled in the art upon reading the following description.

The compositions of the invention are therefore improved oil compositions which contain the usual constituents of an oily solvent or protective base material which is generally a mineral oil product such as "Stoddard solvent," gas oil, lubricating oil, wax, petrolatum or mixtures of the same. To this base material are added the specific anti-corrosion agents which form the subject matter of the present invention. Synthetic oils, e. g., esters such as dibasic acid esters and polyethers may be employed as the base oils.

The anti-corrosion agents contemplated according to the present invention are aliphatic carboxylic acid partial esters of polyhydric alcohols, said alcohols having at least three hydroxyl groups, these preferably though not always necessarily being branched from a single carbon atom, or still more accurately the hydroxy esters of such alcohols. These esters are characterized by having at least one free hydroxyl group in the molecule, and where possible it is preferred to have two or more free hydroxyl groups in the molecule of the ester. Alcohols which may be used as starting materials for producing the esters useful in making the compositions of the present invention are exemplified by pentaerythritol, di-pentaerythritol, poly-pentaerythritol, and trimethylol propane. Glycerol and erythritol also may be used, although they are not quite as effective. Other alcohols having a tertiary or neo-carbon atom structure similar to that of the pentaerythritols may also be used. With these polyhydric alcohols of three or more OH groups, it has been discovered that the mono-esters of the polyhydric alcohol are very proficient and effective anti-corrosion agents. The esterification of each succeeding OH group diminishes the effectiveness of the partial ester as an anti-corrosion agent until the completely esterified polyhydric alcohol shows little or no anti-corrosion properties. Thus the di-ester is usually somewhat less potent than the mono-ester, and the tri-esters or tetra-esters are quite inactive.

The acids useful for the esterification of the polyhydric alcohol compounds are those fatty acids having from about 10 to 22 carbon atoms which are commonly combined with glycerol in naturally occurring animal and vegetable oils and fats and which are derived therefrom upon saponification thereof and are exemplified by the

fatty acids derived from stearin, fish or whale oils, animal fats, and vegetable fats or oils, and the like. The list of preferred esterifying materials includes fatty acids, such as, capric, lauric, myristic, palmitic, oleic, linoleic, linolenic, ricinoleic, stearic, dihydroxystearic, eleostearic, erucic and behenic. The moderately unsaturated long chain acids such as oleic acid are particularly suitable, also hydrogenated or partly hydrogenated, or oxygenated fatty acids. It is also contemplated that mixtures of the foregoing acids may be used in the esterification of the polyhydric alcohols. It is also often advantageous to employ mixtures of such acids with low molecular weight acids such as acetic, propionic, glycolic, lactic, etc., to produce mixed esters. These should be of short chain length, not exceeding 4 carbon atoms. The long chain acids have the advantage of imparting some oil solubility to the ester, although the partial esters are only very sparingly soluble in oil because of the free hydroxyl groups they contain. Esterification of some of these with a short chain acid tends to improve oil solubility.

The anti-corrosion agents of the present invention are made by reacting one mol of the polyhydric alcohol with preferably only one or at most two mols of carboxylic acid or carboxylic acid mixtures either in the presence of or absence of a catalyst as is well understood by those skilled in the art. The catalyst may be acidic, for example, sulfuric or phosphoric acid, or alkaline as, for instance, sodium hydroxide, or it may be a salt such as stannous chloride. The ingredients are commingled and heated in a kettle or other container, preferably closed and equipped with suitable agitating means at a temperature of 125°-300° C. until the esterification reaction reaches completion. It is frequently desirable to maintain an atmosphere of inert gas, such as nitrogen or a carbon oxide over the reacting mass. This may be done by passing an inert gas over or through the reacting mass in order to assist removal of the water of reaction and prevent discoloration of the esters formed or the reaction may be carried out in a refluxing hydrocarbon solvent with means provided for trapping out the water formed. It may be advantageous in some instances to modify the esters by introducing ether groups, for example by reaction with ethylene oxide.

