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RUST INHIBITOR FOR GASOLINE

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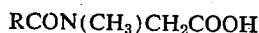
This invention relates to gasolines which contain improved rust inhibiting compositions.

The rusting problem presented in connection with gasoline occurs during the storage and/or transportation thereof. Rusting may occur in storage tanks, pipelines, tanker vessels, automobiles, etc. Any rust inhibitor which is added to the gasoline must not cause the formation of emulsions with water, which water is present in the storage tank, pipeline, tanker compartment, etc. and which causes the rusting to occur. The rust inhibitor must not be precipitated from the gasoline by the high pressures which occur in pipeline transportation. Also, the color of the gasoline must not be changed by the addition of the rust inhibitor, i.e. the rust inhibitor must not cause a color change by reaction thereof with the hydrocarbons, antioxidants, dyes, components of tetraethyllead, sulfur, etc. which might be contained in the gasoline. This color problem is particularly troublesome when a non-dyed gasoline free of tetraethyllead is involved. In addition, the rust inhibitor must not adversely affect the octane rating of the gasoline, must not effect the operation of effectiveness of the other gasoline additives, and must not cause the formation of excessive amounts of gum or sediment.

An object of this invention is to provide an improved rust inhibitor for gasoline. Another object is to provide a highly effective and inexpensive rust inhibiting composition for gasoline which does not adversely affect the other properties of the gasoline during storage, transportation, or use of the gasoline in combustion engines. Other objects and advantages of the invention will be apparent from the detailed description thereof.

It has been found that these and other objects can be achieved by incorporating in a gasoline an amount between about 0.0001 and 0.01 percent by weight of a rust inhibiting composition which consists of an acylsarcosine and a 1,2-disubstituted imidazoline. The rust inhibiting composition may also contain tall oil. For example, an approximately equimolar mixture of N-oleyl sarcosine and 1-hydroxyethyl 2-heptadecenyl imidazoline may be employed as the rust inhibiting composition. While each of the individual components mentioned does have some rust inhibiting properties, the effectiveness of the mixture of the two components is more than additive, i.e. a synergistic and beneficial effect is observed when the mixture is employed, which effect could not have been anticipated from the results obtainable with the individual components. When tall oil is added to the synergistic rust inhibiting composition, an additional synergistic effect in rust inhibition is also obtained by the three component mixture.

The acylsarcosine employed in the rust inhibiting composition is one which has the formula

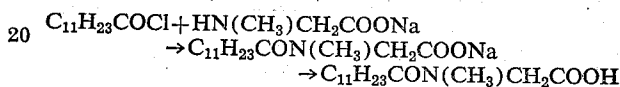


in which R is an alkyl radical having from 8 to 20 carbon atoms. The alkyl radical may be a saturated or unsaturated grouping having either a straight or branched

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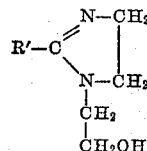
chain. Because the primary purpose of the R grouping is to impart oil solubility to the acylsarcosine molecule, its particular configuration and the exact number of carbon atoms contained in the R grouping are not of critical importance, provided it imparts oil solubility. Mixtures of various acylsarcosine can be employed, or the individual acylsarcosines may be used. Those acylsarcosines whose alkyl radical is derived from a natural fatty acid composition are very satisfactory. For instance lauroyl-, stearoyl-, oleyl-, cocyl- (from coconut oil), sarcosines may be used.

The acylsarcosines may be prepared by reacting the desired acylchloride (having from 8 to 20 carbon atoms) with the alkali metal salt of methyl aminoacetic acid (frequently methyl glycine or sarcosine) to form the alkali metal acylsarcosinate which may then be partially hydrolyzed to the desired acylsarcosine. The reactions which occur may be illustrated as follows:



The acylchlorides which may be used are those suitably derived from natural fatty acid compositions such as have been discussed previously.

The 1,2-disubstituted imidazoline which is used corresponds to the following structural formula:



In the formula, R' represents a hydrocarbon radical of 8 to 20 carbon atoms in length. It may be a saturated or unsaturated alkyl radical, having either a straight or branched chain. Since the primary function of the hydrocarbon radical represented by R' is to impart oil solubility to the molecule, the particular number of carbon atoms contained therein is not of critical importance. It is essential that the hydroxyethyl grouping be present in the disubstituted imidazoline.

