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# RUST INHIBITED DISTILLATE PRODUCTS

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This invention concerns a method and composition for inhibiting the rusting characteristics of petroleum distillate products. The rust inhibitors employed in the invention are directly dissolved in the petroleum distillate in a manner substantially eliminating any rusting of ferrous surfaces in the presence of the distillate. The additives to be employed constitute a mixture of a soap of a hydrocarbon sulfonic acid with either a free alkyl phosphoric acid or a free cyclo-alkyl phosphoric acid or a soap of these acids. Mixed salts of the two constituents may also be employed. Particularly desirable product-soluble rust inhibitors of this class are the ammonium salts of petroleum sulfonic acid and an alkyl phosphoric acid.

A problem which has long existed in the handling and use of petroleum products is the rusting which frequently occurs in pipelines, storage tanks, engines, etc. Old as this problem is, effective means of meeting the problem have only been suggested in recent years. A good deal of technical consideration is now being given to the discovery of effective rust inhibitors for petroleum products. The rusting problem which occurs in storing and using petroleum products occurs as the result of traces of moisture inevitably present in petroleum distillates. Moisture finds its way into the distillates in a variety of ways. While water is not appreciably soluble in petroleum distillates traces of moisture are, in fact, dissolved in heating oil, gasoline, kerosene, etc. Again, it is impossible to prevent entrainment of moisture in such products during storage and handling. In this connection, for example, storage tanks are generally provided with breather devices to permit the intake and exhaust of air during atmospheric changes. As a result, cool, moisture-laden air is generally drawn into a storage tank at night, resulting in the condensation of moisture in the tank. A portion of this moisture is dissolved in or entrained in petroleum products when pumped from the storage tanks.

There have been a number of suggestions for overcoming the corrosion due to moisture carried by oil products. For example, a number of water-soluble rust inhibitors are known and have been employed. Use of water-soluble inhibitors is disadvantageous for several reasons, however. The inhibitor is largely lost when water is separated from oil products during handling so that the desired rust inhibition for remaining residual traces of water may be lost. Addition of water-soluble inhibitors to oil again necessarily requires addition of water to the oil which aggravates the problem intended to be solved. It is therefore a particular object of this invention to provide a rust inhibitor which is soluble in the oil product to be inhibited.

It may be observed that attempts have been made in the past to provide suitable oil-soluble rust inhibitors. The problem of providing such an inhibitor is complicated by a number of factors however. It is clearly necessary that the inhibitor should not degrade the oil product, and thus, should not decrease the octane number of a gasoline for example, and should not otherwise affect critical inspections of the oil products. In this connection a particular problem encountered with gasoline rust inhibitors



is the tendency of many inhibitors to discolor dyed gasolines. A more specific object of this invention therefore is to provide an oil soluble rust inhibitor which will suitably inhibit an oil product against rusting, while in no way affecting the critical inspections or characteristics of the oil product.

These objectives are satisfied in accordance with this invention by a two-component rust inhibitive composition. The makeup of this composition is based on the discovery that two particular classes of rust inhibitors are beneficially employed in combination to obtain rust inhibiting characteristics unobtainable by use of single components selected from either class of inhibitors. In other words the invention is based on the discovery of a synergistic action between two classes of rust inhibitors. In this combination one inhibitor constitutes a salt of a hydrocarbon sulfonic acid. As well known to the art, hydrocarbon sulfonic acids are oil-soluble sulfonic acids obtained by the sulfonation of a hydrocarbon oil. For example, in the course of white oil production, sulfuric acid is employed to treat a hydrocarbon oil. Reaction of the sulfuric acid with the hydrocarbon oil results in the formation of oil-soluble annd water-soluble petroleum sulfonic acids. The oil-soluble sulfonic acids are conventionally called mahogany sulfonic acids. Other sulfonic acids from different sources may be employed such as those of alkylated aromatics, e. g., polypropyl benzene or wax-alkylated toluene, or those formed by the sulfonation of wax. Salts or soaps of these acids are formed by reaction of a basic compound with the sulfonic acid and these soaps are to be employed in this invention. For example, an oil-soluble alkali metal or alkaline earth metal soap or mahogany sulfonic acid may be employed. The ammonium soap or mahogany sulfonic acid may be used advantageously. The ammonium soap is particularly desirable for use in this invention since this soap forms no ash when the oil product, in which the inhibitor is used, is burned.