The compositions of the present invention, as before stated, comprise an oleaginous base, preferably of mineral oil, although vegetable or animal oils or mixtures of oils may be used as the base, blended with a minor proportion of a carboxylic acid partial ester of an aliphatic polyhydric alcohol having at least three hydroxyl groups preferably branching from a single carbon atom. The compositions are produced by blending from 0.1% to 10%, preferably 0.5 to 3%, by weight of the ester in the oleaginous base, using heat and stirring if necessary. The present invention is based upon the further discovery of a synergistic effect of oil soluble metal sulfonates when combined with the esters described above. It is highly desirable to include one or more of such sulfonates as auxiliary agents in the preservative composition in proportion of about 0.5 to 10% by weight, preferably 0.5 to 3%. These include especially the oil soluble sulfonate soaps, of alkali or alkaline earth metals, such as calcium or sodium soaps of mahogany sulfonic acids. For some purposes other known rust inhibitors may be used also, such as metal xanthates,

metal phenolates, metal phenol sulfides, metal naphthenate, metal organo phosphates and thiophosphates, organic bases, vegetable or animal fatty oils, etc. Wool grease (degras) is a particularly suitable additive when a residual coating which will adhere well to the metal is desired. See the patent to Lebo No. 2,182,992.

Metal sulfonate salts of the types mentioned are particularly desirable, in combination with the partial esters of pentaerythritol in rust preventive crankcase lubricants and also in rust preventive coating compositions. These should be employed in most cases. Additional salts which may be used include barium tert.-octyl phenol sulfide, calcium diamyl phenate, aluminum stearate, zinc naphthenate, tin lauryl phenol sulfide, nickel amyl xanthate, reaction product of P_2S_5 and barium tert.-amyl phenol sulfide, zinc diisopropyl salicylate, barium dioctyl thiophosphate, calcium amyl phenol thiophosphate, calcium octadecylate, and the like.

For special purposes, such as to enable the composition to dislodge water from metal surfaces, alkylol amines, alcohols, esters, ethers, ether alcohols and the like may be incorporated in the composition. Also, one or more of the free hydroxy groups present in the hydroxy esters of the present invention may be reacted with phosphorus sulfides or oxides, thio acids, xanthates or carbamic acids to produce multi-functional corrosion preventives, rust inhibitors, detergents and anti-oxidants.

Because of their potent rust preventive properties the esters of the present invention may also be employed in fuel compositions such as Diesel fuels, domestic and industrial heating oils, kerosene, gasoline and the like. They are primarily useful, however as crankcase lubricants for internal combustion engines, and as slushing oils or coating compositions such as are applied to machined or polished ferrous metal surfaces to prevent rust.

The efficiency of rust preventive compositions is best evaluated by actual service or exposure tests, although certain standard laboratory tests, of which the humidifier test is the one most employed, may be used for rapid evaluation.

Test procedure

Sand blasted panels of hot rolled steel are dipped into slushing compound samples, then maintained vertically in a box for 16 hours under ordinary room conditions to allow the rust preventive film to reach an equilibrium condition. Compounds containing petrolatum or waxes are applied at temperatures above their melting point and fluid products are applied at room temperatures. The coated panels are then placed in an upright position in a humidifier chamber maintained at 100-120° F. where they are subjected to continuous moisture condensation. The test pieces are spaced in the cabinet in such a manner that they do not come in contact with each other. The time, in hours, for a panel subjected to these conditions to develop initial evidence of rusting is observed and recorded as the resistance life of the coating composition. According to Government specification AN-VV-C-576b the minimum resistance life for a coating composition tested under these conditions is set at 150 hours.

The following examples illustrate the rust preventive effectiveness of compositions of the present invention on the basis of the above tests.

