

UNITED STATES PATENT OFFICE

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PREVENTION OF RUST

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This invention relates to preventing or retarding rusting, especially rusting due to water dissolved in or settled from light petroleum distillates, particularly gasoline. By light petroleum distillates, I mean petroleum distillates of a viscosity not exceeding that of gas oil.

Rust frequently occurs in gasoline pipe lines, storage tanks, and even in automotive equipment because of traces of moisture inevitably present in the gasoline. Although gasoline as it leaves the refinery is usually free of occluded moisture it may contain as much as 0.005-0.01% dissolved moisture. Part of this dissolved moisture separates when the gasoline is chilled and settles as a separate liquid phase beneath the main body of gasoline. Water may also enter gasoline systems along with air through partially filled tanks provided with breather devices. As such a 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 the next day. Repetition of this cycle eventually leaves appreciable amounts of moisture at the bottom of the tank.

I have discovered that the carboxy acids obtained by the oxidation of microcrystalline wax when present in light petroleum distillates, even in exceedingly small proportions, have the property of inhibiting the rusting of iron and steel surfaces, as in gasoline pipe lines, storage tanks, and automotive equipment. My invention, based on this discovery, thus involves the incorporation of a small amount of the carboxy acids obtained by the oxidation of microcrystalline wax in light petroleum distillates, particularly gasoline, whereby corrosion or rusting of iron or steel surfaces which come into contact with the distillate containing the carboxy acids is markedly inhibited or substantially prevented. The amount of the oxidized product included in the distillate may range from about .5 to about 50 pounds per thousand barrels of distillate, typical concentrations which have been found to be highly useful and to substantially prevent rusting or corrosion of steel surfaces when present in an all-purpose gasoline being from about 3 to about 9 pounds per thousand barrels. I have found that the incorporation of this material in gasoline has no noticeable effect on the lead susceptibility, induction period, octane number or gum formation, so that it has no adverse effect on the properties of the gasoline.

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The carboxy acids obtained by the oxidation of microcrystalline wax may be used in the form in which they are produced, or in purified, i. e., concentrated form; that is, in admixture with unreacted material as obtained from the oxidation reaction, advantageously after acid and water washing to remove the catalyst or the like, but without removal of unreacted wax; or in concentrated form, as, for example, as the overhead obtained by flash distillation of the acid-washed reaction product; or they may be used in saponified or neutralized form, e. g., as the metal, for example, sodium or calcium, ammonium, amine, e. g., triethanolamine, morpholine, cyclohexylamine, salts; or in the form of amides, e. g., as the amide obtained from triethylenediamine or the like. In each of these forms, the microcrystalline wax acids retain their capacity to impart substantial rust inhibition properties to the petroleum distillate in the small quantities of from about one-half to about 50 pounds per thousand barrels of distillate.

The carboxy acids used in accordance with the present invention are obtained by the oxidation of microcrystalline wax with the use of air or oxygen, or oxygen-enriched air as the oxidizing agent, advantageously with the use of a catalyst, for example, potassium permanganate in small quantities, for example, from about .1 to about 1%, and with the use of a small amount of oxidized product from the previous run as seed. Elevated temperatures substantially above 100° F. are used for the oxidizing with a reaction temperature in the range of about 230 to about 275° F. giving good results. The oxidation takes place over a prolonged period of time, for example, from about 40 to over 100 hours, with the degree of conversion of the wax to oxidized product, as determined, for example, by the saponification number of the reaction mixture, increasing with time. The oxidation proceeds more rapidly if oxygen or oxygen-enriched air is used in place of air but the character of the reaction product does not seem to change substantially. The oxidation may advantageously be carried out until the product has a saponification number in excess of 100 and usually in excess of 200, e. g., 260, but the effectiveness of the material in inhibiting rusting or corrosion when incorporated in light petroleum distillates, obtained on the basis of the oxidized material, does not seem to vary greatly as between products which have been oxidized to a saponification number but a little above 100 and products which have been oxidized to a substantially

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higher saponification number, for example, 260. The wax acids in general have a substantially higher saponification number than acid number, perhaps indicating the presence of lactones. Thus, typical products may have a saponification number of 221 with an acid number of 158, a saponification number of 150 with an acid number of 103, saponification number of 135 with acid number of 70, etc. The products have little unsaturation having iodine numbers ranging down from about 20 to almost 0.

