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# RUST INHIBITING COMPOSITION

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This invention relates to light petroleum distillate fractions having improved corrosion inhibiting properties. In particular, the invention relates to fuels containing as a corrosion inhibitor a small amount of a phenol substituted aliphatic carboxylic acid amide of an N-alkyl amine. By light petroleum distillates, I mean normally liquid petroleum distillates having a viscosity not exceeding that of petroleum gas oil.

Rust frequently occurs in light petroleum products pipe lines, storage tanks and equipment using the products because of traces of moisture inevitably present. For example, although gasoline is usually free of occluded moisture as it leaves the refinery, it may contain as much as 0.005 percent to 0.01 percent of dissolved moisture. Part of the dissolved moisture separates when the light oil product is chilled and settles as a separate liquid phase beneath the main body of oil. Water may also enter oil systems along with air through partially filled tanks provided with breather devices. As the tank cools, for example, at night, its contents contract and moisture-laden air is drawn in. This moisture condenses on the walls of the tank, settles to the bottom and dried air is expelled when the contents of the tank again warm up, as from the heat of the sun. Repetition of this cycle eventually leaves appreciable amounts of moisture at the bottom of the tank.

Contact of moisture with steel, in the absence of a corrosion inhibitor, results in the formation of rust. Thus, the presence of inevitable traces of moisture in fuels presents the problem that steel equipment contacted by the fuel will be rusted unless an inhibitor is present. As is obvious, the rust that forms permanently injures expensive equipment and there is additional loss in terms of replacement costs of such equipment and operating time lost during such replacement. For example, where rust forms on interior surfaces of pipe lines carrying petroleum products and no effort is made to prevent it, the rust formation can reduce carrying capacity of the pipe by more than 12 percent in one year. In addition to the decrease in life of rusted equipment such as storage tanks, pipe lines and the like, there is danger of trouble in engine operation from failure of fuel carrying equipment.

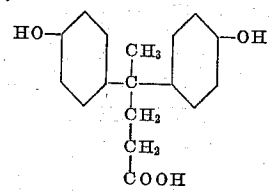
Although several methods have been proposed for preventing rusting in gasoline handling systems, each of these has rather obvious shortcomings. One method, for example, involves drying of the gasoline by absorption on dehydrated alumina before the gasoline is pumped into pipe lines. Another method involves the introduction into the fuel of chemicals such as mercaptobenzothiozole or hydrogen which react with dissolved oxygen and thereby arrest corrosion. Still another method involves the introduction of water-soluble corrosion inhibitors such as sodium nitrite or chromates. Each of these methods is disadvantageous as affording only temporary protection. Sodium nitrite applied to inhibit rusting in pipe lines is frequently decomposed by the action of oxidizing agents present in some crude oils. Hydrogen is quickly lost from vented storage tanks while water-soluble inhibitors are lost when they settle to the bottom of storage tanks and are drawn off. Water-soluble inhibitors are further deficient in many instances in not affording protection in the oil phase.

I have now found that certain carboxylic acid amides



are inhibitors when present in light petroleum distillate. The compositions of this invention incorporate a small amount sufficient to inhibit rusting of iron and steel (ferrous) surfaces, of a di(hydroxyphenyl)-substituted lower aliphatic carboxylic acid amide of an alkyl amine in the petroleum distillate which is the major portion of the composition. The acid amide is usually present in a concentration of about 1 to 100 pounds per 1000 barrels of fuel, preferably at least 10 pounds and not more than about 25 to 50 pounds per 1000 barrels of fuel. The fuels are well known materials and include gasoline, diesel fuel, kerosene, etc.

According to my invention, a small amount of the reaction product of an alkyl amine and a di(hydroxyphenyl) substituted lower carboxylic acid is added to the light petroleum fraction. The novel additive of this invention can be formed by the amidization of a phenol substituted carboxylic acid containing from 4 to 8 carbon atoms in the aliphatic chain containing the carboxyl group. Especially preferred is 4,4-bis(4-hydroxyphenyl) pentanoic acid,




The phenol group may also be substituted with alkyl or other groups which do not destroy the rust inhibiting effect.

These acids may be prepared by the method described by Zu and Day in the Journal of Organic Chemistry 23, pp. 1004–1006 (July 1958). Suitable acids are 3,3-bis(p-hydroxyphenyl) butanoic acid; 3,3-bis(3-methyl-4-hydroxyphenyl) butanoic acid; 3,3-bis(3,5-dimethyl-4-hydroxyphenyl) butanoic acid; 3,3-bis(3-methyl-4-hydroxyphenyl) pentanoic acid and 4,4-bis(3-monochloromethyl-4-hydroxyphenyl) pentanoic acid.

These acids have generally been found to be insoluble in petroleum products, and the number of the carbon atoms in the amine is usually from about 10 to 50 or more, preferably at least 28, to impart oil-compatibility, i.e. soluble, dispersible or miscible properties, to the final product. Primary or secondary amines can be used and I prefer that the amine have at least one alkyl group of at least 16 carbon atoms, e.g. 16 to 24, in a straight chain, most advantageously the amine has two such groups.

