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CORROSION PREVENTIVE COMPOSITIONS

Raymond L. Mayhew, Phillipsburg, N.J., and Charles F. Jelinek, Delmar, N.Y., assignors to General Aniline & Film Corporation, New York, N.Y., a corporation of Delaware

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The present invention relates to corrosion preventive compositions particularly adaptable for protecting metal surfaces.

It is known that not only moisture but corrosive fluids, gases, etc. readily attack metallic surfaces and cause corrosion, rusting, and other damage to such surfaces. This problem is serious where liquid petroleum hydrocarbons are employed, such, as, for example, lubricating oils in internal combustion engines, diesel engines, aircraft engines, turbines and various other machinery and industrial equipment. The damage thus caused is not to the metal surface alone, for rust particles frequently break off and enter the circulating system of engines and cause plugging, clogging and fouling of conduit lines, columns and the like which are very susceptible to corrosion and must be protected.

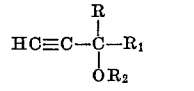
To protect metal surfaces in contact with corrosive contaminants with a composition which is stable and readily miscible with liquid petroleum hydrocarbons constitutes the principal object of the present invention.

Another object is to form film-forming metal protective compositions which possess lubricating properties.

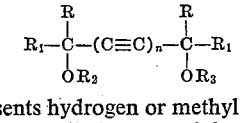
A further object is to provide an oily rust preventing composition comprising a liquid petroleum hydrocarbon having incorporated therein an active amount of a rust inhibiting ingredient.

Other objects and advantages of the invention will become more clearly manifest from the following description.

We have found that various metals which are subject to rusting and corrosive influence when in contact with liquid petroleum hydrocarbons, whether crude or refined, can be protected from such influence by incorporating into the liquid petroleum hydrocarbon a rust inhibiting amount of a fatty acid ester of an acetylenic alcohol containing from 3 to 28 carbon atoms. Such esters are characterized by the following general formulae:



and



wherein R represents hydrogen or methyl group, R_1 represents hydrogen or an alkyl group of from 1 to 6 carbon atoms, e.g. methyl, ethyl, propyl, butyl, pentyl, hexyl, R_2 represents an acyl group of from 10 to 34 carbon atoms, R_3 represents ether hydrogen or acyl group of the same value as in R_2, and n represents 1 or 2.

The esters characterized by the foregoing general formulae are readily prepared in the usual manner by esterifying either propargyl alcohol, 2-butyne-1,4-diol, butyne-3-ol-2; 1,4-dimethyl-butyne-2-diol-1,4; 2-methyl-butyne-3-ol-2; 2,5-dimethylhexyne-3-diol-2,5; n-hexyne-5-ol-4; n-nonyne-8-ol-7; n-hexadecyne-8-diol-7,10; or 2,4-hexadiyne-1,6-diol with a fatty acid or a fatty acid chloride containing from 10 to 34 carbon atoms. The nature of the fatty acid or fatty acid chloride is immaterial and may be of the saturated or unsaturated branch or unbranched type and contains at least 10 carbon atoms in its molecular structure. For the purpose of the present invention, we prefer to form the esters by esterifying 1 mol of the acetylenic alcohol with 1 mol of an acyl halide containing from 10 to 34 carbon atoms in the presence of an acid acceptor, such as pyridine in the conventional manner. Acyl halides which may be used are those that are derived from lauric acid, tridecylic acid, myristic acid, pentadecylic acid, palmitic acid, margaric acid, stearic acid, undecylic acid, behenic acid, tetracosanic acid, oleic acid, elaidic acid, erucic acid, brassidic acid, linoleic acid, stearolic acid, behenolic acid, melissic acid, psyllostearic acid, and the like.

In addition to the foregoing acids which may be converted to the corresponding acid chlorides, the following acids may also be employed in the form of their acid chlorides—tall oil acid, hydrogenated tall oil acids, naphthenic acids, abietic acids; alkyl benzoic acids such as dodecylbenzoic acid, nonylbenzoic acid, octylbenzoic acid; acids from oxo alcohols and aldehydes; acids from oxidized petroleum fractions; acid mixtures from various natural plant and animal oils such as oilve, tallow, palmitic, castor, peanut, coconut, soybean, cottonseed, ucuhuba, linseed; fish oils such as cod, herring, menhaden, etc.; neat's-foot, spern, palm, corn, babassu, kapok, hempseed, mustard, rubberseed, rape, safflower, sesame, etc.

The esters characterized by the foregoing general formulae when incorporated into liquid petroleum hydrocarbons inhibit the rusting of ferrous metals in contact with such hydrocarbons.

The corrosion preventing compositions utilized in accordance with the present invention are employed in all liquid petroleum hydrocarbons and mixtures thereof, and include crude oil, crude oil fraction and derivatives thereof such as gasolene, kerosene, gas oils, petroleum naphtha, petroleum naphtha cuts, mineral spirits, mineral seal oil, benzene, cumene, butylbenzene, paraffins, e.g. hexane, octane, nonane, decane, etc. and mixtures thereof, cycloparaffins, e.g. cyclohexane, isopropyl cyclohexane, n-butyl cyclohexane, etc. and mixtures thereof, chlorinated kerosene transformer oils, diesel oils, cutting oils, lubricating oils and the like, whether in the crude or refined form.

The fatty acid esters of the aforementioned acetylenic alcohols are soluble in all of the aforementioned liquid hydrocarbons to the extent of rust inhibiting amounts which for practical purposes may range from 0.5 to 5% by weight of the liquid petroleum hydrocarbon.