The microcrystalline wax is a common article of commerce. These waxes are obtained from petroleum residues or petrolatum. They are generally regarded as containing some straight chain molecules and a large portion of both branched chain molecules and ring type molecules. Typical waxes have been shown by X-ray analyses to contain hydrocarbons in the C₃₄ to C₅₅ range.

The invention will be illustrated by the following specific examples but it is not limited thereto.

Example 1

Microcrystalline wax obtained from East Texas crude shown by X-ray analysis to consist of mixtures of hydrocarbons in the C₃₄ to C₅₅ range was oxidized after the addition of 0.15% potassium permanganate at a temperature of 110 to 130° C. by blowing with air at the rate of 165 liters of air per hour per kilogram of wax to a saponification number of 135. The product after acid and water washing (to remove potassium and manganese) had a saponification number of 135, an acid number of 70 and an iodine number of 10.3. When added to a gasoline of 76.5 octane number in proportions of 6 and 9 pounds per thousand barrels, this product effectively inhibited corrosion or rusting of steel surfaces in contact with the gasoline.

Example 2

An overhead product from the flash distillation of a crude microcrystalline wax oxidation product, distilled after acid and water washing, with a saponification number of 221, acid number 158, iodine number 21, when added to the same gasoline in proportions of 3, 6 and 9 pounds per thousand gallons effectively prevented corrosion or rusting of steel surfaces in contact with the gasoline.

Example 3

Another flash overhead product having a saponification number of 150, acid number 103 and iodine number 17.9, in proportions of 3, 6 and 9 pounds per thousand barrels of the gasoline effectively inhibited corrosion of steel surfaces in contact with the gasoline.

In each of the foregoing examples the addition of the acids derived by the oxidation of the microcrystalline wax to the gasoline had no appreciable effect on the octane number, lead susceptibility, gum formation or induction period of the gasoline.

Instead of adding the microcrystalline wax acids to gasoline or other light petroleum distillates as such, or in admixture with suitable diluents or solvents, the microcrystalline wax acids may be admixed with tetraethyl lead fluid, and added to the gasoline with it. Thus, where

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tetraethyl lead fluid is to be added to gasoline in proportions of 1 cc. per gallon, incorporation of about 2% of the microcrystalline wax acids in the tetraethyl lead fluid results in incorporation of about 3 pounds of the microcrystalline wax per thousand barrels in the gasoline. Inclusion of 4% of the acids in the tetraethyl lead fluid results in the incorporation of about 6 pounds per thousand barrels in the gasoline where the tetraethyl lead fluid is used at the rate of 1 cc. per gallon. When so incorporated in the tetraethyl lead fluid, the microcrystalline wax acids not only serve to impart corrosion or rust inhibition properties to the gasoline in which the tetraethyl lead fluid is finally incorporated, but also serve to effectively impart anticorrosive or anti-rusting properties to the tetraethyl lead fluid itself. It is well known that corrosion of equipment used for the storage or handling of tetraethyl lead fluid has presented a substantial problem, and when the present invention is practiced in such a way that the microcrystalline wax acids or a portion of them are added to the gasoline by inclusion in the tetraethyl lead fluid, not only are anticorrosive or anti-rusting properties imparted to the gasoline but at the same time the corrosion or rusting problems involved in the handling of the tetraethyl lead fluid are largely overcome.

I claim:

1. A light petroleum distillate to which a rust inhibiting property has been imparted by the incorporation of approximately .5 to 50 pounds per 1,000 barrels of distillate of an oxidized microcrystalline wax having from 34 to 55 carbon atoms per molecule which consists essentially of carboxy acids having a saponification number in excess of 100 and not exceeding 260, having an acid number within the range of about 70 to 160 and having an iodine number less than about 20.

2. The composition according to claim 1 in which said light petroleum distillate is gasoline.

3. A method of preventing the internal corrosion of iron and steel pipe lines, storage tanks and the like which comprises incorporating in a light petroleum distillate introduced thereinto approximately .5 to 50 pounds per 1,000 barrels of distillate of an oxidized microcrystalline wax having from 34 to 55 carbon atoms per molecule which consists essentially of carboxy acids having a saponification number in excess of 100 and not exceeding 260, having an acid number within the range of about 70 to 160 and having an iodine number less than about 20.

4. Method according to claim 3 in which said light petroleum distillate is gasoline.

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