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2,904,415

NON-CORROSIVE PETROLEUM DISTILLATES

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This invention relates to non-corrosive petroleum distillates, and particularly to a method for the prevention of corrosion occasioned by petroleum distillate fuels under conditions of storage and transportation wherein water, containing large amounts of dissolved solids, is present.

Petroleum distillates, when stored or transported in pipelines in the presence of water having relatively large amounts of dissolved solids contained therein, tend to severely corrode the metal containers in which they are contained. Large storage tanks and the storage compartments of tankers are readily subject to attack. The most offensive petroleum distillates are those having an end point of below 800° F. and particularly the distillates having an API gravity of at least 45. Such products are fuel oils, naphthas, kerosene and gasoline. In refinery storage tanks corrosion generally occurs either on the metal in contact with the water layer at the bottom, or on the metal in contact with the vapor phase at the top. With tankers, severe attack occurs because of alternate exposure to distillate fuels, air and sea water.

Gasoline under storage conditions is generally in contact with water. This water may come from several sources viz, leakage into the container, condensation and entrainment.

In ocean going storage tankers the water contacting the petroleum distillates is high in dissolved oxygen and salts. The practice of cleaning empty compartments with hot sea water under pressure places a residue of salts on the surface of the metal walls, which are subsequently dissolved by water-petroleum mixtures.

It is an object of the present invention to provide a petroleum distillate which is non-corrosive to metal containers in the presence of waters containing high dissolved solids.

Another object is to prevent the corrosion of storage tanks, compartments of tankers and pipelines which contain petroleum distillates in the presence of water containing high dissolved solids.

A further object is to prevent the corrosion of storage tanks and compartments of tankers which contain petroleum distillates having an API gravity of at least 45 in the presence of water containing high dissolved solids.

Another object is to prevent the corrosion of ferrous metals by petroleum distillates in the presence of water containing high dissolved solids by providing corrosion inhibiting materials which are effective in low concentrations and which do not adversely effect the petroleum distillates.

Still another object is to prevent the corrosion of metal containers which store gasoline-sea water mixtures. Other objects will appear hereinafter.

In accordance with this invention it has been found that corrosion caused by petroleum distillates, particularly gasolines, which are in contact with water having high dissolved solids, may be prevented by the use of small amounts of a polymerized fatty acid in conjunction with an organic wetting agent capable of lowering

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the surface tension at the interface between the petroleum hydrocarbon distillate and water.

By using the combination of polymerized fatty acid with a wetting agent of the type described, it is possible to obtain corrosion protection by using as little as 2.5 p.p.m. of the acid. The ratio of wetting agent to acid may be from 1:3 to 3:1 with the preferred range being about 1:1. In practice it may be necessary to increase the dosage of the acid to about 400 p.p.m. but generally between 2.5 to 50 p.p.m. will give adequate protection in most cases. It will be noted, however, that in some instances the use of excessive amounts of the inhibiting combinations will produce detrimental results. Routine experimentation can determine optimum dosages.

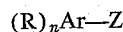
The polymerized fatty acids are well known and have been described in numerous publications. Perhaps the best description of these materials is given in Industrial and Engineering Chemistry, 32, p. 802 et subs (1940). These materials are composed primarily of dicarboxylic acids derived from the bimolecular addition of unsaturated fatty acids. The polymers are formed by an olefinic polymerization of fatty acids which contain at least two unsaturated linkages. These acids are available from commercial sources. Typical properties of two of these materials are given below in Table I:

TABLE I

	Composition I	Composition II
Acid value.....	180 Min.....	150
Saponification value.....	185 Min.....	172
Unsaponifiable matter, percent.....	2.0 Max.....	3.7
Neutralization equivalent.....	290-310.....	
Color, gardner.....	10 Max.....	
Iodine No.....		36
Moisture content, percent.....		0.86

These commercial acids are not pure, but the dicarboxylate polymers which predominate contain about 34-36 carbon atoms. Composition II is a polymerized acid and is a by-product from the caustic fusion of castor oil in the manufacture of sebacic acid.

