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DISTILLATE HYDROCARBON COMPOSITIONS

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This invention relates to the production of distillate hydrocarbon compositions, particularly gasolines, of improved properties attributable to the incorporation of a very small amount of a long chain hydrocarbon phosphonic compound.

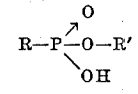
As competition in the marketing of gasoline has forced octane numbers higher and created new indexes of quality, there has been an increasing tendency to rely upon additives to improve fuel quality. The use of additives of course is highly advantageous, but use of add tives of non-petroleum origin may, under particular or limiting engine conditions, create special problems. For example, the simplest means for making an incremental octane improvement is by increasing the addition of anti-knock agent, i.e. tetraethyl lead. The use of higher lead concentrations, however, may cause troubles from spark plug fouling and/or pre-ignition. Recently, special additives, usually containing phosphorus in soluble form, have been proposed to suppress these conditions, but they in turn introduce problems, e.g. increase in engine deposits, thereby increasing the octane requirement of the engine with use. Also, by way of example, the use of an anti-rust additive in the gasoline may be useful, particularly for protection of pipe lines and equipment during transportation and storage. But this adds another additive along with the above and others such as antioxidants, dyes, gum inhibitors, etc., which while performing their intended functions, may interfere in other respects with the efficient operation of the engine.

It is an object of my invention to provide a multifunction additive which, useful in extremely low concentrations, contributes to fuel quality while beneficially reducing or affecting formation of engine deposits. It is also an object of my invention to provide a distillate hydrocarbon composition of improved anti-rust properties. According to my invention a long chain hydrocarbon phosphonic acid compound, most advantageously a monoalkyl ester of a long chain hydrocarbon phosphonic acid, is added to gasoline or to other non-viscous distillate hydrocarbon fractions such as jet engine fuel, diesel fuel, or light volatile solvents. In extremely low concentrations, the phosphonic compound imparts anti-rust properties and functions as a deposit modifier, thus providing improved engine performance in terms of properties such as pre-ignition, octane requirement increase, and average spark plug life. The proportions of phosphonic compound are within the range of about 0.00001 to 0.1 percent by weight. Advantageously, the concentration is about 5 to 10 pounds of additive per 1000 barrels of gasoline, or about 0.002 to 0.004 percent by weight. Because of solubility considerations, the concentration of the free acid will be ordinarily below about 0.002 percent.

The phosphonic additives are characterized by the association of the strongly polar phosphonic group and a long chain hydrocarbon group. The long chain hydrocarbon group must contain an essentially straight aliphatic chain of at least 10 carbon atoms length in order to provide the close molecular packing necessary for good

film forming properties. Octadecyl phosphonic acid is particularly advantageous although hydrocarbon chains of greater length may be used, often with advantages in improving oil solubility, up to very long chains such as in the case of hexatriacontanyl phosphonic acid. In terms of practical availability, however, materials such as dodecyl phosphonic acid and hexadecyl phosphonic acid have special value. In the longer chain products, some chain branching and ring substitution can be tolerated without interfering with close molecular packing for high film strength. The introduction of rings, particularly when close to the phosphonic group, also tends to have a beneficial effect on oil solubility. Alkyl benzene phosphonic acids however should be para-positioned to preserve the essentially straight chain character. The methyl branching in olefin chain polymers such as propylene tetramer, or in polybutene chains, also appears unobjectionable.

The new additives may be characterized structually by the following formula:



It is important that there be at least one free acid group. The R′ may be hydrogen or an aliphatic radical containing less than 10 carbon atoms. The monomethyl ester is superior to the higher alkyl esters such as ethyl, propyl and butyl because the small methyl group appears to interfere less with close molecular packing in film formation. As the alkyl groups lengthen however there is some evidence that their freedom to bend restores close packability.

