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RUST INHIBITOR FOR FUEL FRACTIONS OF MINERAL OIL

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This invention relates to liquid fuel fractions of mineral oil containing an improved rust inhibiting composition.

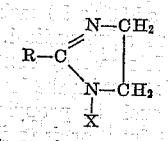
While the general problem of rusting of metal surfaces which are in contact with mineral oils has received considerable research attention in the past, particularly with respect to improving the rust inhibiting properties of lubricating oils and the like, it has only been recently that research attention has been directed to improving the rust inhibiting properties of "light products" i.e. naptha, gasoline, kerosene and burning oils or similar liquid fuel fractions of mineral oil. The rusting problems occurring with lubricating oils are different from those occurring with the liquid fuel fractions of mineral oil. For example, the rust preventive properties of a finished lubricating oil may be affected not only by the type of oil, but also by the presence of other additives, by the type of metal materials from which the engine parts are constructed, by the different types of physical mechanisms used in the engine, and other factors. The presence of other additives in lubricating oil may aggravate the problem of corrosion and rusting. Certain metal materials from which the engine may be constructed may be readily rusted in the corrosive atmosphere of the internal combustion chamber. The use of hydraulic valve lifters in place of mechanical valve lifters has presented another type of rusting problem which has only recently been solved after intensive research.

The rusting problem presented in connection with light liquid fuel fractions such as gasoline, naphtha, kerosene, jet fuels and other light burning oils, occurs because of the storage and/or transportation of the fuel fraction and because of the ingredients of the light liquid fuels. For example, gasoline may be stored in tanks, shipped in tankers over fresh water or salt water, or pumped through pipelines. Any rust inhibitor which is added to gasoline must not allow or cause the formation of emulsions of water which might be present in the storage tank, tanker compartment, or pipeline. 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 affected by the addition of the rust inhibitor i.e. the rust inhibitor must not cause a color change by reaction thereof with the hydrocarbons, anti-oxidants, dyes, components of tetraethyl lead, sulfur, etc., which may be contained in the gasoline. The color problem is a particularly difficult one when a non-dyed gasoline free of tetraethyl lead is involved. In addition the rust inhibitor must not affect the octane rating of the gasoline. The presence of the rust inhibitor must not increase the amount of color formation beyond acceptable standards.

An object of this invention is to provide an improved rust inhibitor for liquid fuel fractions of mineral oil. An additional object is to provide a highly effective and inexpensive additive for liquid fuel fractions such as gasoline which does not affect the qualityof the gasoline nor the storage or transportation thereof and which reduces

the amount of rusting of metals in contact therewith. Other objects and advantages of the invention will become apparent from the following description thereof.

It has been found that these and other objects can be achieved by incorporating in a liquid fuel fraction of mineral oil from between about 0.0001 and 0.01% by weight of tall oil and a 1,2-di-substituted imidazoline. The di-substituted imidazoline corresponds with the following formula:



in which R is a hydrocarbon radical of 10 to 30 carbon atoms in length and X is a substituted alkyl group having from 2 to about 6 carbon atoms selected from the class consisting of hydroxyalkyl, aminoalkyl, and aminoalkylene iminoakyl radicals. While tall oil or the disubstituted imidazoline individually have some rust proofing ability, it has been discovered that the combined use of the two produces a rust inhibiting effect which is much greater than the additive effects of the two components, i.e., a synergistic rust inhibiting effect is obtained when both the tall oil and the imidazoline are employed together in a liquid fuel fracton. This synergistic effect is most pronounced when employing molar ratios of tall oil to the substituted imidazoline of between 10:1 and 0.7:1, such as between 7:1 and 0.7:1. A preferred disubstituted imidazoline is 1-hydroxyethyl 2-heptadecenyl imidazoline. For example, tall oil and 1-hydroxyethyl 2-heptadecenyl imidazoline may be added in a molar ratio of about 7 moles of tall oil per mole of the substituted imidazoline to a gasoline in an amount between 0.001 and 0.008% by weight as a rust inhibitor.