Specific classes of wetting agents useful in the invention are compositions having the following general structure:



wherein R is an alkyl radical having at least two carbon atoms and preferably not more than 32. n is a small whole number not greater than 3. Ar is a carbocyclic structure from the group consisting of aromatic and polyaromatic radicals. Z is a nuclear substituent of Ar from the group consisting of:

- Alkali metal sulfonate groups.
 - Alkali metal salts of sulfonated phenols.
 - Polyoxyethylene glycol ether groups containing from 3-15 ethoxy groups and preferably 5-9.
 - The alkali metal sulfonates of C.
- In the above and hereinafter, the expression alkali metal is also meant to include ammonium.

Wetting agents which fall within A, above, are the petroleum sulfonates or mahogany acid salts. In this instance R would be an alkyl group of varying length, being either straight or branched chained. The aryl nucleus would be predominantly phenyl but might contain other polynuclear aromatic groups such as naphthalene, anthracene, phenanthrene and derivatives thereof. It is preferred to use a petroleum sulfonate having a molecular weight of 400 or more.

A mahogany acid salt that has given good results is a commercial product containing hydrophilic oleophilic components and is primarily oil soluble; however, it dis-

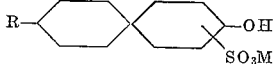
perses in water. The typical characteristics of the sodium salt of this mahogany acid are:

Sulfonates	42
Mineral oil	54
Inorganic salts	Trace
Water	4
Free alkalinity	None
Fural viscosity at 210° F.	55
Molecular weight	400-415

The material is supplied as the sodium salt and in this form is excellent for the purposes of the present invention.

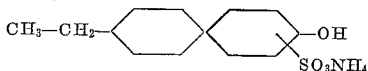
Other alkyl aryl sulfonates that can be used are the sulfonated alkyl benzenes. In a similar fashion the sulfonated alkylated naphthalenes can also be used.

Type B wetting agents are the specific class of compounds having the formula:



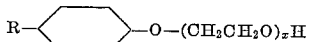
wherein R is a short chain alkyl group preferably having not more than ten carbon atoms. M is alkali metal.

A compound that has shown particular effectiveness is the ammonium salt of monoethylphenyl phenol sulfonic acid having the probable structural formula:



A commercial grade of this material contains about 25-50% water.

The wetting agents of type C are formed by the reaction of an alkyl phenol with ethylene oxide. A class of commercial wetting agents which have proven useful have the general formula:

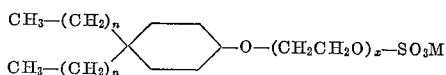


wherein R is an alkyl radical preferably having from about 4 to 18 carbon atoms and x is an integer having the value, 3-15 and preferably 5-9.

The derivative wherein R is an alkyl group of 9 carbon atoms and x is about 5 has given excellent results. A typical product as supplied by the manufacturer has the following characteristics:

Active ingredient, minimum by weight..	95%.
Color, maximum	200 Pt-Co.
Odor	Mild, pleasant.
Cloud point (0.5% aqueous solution), min.....	55° C.
Specific gravity at 20/20° C.	1.0643.
Average weight per gallon at 20° C.	8.86 lb.
Fire point	590° F.
Solidification temperature, maximum	23° F.

Class D type wetting agents are those having the following structural formula:



Wherein n is an integer and x has the value previously shown. They may be considered as the metal sulfonates of Class C type.

EVALUATION OF THE INVENTION

In evaluating the inhibitors of the present invention a test procedure, which is described in detail below, was devised. This test is believed to give reproducible results and to simulate conditions which are often found in actual storage of gasoline. For convenience, and for purposes of uniformity in results, all the tests were run with a commercial non-leaded gasoline. The synthetic sea water used was prepared in accordance with ASTM (D665-52T). This test water was prepared by adding the following inorganic salts and acid to deionized water.