Some amines which can be used to supply the amide portion of the novel compounds of the invention are commercially available fatty amines such as: Armeen HT, a hydrogenated tallow amine comprising approximately 71% octadecyl, 24% hexadecyl, 3% octadecenyl and 2% tetradecylamines; Armeen HTD (distilled Armeen HT); Armeen O, a mixture of 85% oleyl, 6% linoleyl, 5% hexadecyl, 4% tetradecyl and 1% stearylamines; Armeen OD (distilled Armeen O); Armeen 18D, distilled octadecylamine; Armeen C, a mostly $C_{12}$ amine derived from cocoanut; Armeen CD (distilled Armeen C); Alamine H26D, another distilled tallow amine; Primene 81R, a mixture of branched chain amines containing 12 to 14 carbon atoms; and Primene JMT, a mixture of branched chain primary amines containing 18 to 21 carbon atoms. Secondary amines useable in this invention include those corresponding to the named primary amines, e.g. dioctedecylamine, dihexyldecylamine, dioleylamine, etc. Aliphatic primary diamines, such as those commercially available in the "Duomeen" series which have the requisite carbon content are also suitable materials for use in this invention. For example, Duomeen T, a hydrogenated reaction product of tallow amine and acrylonitrile having

a 32 to 50 iodine value and the structure

$$R—NH—CH_2—CH_2—NH_2$$

where R is an alkyl group of 16 to 18 carbon atoms obtained from tallow, may be used.

The additive is prepared by heating and stirring equimolecular quantities of the acid and appropriate amine with sufficient water entraining agent, such as xylene, to obtain a temperature of about 150 to 200° C. for say from about 10 to 25 hours. Boric acid may be used to increase the speed of the reaction. After the theoretical amount of water is removed, the water entraining agent is removed and the product needs no further purification.

The following examples are illustrative.

## EXAMPLE I

*(Sample -602)*

To a 3-liter round bottom 4-necked flask equipped with a thermometer, motor driven stirrer, reflux condenser, water trap and heating mantle were charged, 214 g. (0.75 mole) 4,4-bis(p-hydroxyphenyl) pentanoic acid, 400 g. (0.75 mole) dioctadecyl amine from hydrogenated tallow and 180 g. of xylene. The mixture was heated and stirred for 14 hours, removing the xylene meanwhile to raise the flask temperature to 200° C. A total of 16.5 cc. of water was obtained. The remainder of the xylene was then removed by heating the product to 225° C. while blowing it with nitrogen. The product weighed 580 g. and represented a 97% yield.

## EXAMPLE II

*(Sample -603)*

Into a 3-liter round bottom 4-necked flask equipped with a thermometer, motor-driven stirrer, reflux condenser, water trap and heating mantle were charged, 218 g. (0.75 mole) 4,4-bis(p-hydroxyphenyl) pentanoic acid, 400 g. 0.75 mole) dioctadecyl amine and 200 g. of xylene. The mixture was stirred and heated to 156° C. over 15 minutes. Fifty grams of xylene were then added and after cooling to 141° C., 12 grams of boric acid were added. Stirring and heating were continued. During the next 4.25 hours 13 cc. of water were obtained in the trap and the flask temperature rose to 154° C. During the next 5.5 hours, 245 cc. xylene and 28.5 cc. water were removed at a final flask temperature of 225° C. The remaining residual xylene was blown out with nitrogen. The product weighed 600 g. and represented a 99% yield.

The properties of the amide are shown in Table I.

| Amide Sample | Properties of the Amide | | Hydroxyl Value | Percent Yield | Percent Boron |
|---|---|---|---|---|---|
| | Saponification Number | Acid Number | | | |
| -602 | 8 | 6 | 131 | 97 | |
| -603 | 4.5 | 0.2 | 134 | 99 | 0.19 |

The inhibitor samples were added to distillate fuels and tested by a modification of ASTM test D665–47T: "Rust-Preventing Characteristic of Steam-Turbine Oil in the Presence of Water." In this modified procedure, a freshly-ground rust test coupon consisting of a ½-inch diameter by 5½ inch long mild steel rod is suspended in a 400-ml. beaker equipped with a stirrer and placed in a temperature controlled bath capable of maintaining the temperature at 100±1° F. The test fuel (350 ml.) is added and stirred for thirty minutes to allow rust



inhibitor to precoat the test specimen. Part (50 ml.) of the test fuel is then removed and 30 cc. of distilled water is added and the mixture stirred for 3½ hour test period. At the end of this period, the coupon is removed, dried with suitable solvents, inspected and rated according to the following scale.

A—No rust
B++—Trace of rust (covering a maximum of 0.25% of total surface area)
B+—Less than 5% of surface area covered by rust
B—5 to 25% of surface area covered by rust
C—25 to 50% of surface area covered by rust
D—50 to 75% of surface area covered by rust
E—75 to 100% of surface area covered by rust

The test conditions are substantially more severe than ordinary conditions encountered so the results give a clear indication of the effectivness of the inhibitor mixture.

TABLE II

| Sample No. | Corrosion Inhibitor Concentration No.,lbs./1,000 bbls. | Rating | |
|---|---|---|---|
| | | Diesel Oil | Gasoline |
| -602 | 10/1,000 | B | B+ |
| | 20/1,000 | B+ | |
| | 30/1,000 | B++ | |
| -603 | 10/1,000 | B | |
| | 20/1,000 | B++ | |
| | 30/1,000 | B++ | |
| Diesel Oil | | E | |
| Gasoline | | | E |

I claim:

1. A light, normally liquid petroleum distillate having a viscosity not exceeding that of petroleum gas oil into which has been incorporated an amount sufficient to inhibit corrosion of ferrous surfaces of a petroleum distillate compatible, N-di-alkyl, bis(hydroxyphenyl) carboxylic acid amide, wherein the carboxylic acid radical is in an aliphatic chain of 4 to 8 carbon atoms, each alkyl group of said N-di-alkyl group containing at least 16 carbon atoms.

2. The composition according to claim 1 wherein the N-di-alkyl is dioctadecyl.

3. The composition according to claim 1 wherein the acid amide is dioctadecyl 4,4-bis(4-hydroxyphenyl (pentamide.

4. The composition according to claim 1 wherein the amide is present in an amount of about 10 to 50 pounds per thousand barrels of distillate.

5. The composition of claim 1 in which the N-dialkyl group has up to about 50 carbon atoms.


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