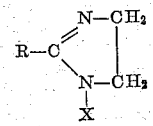
Tall oil is the name by which the mixture of saturated and unsaturated fatty acids, rosin acid, non-acid materials such as esters, lactones, estolides, alcohols such as sterols, which is obtained by acidifying the black liquor skimmings obtained in the pulping of wood, usually pine, by the sulfate (kraft) process. The black liquor produced during the pulping of wood is partially concentrated, then settled and the curdy soap skimmed from the top of the settling liquor. The skimmings are acidified with sulfuric acid (usually of 50 to 98% concentration) and the mixture heated to about 100° C. followed by decantation of the liberated tall oil. The manufacture, purification, composition, etc., of tall oil is described in "Encyclopedia of Chemical Technology," volume 13, pages 572–7 (1954).

The crude tall oil may contain a mixture of unsaturated fatty acids such as oleic, linoleic, linolenic, and the like, rosin acids, all of which have not been identified, but some of which are of the abietic type or the pimaric type, alcohols such as sterol, esters of alcohols with the fatty acids and rosin acids, lactones, hydrocarbons, and compounds which have not as yet been identified. During purification of the tall oil by many of the usual processes such as treatment with mineral oil, distillation under reduced pressure, solvent extraction, or other methods, a series of chemical reactions may occur among the tall oil constituents so as to modify further the composition of tall oil.

Either the crude tall oil or purified tall oil may be used in our invention. Typical American tall oils will 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%, rosin acids content of between about 30 and 70% and an unsaponified content of between 4 and 12%. Commercial tall oils are obtainable under the

trade name, Unitol, Facoil, Liqro, Rosoil, Indusoil, Opoil, Deoil. The properties of five commercial American tall oil products are shown in the Encyclopedia of Chemical Technology volume 13, page 575 (1954).

The 1,2-di-substituted imidazoline which may be used corresponds to the following structural formula:



In the formula, R represents a hydrocarbon, essentially straight chain radical of 10 to 30 carbon atoms in length. It may be a saturated alkyl radical, or it may contain unsaturated bonds. It also may contain methyl branching of the type associated with the lower, normally liquid polymers of olefins such as propylenes and butylenes. Since its predominant function is to impart oil solubility, it may contain a ring structure such as a phenylene radical provided the essentially straight chain character of the chain is not destroyed. In the formula, X represents a hydroxyalkyl, aminoakyl or an aminoalkylene iminoalkyl radical, preferably containing two to not more than about six carbon atoms in the chain.

The 1-2-disubstituted imidazolines used in the invention are of a type well known in the art. See for example, U.S. Patent 2,214,152 to Wilkes. We have found, however, that it is essential that the 2-substituent include a polar group such as a hydroxy or an amino radical. Apparently, the polar sidechain contributes to the film forming capacity of the molecule in oil solution, but preferably it should not be over about 6 carbon atoms in length. The sidechain however may contain more than one polar grouping; for example, radicals derived from ethylene diamine, propylene diamine, di-ethylene triamine are suitable. Examples of useful imidazolines include 1-hydroxyethyl 2-heptadecenyl imidazoline, 1-aminoethyl 2-undecyl imidazoline, 1-hydroxyethyl 2-pentadecyl imidazoline, 1-aminoethyl 2-heptadecenyl imidazoline, 1-aminoethyl 2-heptadecyl imidazoline, 1-hydroxyethyl 2-heptadecyl imidazoline, 1-aminoethyl-ethylimino 2-heptadecenyl imidazoline, and the like.

The molar ratio of tall oil to the disubstituted imidazoline which may be used may be between about 10:1 and 0.7:1. The synergistic effect on rust proofing when using both constituents shows up most strikingly when using a molar ratio of tall oil to the imidazoline between 7:1 and 0.7:1. Since tall oil is much cheaper than the imidazoline it is preferred to use a molar ratio of tall oil to imidazoline which is between 5:1 and 10:1 whereby advantage can be taken of the cheapness of tall oil while still obtaining the highly synergistic effects of using the proper molar ratios.