Inorganic Salts and Acid		Grams per liter
5	Sodium chloride.....	24.54
	Magnesium chloride . 6H ₂ O.....	11.1
	Sodium sulphate.....	4.09
	Calcium chloride.....	1.16
	Potassium chloride.....	0.69
	Sodium bicarbonate.....	0.20
	Potassium bromide.....	0.10
	Boric acid.....	0.03
10	Strontium chloride . 6H ₂ O.....	0.04
	Sodium fluoride.....	0.003

Procedure

Forty ml. of the hydrocarbon are introduced into a screw-cap tube. The desired amount of treatment is added. If the volume of the latter is too small to measure conveniently, a more dilute solution of the treatment may be made, preferably with the hydrocarbon under test. Not more than 1 ml. of treatment is used.

Four ml. of synthetic sea water which has been equilibrated with air is added, the tube capped and rotated end-over-end for six hours.

The entire contents of the tube are transferred to a test tube and the two phases permitted to separate. A mild steel, rod shaped specimen is attached to a hook in a cork and the position of the hook adjusted so that the specimen hangs with its lower end just above the bottom of the tube, but not in contact with any part of the container.

The tube is allowed to remain undisturbed for 72 hours. The specimen is then removed and examined.

Evaluation

If visual inspection reveals no rusting in duplicate tests, the treatment is considered to pass the test.

If both specimens from duplicate tests show rusting, the treatment is considered to fail the test.

If one specimen shows rusting, but not the other, tests on two additional specimens are made. If neither of these shows rusting, the treatment passes; if either shows rusting, the treatment fails.

The polymerized fatty acid, Composition II, was tested at varying concentrations. It was found the lowest dosage at which protection was afforded was about 1,000 p.p.m. At 750 p.p.m. corrosion was present on the specimens.

It was decided that perhaps the combination of Composition II, with other known corrosion inhibitors, and organic compounds would give protection not afforded by Composition II alone. Accordingly, the following materials were tested at 250 p.p.m. with 750 p.p.m. of Composition II; sodium nitrite, glassy sodium polyphosphate, mercaptobenzothiazole, sodium polyacrylate, lecithin, dibutyl phosphite and formaldehyde. Each of these combinations failed to give adequate protection to the specimens.

EXAMPLE I

Several preferred wetting agents were combined with Composition II, in the proportions shown below in Table II.

TABLE II

Wetting agent	Concentration of composition II, Table I in p.p.m.	Concentration of wetting agent in p.p.m.
Petroleum sulfonate (average molecular weight 400).....	125	375
70 Monoethylphenyl phenol ammonium sulfonate (50% by weight aqueous solution).....	50	25
Nonyl phenoxy tetraethoxy ethanol.....	150	50

The results of the tests were that all of the specimens passed with no evidence of corrosion being present.

EXAMPLE II

In this example the test method described above was used and also the ASTM test designation: D665-49T; issued 1942, renewed 1944, 1946, 1947, 1949, entitled "Rust Preventing Characteristics of Steam-Turbine Oil in the Presence of Water." The fuel used was a number 2 diesel fuel. A synthetic sea water was employed in both tests.

The formula under evaluation was as follows:

Composition	Percent by weight
Composition II.....	28.5
Monoethylphenyl phenol ammonium sulfonate (50% by weight aqueous solution).....	57.2
Butyl Carbitol.....	14.3

The above composition passed the first described test at 25 p.p.m. and the second described test at 50 p.p.m. It should be noted that when the concentration of the formula was raised to 1,000 p.p.m. it failed the first test.

For purposes of comparison varying amounts of Composition I were tested alone using the test method shown in Example I. Not until 1250 p.p.m. were reached was protection achieved.

EXAMPLE III

In this series of tests all of the wetting agents shown in Example I using the test method of Example I, were tested individually at 250 p.p.m. and afforded no protection to the specimens.