The combined amount of the acylsarcosine and the disubstituted imidazoline which is added to the gasoline may be between 0.0001 and 0.01 percent by weight. This corresponds to a range of 1 p.p.m. to 100 p.p.m. Under severe rusting conditions such as occurs in seagoing tankers, amounts in the neighborhood of 0.001 to 0.003 percent by weight (10 to 30 p.p.m.) will be satisfactory. Under conditions less conducive to rusting, amounts in the range of about 0.0005 to 0.001 percent by weight can be used satisfactorily. The amount of 0.001 percent by weight is approximately 2½ lbs./1000 barrels of gasoline. While equimolar mixtures of the acylsarcosine and the disubstituted imidazoline are very satisfactory, a wide range of ratios of these two components may be employed. Thus, a molar ratio of from 0.1 to 10 mols of acylsarcosine per mol of disubstituted imidazoline may be contained in the rust inhibiting composition.

Tall oil, which has some rust inhibition properties of its own, can be employed in the rust inhibiting composition added to the gasoline. When it is employed together with the mixture of acylsarcosine and disubstituted imidazoline, it displays a synergistic and beneficial effect. It is attractive to use due to its low cost. It may be employed in the amount of about 1 to 10 mols per total number of mols of acylsarcosine and disubstituted imidazoline contained in the rust inhibiting composition. Tall oil, which consists of a mixture of saturated and unsaturated fatty acids, rosin acids, non-acid materials such as esters, lactones, estolides, alcohols, etc. is ob-

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 tained by acidifying the black liquor skimmings obtained from pulp wood in the sulfate (kraft) process. The manufacture, purification, composition, etc. of tall oil is described in the "Encyclopedia of Chemical Technology," volume 13, pages 572-7 (1954). Either crude tall oil or purified tall oil may be used. Typical whole tall oils have a color (Gardner) of 9-12, an acid number of about 155-185, a saponification number of about 158-185, an iodine number of about 140-210, fatty acids content of between about 35 and 55 percent, rosin acid content of 30 to 70 percent and an unsaponified content of between 4 and 12 percent. Fractions of whole tall oils such as contain 70 to 95 percent fatty acids, 1 to 4 percent rosin acid, and 2 to 5 percent of unsaponified materials are also satisfactory for use.

The acylsarcosine and disubstituted imidazoline (and the tall oil when desired) may be added separately or together to the gasoline. A very convenient way of incorporating the rust inhibiting composition within the gasoline consists of forming a gasoline concentrate containing between 1 and 50 percent by weight of the rust inhibiting composition. This concentrate may be heated, e.g. to a temperature of 100-175° F. (temperatures higher than 200° F. are believed to cause a reaction which reduces the effectiveness of the rust inhibiting composition).

The effectiveness of the acylsarcosine, the disubstituted imidazoline and the tall oil when each was employed individually as a rust inhibiting composition was determined. Tests were also carried out which show that a mixture of the acylsarcosine with the disubstituted imidazoline and a mixture of the acylsarcosine plus disubstituted imidazoline plus tall oil provided unexpectedly greater effectiveness than the effectiveness of the individual components would have predicted. The test procedure consisted of a standard ASTM D-665-54T rust test which as modified by employing synthetic seawater (to make the test much more severe) in place of distilled water, and carrying out the test at 80° F. rather than 140° F. because of the volatility of the gasoline. Basically, the test is carried out by stirring a mixture of gasoline and the synthetic seawater at 80° F. with cylindrical polished steel specimens at a stirring rate of about 1,000 r.p.m. for 20 hours. In order for a specimen to pass the test, it must not show a single rust spot or streak when subjected to 60-foot candles illumination. The effectiveness of the rust inhibitor is determined by repeating the tests with varying amounts of the inhibitor until the minimum amount of inhibitor necessary to pass the rust test is determined. A comparison of the minimum amounts of the different rust inhibitors necessary to pass the test shows the relative effectiveness of the different rust inhibitors.