The second constituent of the rust inhibiting composition of this invention is an alkyl or cyclo-alkyl phosphoric acid or a salt of an alkyl or cyclo-alkyl phosphoric acid. Consequently, as used herein, the terms "alkyl" and "aliphatic" include cyclo-alkyl and cyclo-aliphatic. These acids are preferably prepared by the reaction of $P_2O_5$ with an alcohol. The preferred alcohols to be reacted are the monohydric primary alcohols having 6 to 18 carbon atoms. While aliphatic alcohols of this character are preferred, aryl alcohols may also be employed. The reaction between $P_2O_5$ and the alcohol results in the formation of what may be called esters or acid-esters of phosphoric acid. Depending upon the reactant proportions and the reaction conditions, mono-, di-, or tri-alkyl phosphoric acids may be obtained. Practically the reaction product constitutes a mixture of the esters. For this reason this constituent of the rust inhibiting composition is best defined as the reaction product of $P_2O_5$ and an alcohol.

The two-component rust inhibiting composition may also be prepared by mixing a hydrocarbon sulfonic acid with an alkyl phosphoric acid and forming a mixed salt of these acids. As examples of this procedure, ammonia or sodium hydroxide may be reacted with the mixed acids to form mixed soaps of the sulfonic acid and alkyl phosphoric acid.

In order to obtain the desired synergism between the salt of hydrocarbon sulfonic acid and the alkyl phosphoric acid or its salt, these constituents should be combined in proportion ranging from about 1 to 0.5, to 1 to 12. A preferred synergistic combination of the two additives employs about 1 part of the soap of sulfonic acid and about 3 parts of an alkyl phosphoric acid or its

salt. In this identification of synergistic compounds, the ratios given are expressed on a weight basis.

Examples of suitable alkyl phosphoric acid soaps are mono-lauryl phosphoric acid, di-octyl phosphoric acid, di-2-ethyl-hexyl phosphoric acid, di-lauryl phosphoric acid, di-butyl phosphoric acid, mono-octadecyl phosphoric acid, cyclo hexyl phosphoric acid, methyl cyclo hexyl phosphoric acid, etc. Of these compounds, $C_8$ alkyl phosphoric acids are particularly preferred for use in this invention.

The combined rust inhibiting additives, in the ratios indicated, may be employed economically in petroleum products in the concentration of about ¼ pound per 1,000 barrels up to 25 pounds or more per 1,000 barrels. In this range of concentrations it is generally suitable and preferred to use a concentration of about 1 to 5 pounds of combined rust inhibitors per 1,000 barrels of product. Of course, in special circumstances where the primary function of the oil composition may be that of rust prevention, it is practicable and desirable to use higher concentrations of the combined rust inhibiting additives up to the limit of their solubility in oil. The oil products which may be successfully inhibited in this way may be defined as the distillate petroleum products. Thus, the oil product may constitute gasoline, kerosene, lubricating oil, heating oil, gas oil, etc.

In order to demonstrate the utility and benefits of this invention, the following examples are presented. In these a rusting test was employed which generally corresponds to A. S. T. M. test method D–665. This test was modified however, by lowering the temperature to 77° F. The test required stirring of a mixture of 300 cc. of oil product with 30 cc. of distilled water at 77° F. with a cylindrical steel rod immersed therein. At the end of 24 hours the rod was examined and rated in accordance with the amount of rust which had formed.