The wetting agent and polymerized fatty acid are sometimes desirably dissolved in a common solvent or carrier. The nature of the carrier must be such that it will readily blend the active ingredients into the petroleum distillate treated. Where mahogany acid salts are used, organic solvents such as kerosene, xylene and toluene give good results. Cellosolve and Carbitol solvents are good solvents for alkyl aryl sulphonated phenols. These solvents may be represented by the following general formula:



were R and R' are from the group consisting of acyclic hydrocarbon radicals having from 1-5 carbon atoms, phenyl and hydrogen with the proviso that R and R' are not both hydrogen. x is an integer having a value from 1-4. Several such compounds are ethylene glycol monomethyl ether, ethylene glycol monoethyl ether, ethylene glycol monobutyl ether, ethylene glycol ethylbutyl ether, ethylene glycol monophenyl ether, diethylene glycol monomethyl ether, diethylene glycol monoethyl ether and diethylene glycol monobutyl ether.

The corrosion inhibiting compositions may be advantageously combined with other chemical treatments for petroleum distillates. Especially good results are afforded when fuel oil stabilizers are used in conjunction with the composition of the invention.

The expression, "waters having high dissolved solids," refers to waters occurring in normal storage conditions under which petroleum distillates are kept. More specifically, it refers to waters having at least 1,000 p.p.m. of dissolved solids. The term "organic wetting agent" as used in this invention refers to compounds which are capable of lowering the surface tension between the interface of the petroleum distillate and water.

While gasoline and a No. 2 diesel fuel were used in the above examples, other hydrocarbon petroleum distillates may be rendered non-corrosive by using the inhibitors of the present invention. Kerosene, other diesel fuels and range oils are but a few. The dosages set forth may be used with these hydrocarbons and the results will be beneficial.

Having thus described our invention in its useful and novel aspects it is claimed as follows:

1. A non-corrosive petroleum distillate having an end point below 800° F., in contact with a corrosive water which contains at least 1,000 parts per million of dissolved inorganic salts, containing at least 2.5 parts per million of the combination of a polymerized fatty acid, containing at least two carboxylic acid groups per molecule and which is formed by the addition polymerization of fatty acids containing at least two olefinic linkages, and an alkylaryl substituted alkali sulfonate wetting agent from the group consisting of alkali metal petroleum sulfonates and monoethylphenyl phenol ammonium sulfonate with the ratio of organic wetting agent to polymerized fatty acid being from 1:3 to 3:1.

2. The composition of claim 1, where the petroleum distillate is gasoline.

3. The composition of claim 1, where the ratio of organic wetting agent to polymerized fatty acid is 1:1.

4. A non-corrosive petroleum distillate having an end point below 800° F., in contact with a corrosive water which contains at least 1,000 parts per million of dissolved inorganic salts, containing at least 2.5 parts per million of the combination of a polymerized fatty acid containing at least two carboxylic acid groups per molecule and which is formed by the addition polymerization of fatty acids containing at least two olefinic linkages, and the organic wetting agent, monoethylphenyl phenol ammonium sulfonate; with the ratio of organic wetting agent to polymerized fatty acid being from 1:3 to 3:1.

5. A non-corrosive petroleum distillate having an end point below 800° F., in contact with a corrosive water which contains at least 1,000 parts per million of dissolved inorganic salts, containing at least 2.5 parts per million of the combination of a polymerized fatty acid containing at least two carboxylic acid groups per molecule and which is formed by the addition polymerization of fatty acids containing at least two olefinic linkages, and an alkali metal petroleum sulfonate with the ratio of the alkali metal petroleum sulfonate to polymerized fatty acid being from 1:3 to 3:1.

6. The composition of claim 5 wherein the alkali metal petroleum sulfonate has an average molecular weight of at least 400 and the ratio of the alkali metal petroleum sulfonate to polymerized fatty acid is 1:1.

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