The rust inhibitors were tested in a gasoline which contained no dye or tetraethyllead fluid. Oleyl sarcosine (sold under the trade name Sarkosyl-O), 1-hydroxyethyl 2-heptadecenyl imidazoline (sold under the trade name Amine-O), and tall oil (sold under the trade name Acintol FA-1) were individually tested in the modified ASTM rust test to determine the minimum amount of each component necessary to pass the rust test when the component was employed individually. The tall oil was a fraction of whole tall oil having the composition 92.5 percent fatty acids, 3.5 percent rosin acids, and 4 percent unsaponified material. An equimolar mixture of oleyl sarcosine and 1-hydroxyethyl 2-heptadecenyl imidazoline was heated to about 180° F. for one hour and the mixture was then tested to determine its rust inhibiting effectiveness. To a portion of this heated equimolar mixture was added 14.88 mols of the defined tall oil (7.44 mols of tall oil per mol of either the oleyl sarcosine or the Amine-O), and the resultant three component mixture was heated for an additional hour at about 180° F. This resultant three component mixture was then tested to determine its rust inhibiting effectiveness. The mini-

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 mum quantity (expressed as weight percent based upon gasoline) of the different rust inhibitors necessary in order to pass the rust test is shown in the table which follows:

Table

| 10 Run No. | | Concentration (Wt. Percent) Required to Pass Test |
|------------|--|---|
| 1----- | Oleyl sarcosine+disubstituted imidazoline ¹ | 0.003 |
| 2----- | Oleyl sarcosine+disubstituted imidazoline ¹ +tall oil | 0.0055 |
| 15 3----- | Oleyl sarcosine----- | 0.0055 |
| 4----- | Disubstituted imidazoline ¹ ----- | >0.5 |
| 5----- | Tall oil----- | >0.1 |

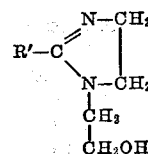
¹ 1-hydroxyethyl 2-heptadecenyl imidazoline.

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 Of the individual components tested in runs 3, 4, and 5, oleyl sarcosine is by far the most effective. Only 0.0055 percent is necessary to pass the rust test. More than 0.1 weight percent of tall oil and more than 0.5 weight percent of the disubstituted imidazoline are needed to pass the test when they are employed individually. Theoretically then, if the disubstituted imidazoline is added in an equal amount to the oleyl sarcosine, it would be expected that the total amount necessary to pass the test would lie half way between 0.0055 and 0.5 weight percent, i.e. about 0.25 weight percent should be necessary. Surprisingly, only 0.003 weight percent is needed to pass the test. This clearly demonstrates the synergistic effect obtained by using a mixture of the acylsarcosine and the disubstituted imidazoline. Similarly, if tall oil is added to a mixture of oleyl sarcosine and the disubstituted imidazoline, the expected additive type of effect would indicate that approximately 0.09 weight percent of this combination would be necessary in order to pass the test; whereas run No. 2 shows that only 0.0055 weight percent is needed.

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 While the invention has been described with reference to certain specific examples, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as would occur to one skilled in the art.

Thus having described the invention, what is claimed is:

1. A gasoline containing between about 0.0001 percent and 0.01 percent by weight of a rust inhibiting composition consisting of an acylsarcosine corresponding to the formula $RCON(CH_3)CH_2COOH$ and a 1,2-disubstituted imidazoline corresponding to the formula



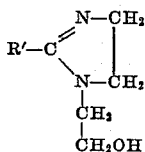
wherein R and R' are alkyl radicals having 8 to 20 carbon atoms, wherein the molar ratio of the acylsarcosine to the 1,2-disubstituted imidazoline is between 0.1:1 and 10:1, and said rust inhibiting composition having been subjected to heating to a temperature between about 100 to 200° F.

2. The composition of claim 1 in which the rust inhibiting composition contains tall oil in an amount between about 1 to 10 mols per mol of N-oleyl sarcosine.

3. A concentrate for addition to gasoline to produce a rust inhibited gasoline, which concentrate consists essentially of a gasoline containing between about 1 and 50 percent by weight of a rust inhibiting composition consisting of an acylsarcosine corresponding to the

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formula $RCON(CH_3)CH_2COOH$ and a 1,2-disubstituted imidazoline corresponding to the formula



wherein R and R' are alkyl radicals having from 8 to 20 carbon atoms, wherein the molar ratio of the acyl-sarcosine to the 1,2-disubstituted imidazoline is between 0.1:1 and 10:1, and said rust inhibiting composition having been subjected to heating to a temperature between about 100 to 200° F.

4. A gasoline containing between about 0.0001% and 0.01% by weight of a rust inhibiting composition consisting of N-oleyl sarcosine and 1-hydroxyethyl 2-hepta-

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decenyl imidazoline, the molar ratio of the sarcosine compound to the imidazoline compound being from 0.1:1 to 10:1, and said rust inhibiting composition having been subjected to heating to a temperature between about 100 to 200° F.

5. The composition of claim 4 in which the rust inhibiting composition contains tall oil in an amount between about 1 to 10 mols per mol of said N-oleyl sarcosine.

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