The combined amount of both the tall oil and the substituted imidazoline which may be added to the liquid fuel fraction may be between 0.0001 and 0.01% by weight, preferably between about 0.001 and 0.008% by weight. This corresponds to a broad range of 1 p.p.m. to 100 p.p.m., preferably between 10 and 80 p.p.m. on a weight basis. 0.001% by weight is approximately 2½ lbs./1,000 bbls. of product. The specific amount used will vary to some extent with the particular gasoline, kerosene, jet fuel, or the like which is used and the severity of the conditions conducive to rusting. Ordinarily about 0.002% (5 lbs./1000 bbls. of product) will be sufficient even under highly corrosive conditions such as those which occur in tanker compartments. Under certain conditions somewhat larger amounts e.g. 0.004 or 0.006% by weight may be desirable.

The tall oil and the disubstituted imidazoline may be added separately or together to the liquid fuel fraction. A very convenient way of adding our rust inhibitor consists of forming liquid concentrates comprising between 1 and 50% by weight or more of the tall oil and disubstituted imidazoline in a hydrocarbon solvent such as naphtha, gasoline, kerosene, toluene, xylenes or the like. While slight heating e.g. to about 100° F. or so may be desirable, care should be taken to avoid subjecting either the concentrate or the fuel fraction containing the rust inhibitor to a temperature higher than about 200° F. At higher temperatures it is believed that a reaction occurs which causes a reduction in the effectiveness of the rust inhibitor.

The effectiveness of tall oil, the disubstituted imidazoline, various molar mixtures of the two, as well as commercial rust inhibitors were determined by a modified ASTM D–665–54T rust test. The ASTM rust test was conducted for 24 hours using synthetic sea water. Because of the volatility of some of the products tested the test temperature was lowered from 140 to 80° F. In order for a specimen to pass the test it must not show a single rust spot or streak under 60-foot candles illumination.

The rust inhibitors were tested in various light oils including gasoline containing no dye nor tetraethyl lead fluid, gasoline containing tetraethyl lead fluid and dye, and kerosene. The tall oil used was Unitol S, a product of the Union Bag and Paper Corp. It contained approximately 50% fatty acids, 43% rosin acids, and 7% unsaponifiable material. The disubstituted imidazoline was 1-hydroxyethyl 2-heptadecenyl imidazoline (Amine O, a product of Geigy Industrial Chemicals). When mixtures of tall oil and the disubstituted imidazoline were evaluated, the various molar ratios of the mixtures were prepared by dissolving the proper amounts of tall oil and disubstituted imidazoline in alcohol, warming slightly and mixing well, and evaporating the alcohol. The resultant mixtures which had varying molar ratios of tall oil to disubstituted imidazoline were then added to the light oil product and their rust inhibiting effect evaluated. The concentration in weight percent of the rust inhibitor which is necessary in order for the test specimen to pass the modified ASTM rust test was determined by conducting separate tests employing amounts of the rust inhibitor which differed usually by about 0.002% by weight in concentration. For example, Sample No. 7 required 0.005% of the rust inhibitor to pass the test whereas it failed the test at a concentration of 0.003% by weight. The ASTM Glass Dish Gum, in mg./100 ml., was determined for most samples. Results of the evaluation of various rust inhibitors is shown in the table which follows:

Table

Sample No.	Light Oil	Mole Ratio		Concentration (Wt. Percent) Required for Complete Rust Inhibition	ASTM Glass Dish Gum, mg/100 ml.
		Tall Oil	Disubstituted Imidazoline		
1	Gasoline A [1]	Yes	none	0.2	
2	do	none	yes	0.5	
3	do	14.7	1.0	0.01 failed	
4	do	10.0	1.0	0.01	4.2
5	do	7.0	1.0	0.006	2.6
6	do	2.33	1.0	0.006	2.0
7	do	1.0	1.0	0.005	3.4
8	do	0.77	1.0	0.006	3.4
9	do	0.26	1.0	0.02	14.4
10	do	0.087	1.0	0.05	29.0
11	Gasoline B [2]	1.0	1.0	0.006	3.0
12	Kerosene	1.0	1.0	0.006	
13	Gasoline A [1]	Commercial Inhibitor		0.012	

[1] Gasoline A did not contain any dye or TEL fluid.
[2] Gasoline B contained TEL fluid and dye.