In a first series of tests which were conducted, the ammonium salt of petroleum sulfonic acid was employed as the first constituent of the rust inhibiting composition. The second constituent constituted the ammonium soap of the reaction product of phosphoric pentoxide and iso-octyl alcohol synthesized by the Oxo process. To obtain the phosphoric acid, 66 g. (0.5 mole) of phosphorus pentoxide was added portionwise with stirring to 260 g. (2 moles) of iso-octyl alcohol at about 60° C., following which stirring was continued for 2 hours at 60° C. The reaction product was heated to 140° C. and blown with nitrogen under reduced pressure for 4 hours to expel unreacted alcohol and water formed during the reaction. To prevent darkening the product during the heating period, a trace of tri-sodium phosphate may be added if desired. A stream of ammonia was passed into this reaction product that had been diluted with a solvent until ammonia was no longer absorbed. Excess ammonia was removed by blowing with nitrogen at elevated temperatures.

Rust tests were then conducted on a heating oil containing small portions of the constituents described. The heating oil employed had the following inspections:

TABLE I

*Inspections on heating oil*

| | |
|---|---|
| A. P. I. gravity | 29.1 |
| Color (R) | 1¾ |
| Carbon residue (10% bottoms) (percent) | 0.167 |
| Sulfur (percent) | 0.84 |
| Neutralization No. (mg. KOH/g.) | 0.00 |
| Olefins and aromatics (percent) | 48.0 |
| Bromine No. (cg. Br./ml.) | 9.5 |
| Distillation: | |
| Initial | 374° F. |
| 10% | 442° F. |
| 20% | 458° F. |
| 50% | 492° F. |
| 80% | 534° F. |



The data obtained from the rusting tests is indicated in the following Table II:

TABLE II

*Modified A. S. T. M. rust tests (24 hours at 77° F.)*

[Blends in heating oil.]

| Inhibitor | Active Ingredients Concentration | Extent of Rusting |
|---|---|---|
| Mixed Ammonium salt [1] | 1#/1,000 bbls. | None. |
| Ammonium salt of petroleum sulfonic acid. | 1#/1,000 bbls. | Heavy. |
| Ammonium salt of isooctyl phosphoric acid. | 1#/1,000 bbls. | Light. |
| No additive | | Heavy. |

[1] Two acids were combined and neutralized with ammonia.

It will be noted that as shown by these data that heating oil alone was characterized by heavy rusting under the conditions of the test. When one pound per 1,000 barrels of either of the ammonium salts were employed individually, rusting was still encountered. However, when using only 1 pound per 1,000 barrels of an equal weight proportion mixture of the ammonium salt of petroleum sulfonic acid and the ammonium salt of Oxo phosphoric acid, the rusting was completely eliminated.

Similar tests were then conducted employing the sodium salt of petroleum sulfonic acid and the free isooctyl phosphoric acid. The data obtained in rusting tests is shown in the following Table III:

TABLE III

*Modified A. S. T. M. rust tests (24 hours at 77° F.)*

[Blends in No. 2 heating oil.]

| Inhibitor (conc. in wt. percent) [1] | Extent of Rusting |
|---|---|
| 0.00025% isooctyl phosphoric acid | Heavy. |
| 0.0005% Sodium petroleum sulfonate | Heavy. |
| 0.000125% Isooctyl phosphoric acid+0.000125% sodium petroleum sulfonate. | Trace. |
| 0.000125% isooctyl phosphoric acid+0.000063% sodium petroleum sulfonate. | Very light. |
| None | Heavy. |

[1] 1#/1,000 bbls.=0.00033 wt. percent approximately.

Again it will be observed that the two additives in combination provided a synergistic effect in inhibiting rusting. The heating oil containing the combined additives in substantially smaller quantities than when employed in the individual tests exhibited appreciably less rusting.

Additional experiments were then conducted to determine the effectiveness of the synergistic rust inhibiting additives of this invention in other petroleum distillate stocks. The results of these experiments are given in Table IV:

TABLE IV

*Effect of rust inhibitors[1] in various base stocks*

[Modified A. S. T. M. rust test-24 hrs. at 77° F.]

| Base Stock | T. E. L. Content, cc./gal. | Boiling Range (°F.) | Rust Rating at Following Inhibitor Conc. (#/1000 bbls.) | | | |
|---|---|---|---|---|---|---|
| | | | None | 1# | 2# | 3# |
| Regular Gasoline | 1.75 | 100–425 | R-6 | R-4 | R-1 | R-1 |
| Premium Gasoline | 2.7 | 100–400 | R-4 | R-1 | R-1 | R-1 |
| 91/98 Aviation Gas | 4.0 | 100–330 | R-7 | R-6 | R-3 | R-1 |
| 115/145 Aviation Gas | 4.6 | 100–330 | R-7 | R-1 | R-1 | R-1 |
| Kerosene | | 300–550 | R-7 | R-1 | R-1 | R-1 |

[1] Inhibitor consists of ammonium salts of mahogany sulfonic acid and isooctyl phosphoric acid in 1/2 weight ratio.