Example I

Using a high grade phenol extracted aviation engine lubricating oil of 120 S. S. U. viscosity at 210° F. and viscosity index of 105 as a basic material, the following data were obtained in the standard Army-Navy humidity cabinet tests mentioned above. The times indicated are hours to incipient rusting:

Test No.		Hours
0	Base Oil.....	2
1	Base Oil+1% pentaerythritol monooleate.....	48
2	Base Oil+1% calcium sulfonate.....	72
3	Base Oil+0.5% pentaerythritol monooleate and 0.5% calcium sulfonate.....	72
4	Base Oil+2% pentaerythritol monooleate.....	72
5	Base Oil+2% calcium sulfonate.....	96
6	Base Oil+0.5% pentaerythritol monooleate and 1% calcium sulfonate.....	120
7	Base Oil+0.5% pentaerythritol monooleate and 2% calcium sulfonate.....	312+
8	Base Oil+1% pentaerythritol monooleate and 0.5% calcium sulfonate.....	120
9	Base Oil+1% pentaerythritol monooleate and 1% calcium sulfonate.....	288
10	Base Oil+1% pentaerythritol monooleate and 2% calcium sulfonate.....	312+
11	Base Oil+3% pentaerythritol monooleate.....	96
12	Base Oil+3% calcium sulfonate.....	72
13	Base Oil+2% pentaerythritol monooleate and 0.5% calcium sulfonate.....	312+
14	Base Oil+2% pentaerythritol monooleate and 2% calcium sulfonate.....	312+

¹ It will be noted that in tests Nos. 7, 10, 13 and 14, the tests were discontinued after 312 hours with no incipient rusting. The total of ester and sulfonate was 2.5% in test No. 7, 3% in No. 10, 2.5% in No. 13, and 4% in No. 14. With as much as 3% of the individual components, protection against rusting was obtained for a maximum of only 96 hours. The combined inhibitors, even in smaller total quantities, are much more effective than would be expected from their individual inhibiting powers. These data are represented graphically in the drawing. It will be noted particularly that after the combined inhibitors exceed 1%, they are far more effective than either component alone and far beyond the expected additive effect of the combined inhibitors. Where the pentaerythritol ester is added to the extent of at least 1% by weight, based on the total composition, the further addition of as little as 0.5% of the sulfonate produces a very satisfactory rust inhibitor. Where the quantity of ester is only 0.5% apparently the sulfonate should be in excess of 1%, preferably about 2%, although the data are not entirely conclusive.

Example II

A typical naphthenic lubricating oil of 45 S. S. U. viscosity at 210° F. was tested in the same manner as in Example I.

Test No.		Hours
15	Base Oil.....	1
16	Base Oil+3% glycerol trioleate.....	4
17	Base Oil+3% pentaerythritol monooleate monoacetate.....	200+
18	Base Oil+3% pentaerythritol monooleate.....	200+

From these data (Test No. 17) it appears that a long chain pentaerythritol monoester having also a short chain partial esterification retains its inhibiting effect to a satisfactory degree.

Example III

Petrolatum of 165° F. melting point was tested as follows:

Test No.		Hours
19	Petrolatum.....	72
20	Petrolatum+1% pentaerythritol monooleate.....	200+
21	Petrolatum+1% di(pentaerythritol monooleate).....	200+

Example IV

Diocetyl sebacate, an ester which is known to have good lubricating qualities, was tested with results as follows:

Test No.		Hours
22	Diocetyl sebacate.....	1
23	Diocetyl sebacate+3% trimethylol propane.....	200+
24	Diocetyl sebacate+3% B-hydroxyethyl ether of pentaerythritol monooleate.....	200+
25	Diocetyl sebacate+1% degreas and 1% sodium sulfonate.....	24
26	Diocetyl sebacate+1% degreas, 1% sodium sulfonate and 1% pentaerythritol monooleate.....	214

Other synthetic lubricants such as the dibasic acid esters (e. g., sebacates, adipates, etc., for example, di-2-ethyl hexyl sebacate), the polyether synthetic oils and the like may be successfully inhibited in a similar manner. The degreas and sulfonate type inhibitor which is not very satisfactory per se for synthetic oils, is materially improved by adding the polyhydric alcohol partial ester.