It should be noted that when tall oil alone was used as the inhibitor, 0.2% was necessary in order to pass the rust test. The use of such a large amount of tall oil was undesirable since it caused discoloration of the gasoline. The discoloration of a water-white gasoline which occurs when using the amount of tall oil necessary for adequate rust inhibition is so great as to prohibit the use of tall oil alone for this purpose. Sample No. 2 shows

that when 1-hydroxyethyl 2-heptadecenyl imidazoline is used, 0.5 weight percent is necessary in the gasoline in order to pass the test. Samples 4 through 8 show the synergistic effect which occurs when a mixture of between 10.0 and 0.7 moles of tall oil per mole of the imidazoline is used. These samples show that about 0.005 or 0.006 weight percent of the proper molar ratios of tall oil to substituted imidazoline will produce passing results. This is in marked contrast with Samples 1 and 2 wherein 40 and 100 times (respectively) this amount was needed when the individual constituents of the mixture were employed alone in order to obtain a passing result. Outside this range of 10.0 to 0.7 moles of tall oil per mole of the disubstituted imidazoline, the synergistic effect is diminished. In addition the formation of gum in the gasoline begins to increase rapidly. Samples 3 and 9 point this out. It should be noted that the commercial inhibitor of Sample No. 13 must be employed in larger amounts than that necessary when employing the preferred mixtures of tall oil and disubstituted imidazoline of our invention.

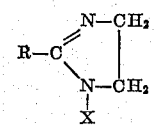
While the present invention has been described particularly in connection with the use of our rust inhibiting mixture in gasoline, other light oil fractions may be used. Examples of such other light oil fractions are liquid fuel fractions of mineral oil such as kerosene, light burning oil, jet fuel, and the like.

Unless otherwise stated, the percentages expressed herein and in the claims are weight percentages.

Although the present invention has been described with reference to specific preferred embodiments thereof, the invention is not to be considered as limited thereto but includes within its scope such modifications and variations as come within the spirit of the appended claims.

We claim:

1. A light liquid fuel fraction of mineral oil containing between about 0.0001% and 0.01% by weight of tall oil and 1,2-disubstituted imidazoline corresponding to the following formula:



in which R is a hydrocarbon radical of 10 to 30 carbon atoms in length and X is a substituted alkyl group having from 2 to about 6 carbon atoms selected from the class consisting of hydroxyalkyl and aminoalkylene iminoalkyl radicals, and wherein the molar ratio of tall oil to the disubstituted imidazoline is between 10:1 and 5:1.

2. The composition of claim 1 wherein the disubstituted imidazoline is 1-hydroxyethyl 2-heptadecenyl imidazoline.

3. The composition of claim 1 wherein the amount of tall oil and disubstituted imidazoline is between about 0.001 and 0.008% by weight.

4. A gasoline containing between about 0.0001 and 0.008% by weight of tall oil and 1-hydroxyethyl 2-heptadecenyl imidazoline, wherein the molar ratio of tall oil to 1-hydroxyethyl 2-heptadecenyl imidazoline is between 5:1 and 10:1.

5. The composition of claim 4 wherein said molar ratio is approximately 7:1.

6. A gasoline containing between about 0.001 and 0.01 percent by weight of tall oil and 1-aminoethyl-iminoethyl 2-heptadecyl imidazoline, wherein the molar ratio of tall oil to 1-aminoethyl-iminoethyl 2-heptadecyl imidazoline is between 10:1 and 5:1.

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