Rating System:
R-1, No rusting.
R-2, Trace rusting.
R-3, Less than 5% surface rusted.
R-4, Between 5 and 50% of surface rusted.
R-5, Between 50 and 99% of surface rusted.
R-6, 100% of surface with light rust.
R-7, 100% of surface with heavy rust.

Finally, additional experiments were conducted in which varying proportions of the rust inhibiting constituents were employed in combination. The base stock employed in these tests was a commercial 100/130 aviation gasoline containing 4.0 cc. of tetraethyl lead per gallon. The rust inhibitor composition used was a mixture of the mixed ammonium salts of mahogany sulfonic acids and isooctyl phosphoric acid. The rust rating system employed was that set forth in Table IV. The results of rusting tests with varying proportions of the two inhibtor constituents are shown in Table V.

TABLE V

*Effect of varying the sulfonate to phosphate ratio*

[Modified A. S. T. M. rust test—24 hrs. at 77° F.]

| Wt. Ratio of Sulfonate to Phosphate | Rust Rating at Following Inhibitor Conc. (#/1000 bbls.) | | | | | |
|---|---|---|---|---|---|---|
| | None | 1# | 2# | 3# | 4# | 5# |
| 1/2 | R-7 | R-4 | R-4 | R-2 | R-1 | R-1 |
| 1/3 | R-7 | R-3 | R-2 | R-1 | R-1 | R-1 |
| 1/12 | R-7 | R-5 | R-5 | R-5 | R-5 | R-3 |

It will be noted from the data of Table V that rust inhibition was secured over the range of inhibitor proportions used. However, substantially better rust inhibition was obtained at sulfonate to phosphate ratios of 1/2 or 1/3 than at 1/12. Again, the data shows that more than about 3 pounds of inhibitor composition are preferably employed for 1000 barrels of product.

The combination additive exhibits an additional advantage in that in a concentrated oil solution the ammonium mahogany sulfonate prevents the crystallization of the ammonium isooctyl phosphate. The latter, by itself, tends to precipitate from an oil solution of 10% or higher concentration, whereas in the presence of the sulfonate, a 50% concentrate shows no crystallization. This ability to prepare concentrates is important in the manufacture, transportation and application of rust inhibiting additives.



The rust inhibiting additives of this invention are advantageously prepared for use by solution in an oil vehicle. The particular oil chosen for preparation of the inhibitor concentrate is chosen with regard to the product in which the concentrate is to be used; preferably having about the boiling range of the product.

What is claimed is:

1. A fuel composition comprising a petroleum distillate fuel and from 0,00008 to about 0.00825 wt. percent of a mixture of a soap of an oil-soluble petroleum sulfonic acid selected from the group consisting of sodium and ammonium petroleum sulfonates, and a compound selected from the group consisting of isooctyl phosphoric acid and an ammonium salt of an isooctyl phosphoric acid, the proportions of said petroleum sulfonate to said last-named constituent being in the range of from 1:0.5 to 1:10.

2. The composition of claim 1 in which said petroleum sulfonate is an ammonium petroleum sulfonate.

3. The composition of claim 2 in which the last-named constituent is an ammonium salt of isooctyl phosphoric acid.

**References Cited in the file of this patent**

UNITED STATES PATENTS

| | | |
|---|---|---|
| 2,080,299 | Benning | May 11, 1937 |
| 2,550,982 | Eberz | May 1, 1951 |
| 2,594,266 | Watkins | Apr. 22, 1952 |
| 2,632,694 | Watkins | Mar. 24, 1953 |
| 2,650,198 | Kronig | Aug. 25, 1953 |