Example V

The synergistic action of pentaerythritol monooleate and the sulfonates is further illustrated and emphasized by the following:

Mineral oil of 120 S. S. U. viscosity at 210° F., having a viscosity index of about 105, being of the same general specifications as the oil of Example I but taken from an entirely different supply, was subjected to the following humidity cabinet tests with the various inhibitors indicated:

Test No.		Hours
27	Base Oil.....	Less than 1.
28	Base Oil+0.5% calcium sulfonate.....	Less than 24.
29	Base Oil+0.5% sodium sulfonate.....	Less than 24.
30	Base Oil+1% calcium sulfonate.....	24-48.
31	Base Oil+1% sodium sulfonate.....	24-48.
32	Base Oil+0.5% pentaerythritol monooleate.....	Less than 24.
33	Base Oil+0.5% pentaerythritol monooleate and 0.5% calcium sulfonate.....	200+
34	Base Oil+0.5% pentaerythritol monooleate and 0.5% sodium sulfonate.....	200+
35	Base Oil+1.5% pentaerythritol monooleate.....	48.
36	Base Oil+1.5% pentaerythritol monooleate and 0.5% calcium sulfonate.....	412.
37	Base Oil+1.5% pentaerythritol monooleate monoacetate.....	100.
38	Base Oil+1.5% pentaerythritol monooleate monoacetate and 0.5% sodium sulfonate.....	300+

Although the above results show some divergence from the tests of Example I, being taken at a different time with oils and other materials from different batches, the remarkable synergistic effect of the sulfonates, employed in small quantities, with varying amounts of the partial esters of pentaerythritol are manifested in the above data. The monooleate monolactate ester shows good results which further justify the conclusion mentioned previously that the mixed partial esters, where one esterifying group is a short chain group, may be quite as useful as the monoesters, in some cases at least. In this example, total quantities as low as 1% of sulfonate and partial ester were highly effective.

By adding wool grease (degreas) to any of the above compositions, an excellent rust-proofing coating composition may be prepared. A light hydrocarbon solvent may be used in lieu of lubricating oil. The use of degreas for giving body to a rust preventive composition is well known per se as shown in the Lebo patent mentioned above but in combination with the ester, and especially with a small amount of ester and sulfonate, the rust-proofing properties are outstanding. The proportions may vary, but about 0.5 to 3% of the ester, 0.5 to 10% of sulfonate and

2 to 15% degreas by weight, preferably about 10%, based on the finished composition, are quite suitable. The remainder of the composition in any case is preferably a petroleum base and may be a solvent which evaporates, such as Stoddard's solvent, or an oil of lubricating grade, e. g., mineral oil base of 35 to 1000 S. S. U. at 210° F. viscosity, or a petrolatum. Paraffin wax or various other waxes, such as those of animal or vegetable origin, may be added where a heavier residual coating is needed.

Even with as long an esterifying chain as the oleic radical, the solubility of the partial esters may not be too good in some oils or hydrocarbon solvents. The use of the sulfonates, which are highly oil soluble, makes it possible to obtain the required rust inhibiting properties with the small quantities of the partial esters which will readily dissolve. The oil solubility of the partial esters may be improved by esterifying an additional hydroxyl group on the polyhydric alcohol with a short chain acid such as lactic acid, or acetic acid, or by etherification with a short chain alcohol radical, by conventional methods.

It will be noted that it is desirable that the ester shall (1) be soluble in the proportions used, and (2) have one and preferably two or more unesterified hydroxyl groups. These properties are somewhat incompatible, hence it is desirable either to improve oil solubility by further partial short chain esterification (which reduces the number of free hydroxyl groups on the polyhydric alcohol) or, which is preferable, to supplement the inhibiting effect of the partial ester, which is limited in effectiveness by its limits as to oil solubility, by using a synergistic inhibitor selected from the metal sulfonates, preferably calcium and/or sodium sulfonate. As with previous examples, degreas, wax, and the like may be added where a residual coating is desired after the hydrocarbon oil or solvent has evaporated.