The corrosion preventive composition is incorporated into the liquid petroleum hydrocarbon in corrosion inhibiting amounts, of the aforestated range, and the mixture may be heated if desired in order to hasten the dissolution. Such mixtures exhibit outstanding corrosion inhibition in the presence of steel drums, storage tanks, and in the presence of ferrous metals under severe rust producing environment as will be noted from the following working examples.

The unusual feature of the corrosion inhibiting substance utilized in accordance with the present invention is that when used with gasolenes, diesel oils and other fuels for internal combustion engines they leave no residue upon ignition.

The following examples will illustrate the manner in which the aforementioned mono esters are utilized in the preparation of stable corrosion preventive compositions, It is to be clearly understood however, that these examples are merely illustrative and are not intended in any way to limit the scope of the invention claimed.

The method utilized in the determination of the rust inhibiting properties of the aforementioned esters is that described by H. R. Baker et al. in Industrial and Engineering Chemistry 41, pages 137–144 (1949).

Example I

A 2% solution and a 0.5% solution were prepared of the monoleate of 2-butyne-1,4-diol in an oil of the type used in the lubrication of internal combustion engines. Each solution as well as the untreated oil was subjected to the static drop test of Baker, Jones and Zisman referred to above. While rusting occurred within a few hours with the untreated oil, the treated oil protected the steel both at 2% and 0.5% concentrations. An inspection after several days showed no traces of rust in the treated oil.

Example II

The solutions of Example I were used to protect steel turnings as follows:

The turnings, as produced, were allowed to fall into the solutions. Then the turnings were drained for a matter of hours. The turnings were then put into a corrosion environment which periodically cycled through 100% relative humidity at about 55° C. Untreated oil allowed rusting to occur in a few hours, the treated oils allowed only traces of rusting in two weeks.

Example III

A solution of 0.5% oleic ester of propargyl alcohol in a high boiling (90°–100° C.) petroleum ether was used to protect steel turnings in the same manner as Example II. While untreated petroleum ether allowed rusting to occur overnight, the treated petroleum ether allowed, in one case, only 10% of the chips show visible rust after three days, and in another case, no rust was visible at three days.

Example IV

2% and 0.5% solutions in petroleum ether were prepared of EPW 3530–173, the monooleate of 2,4-hexadiyne-1,6-diol. These solutions were tested in the manner of Example II. After six days in the corrosive environment, only 10% of the turnings exhibited some rust.

Example V

A product of Emory dimer acid, produced by polymerization of naturally occurring unsaturated fatty acids with a molecular weight of approximately 600 and having the following characteristics:

Acid value, mg. KOH per gram	min.	180
Saponification value, per gram	min.	180
Neutralization equivalent		289–304
Dimer content	percent	75
Trimer content	do	22
Monomer content	do	3
Sp. gr., 15.5° C./15.5° C.		0.95
Viscosity at 25	centistokes	10,000

was completely esterified with propargyl alcohol and tested as Example II At 2% concentration, after six days, 5% of the turnings exhibited rust, and at the 0.5% concentration only 10% of the turnings exhibited some visible rust after four days.

Example VI

A product of the esterification of 2-methyl-3-butyn-2-ol and oleic acid was dissolved in petroleum ether at 0.5%, and the resulting solution tested as Example II. At the end of six days, only 10% of the chips exhibited some rust.

Example VII

The ester of Example VI was dissolved in 2% lubricating oil and tested as Example II. At the end of four days, only 10% of the chips exhibited visible signs of rust.

Example VIII

The compound, 2,4-hexadiyne-1,6-diol, was completely esterified using two mols of oleic acid. The resulting product was tested as Example I. At the end of two days, no signs of rust were visible at either concentration.

Example IX

The compound of Example VIII was tested as Example II using 0.5% dissolved in petroleum ether. After 10 days only 5% of the turnings had visible signs of rust.

Example X

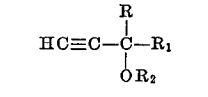
The compound of Example VIII was dissolved in lubricating oil at 2% and 0.5% and tested as Example I. At the end of two days there were no traces of rust.

Example XI

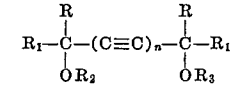
The compound of Example VIII was tested in lubricating oil solution (2% and 0.5%) as Example II. At the end of 3 days the 2% solution had resulted in no rust. At the end of 6 days the 0.5% solution had resulted in only 10% of the chips exhibiting some rust.

We claim:

1. A corrosion preventing composition consisting essentially of a major proportion of a liquid petroleum hydrocarbon and a corrosion inhibiting amount of an acetylenic alcohol fatty acid ester selected from the group consisting of esters of the following general formulae:



and



wherein R represents a member selected from the group consisting of hydrogen and methyl, R_1 represents a member selected from the group consisting of hydrogen and alkyl of from 1 to 6 carbon atoms, R_2 represents an acyl group of from 10 to 34 carbon atoms, R_3 represents a member selected from the group consisting of hydrogen and an acyl of from 10 to 34 carbon atoms, and *n* represents a positive integer of from 1 to 2.

2. A corrosion preventive composition according to claim 1 wherein the acetylenic alcohol fatty acid ester is monooleate of 2-butyne-1,4-diol.

3. A corrosion preventive composition according to claim 1 wherein the acetylenic alcohol fatty acid ester is monooleate of propargyl alcohol.

4. A corrosion preventive composition according to claim 1 wherein the acetylenic alcohol fatty acid ester is monooleate of 2,4-hexadiyne-1,6-diol.

5. A corrosion preventive composition according to claim 1 wherein the acetylenic alcohol fatty acid ester is monooleate of 2-methyl-3-butyne-2-ol.

6. A corrosion preventive composition according to claim 1 wherein the acetylenic alcohol fatty acid ester is dioleate of 2,4-hexadiyne-1,6-diol.

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