Example VI

An excellent hydraulic oil which passed the rather severe U. S. Air Forces test AN-0-7 for airplane rust preventive hydraulic fluids was prepared using as a base oil an oxidation inhibited mixture of substantially equal parts of highly acid treated Coastal (naphthenic) gas oil and a phenol and acid treated naphthenic transformer oil of about 60 S. S. U. viscosity at 100° F. This oil contained a small amount of a commercial viscosity index improver of the acrylate polymer type in order to raise the index to about 130. 0.2% 2,6-butyl 4-methyl phenol was used as the oxidation inhibitor in the base oil. The base oil had a viscosity of about 43 S. S. U. at 100° F.

To 94 parts by weight of the above oil, there were added 6 parts of a commercial 50-50 oil solution of sodium sulfonate, thereby incorporating about 3% of the sodium sulfonate in the oil. Calcium sulfonate can be used if desired. To this was further added 0.5% of pentaerythritol monooleate and a further quantity, about 0.2%, based on the total composition, of the alkylated phenol oxidation inhibitor mentioned in the preceding paragraph, thus raising the oxidation inhibitor content to about 0.4%.

In general, 90 to 98 parts by weight of a light mineral oil or synthetic oil of low viscosity such as 35 to 100 S. S. U. at 100° F. and of high viscosity index, 100 to 150 or more, may be combined with 1 to 7% of oil soluble sulfonate of alkali or alkaline earth metal, especially sodium

or calcium or a mixture, 0.2% to 3% of pentaerythritol monooleate, about 0 to 1% of oxidation inhibitor and 0 to 1.0% of viscosity index improver.

While numerous esters of complex alcohols have been proposed in the prior art as additives for lubricating oils, including some of the pentaerythritol esters, esters of hexitols, and the like, the specific combination of a small amount of long chain acid partial ester of a tri- or tetrahydroxy alcohol, especially pentaerythritol monooleate or its equivalent, with or without addition of short chain ester or ether groups, with a small amount of an oil soluble alkali or alkaline earth metal sulfonate as a potent rust inhibitor in mineral base oils, petrolatum and the like, for lubricating and/or coating ferrous metal surfaces characterizes the present invention. The range of proportions may be from about 0.1 to about 10% of the ester and a similar range for the sulfonate, based on the total composition. For lubricating oil compositions, the narrower limits of 0.5% to 3% of each are specifically preferred since larger quantities of ester are commonly insoluble and larger quantities of the sulfonate are commonly unnecessary. Quantities of either, smaller than 0.5%, are useful but less effective. The mixed esters of low molecular weight carboxylic acids and long chain acids also may be used as previously indicated.

It will be understood that other conventional ingredients, such as fats, waxes, oiliness agents, emulsifiers, adhesive materials, thickeners, antioxidants, viscosity index improvers, and the like may be added as may be required for coating compounds, lubricating oils and greases, cutting oils, soluble cutting oils, slushing oils and the like.

What is claimed is:

1. A rust inhibiting oil composition consisting essentially of a mineral base oil of lubricating grade containing 0.5 to 3%, based on the total composition, of a mono-oleic ester of pentaerythritol, 0.5 to 3% of an oil soluble petroleum sulfonate selected from the class which consists of sodium and calcium sulfonates, and 0 to 1% of degreas.

2. Composition according to claim 1 in which the monooleic ester of pentaerythritol also contains one lower carboxylic acid esterifying group of not more than 4 carbon atoms in chain length.

3. A rust inhibiting composition consisting essentially of a mineral base oil of lubricating grade containing 0.5 to 3% by weight of pentaerythritol monooleate and 0.5 to 2% of oil-soluble calcium petroleum-sulfonate.

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