Surprisingly, the mono-ester long chain phosphonic acids have shown superior rust preventative properties in use although the free acids, based upon film balance studies of film forming properties, show significantly higher film strengths. For example, the collapse pressure, measured in dynes per centimeter of a mono-molecular film of the monomethyl ester of octadecyl phosphonic acid is 48 determined by a Langmuir-Adam-Harkins film balance as compared to 53 for the free acid. The elimination of both acid groups of the phosphonic radical by esterification, on the other hand, reduces film strength to an extent seriously interfering with anti-rust properties. The use of the free acids in gasoline also requires special handling occasioned by their low solubility. Although the additives may be introduced directly into gasoline, it is usually more practicable to dissolve the additive, particularly the free acid which has low oil solubility, in a carrier solvent which is added to the gasoline or other distillate hydrocarbon product. Examples of useful carrier solvents include high octane aromatics such as benzene, toluene, xylene, the polymethyl benzenes and ethyl benzenes. Other solvents are cymene and terpenes such as dipentene. Chlorohydrocarbons such as dichloroethane and cloroform also may be used.

The phosphonic acid compounds may be made in a number of ways. A dialkyl phosphite, e.g. diethyl phosphite, can be reacted with a long chain alkyl halide e.g. octadecylbromide, in the presence of metallic sodium. The resulting dialkyl ester then can be hydrolyzed or partially hydrolyzed with hydrochloric or hydrobromic acid to obtain the free acid or the mono-ester. Alternatively the long chain halide, e.g. octadecyl bromide, can be reacted with a trialkyl phosphite, e.g. triethyl or trimethyl phosphite. At about 130 to 150° C. the diester of the long chain phosphonic acid is formed and the volatile ethyl or methyl halide may be distilled off permitting the reaction to go to completion. In another method, a long chain olefin, e.g. octadecene-1, is reacted with a dialkyl phosphite, e.g. diethyl phosphite in the

presence of a peroxide catalyst or other free radical initiator such as a hypochlorite, or under the influence of ultraviolet light, at about 200 to 300° C. to obtain the diester. Many of the free long chain phosphonic acids and certain of the esters are commercially available. The mono-esters then may be prepared by partial hydrolysis of the dialkyl ester, for example, with hydrogen chloride, or by partial esterification of the free acid in cases where separation of the mono-ester from the reaction mixture permits selective production of the mono-ester, as for example in the case of the monomethyl ester of octadecyl phosphonic acid.

The usefulness of the new additives in distillate hydrocarbon compositions is illustrated by addition of the monomethyl ester of octadecyl phosphonic acid to a regular grade gasoline in a concentration of 5 pounds of additive per 1,000 barrels of product. The gasoline also contained 7 pounds per 1,000 barrels of a commercial anti-oxidant of the phenylene diamine type and 9 pounds per 1,000 barrels of a commercial metal deactivator of the salicyl aldehyde-diamine condensation product type. The composition of the invention was tested in a 16 hour rust test in comparison with the untreated gasoline and also in comparison with a gasoline blend containing 10 pounds per 1,000 barrels of a commercial anti-rust additive of the fatty acid type. The rust test was conducted as follows: SAE–1020 steel panels ½ x 6 x ⅛" were belt sanded clean of discoloration and pits. After cleaning with hot naptha followed by hot acetone they were placed in 100 ml. of the test fuel in a tall form 4 oz. bottle and allowed to stand for ½ hour. After this period of contact, 10 ml. of tap water was added and the capped bottle was rolled for 1 minute. The bottle was then stored in an upright position. The appearance of the strips was examined and evaluated after 16 hours exposure to the fuel layer and the water layer.

Under the test conditions, the untreated gasoline control showed 20 percent rusting of the test panel exposed to gasoline and 80 percent rusting of the panel exposed to water. The composition of the invention reduced rust formation in gasoline to 10 specks (where a speck is defined as less than one millimeter in diameter) and the rusting in water was reduced to 50 percent. The gasoline composition containing the commercial anti-rust showed 15 spots (where a spot is defined as an area of 1 to 3 mm. in diameter) in gasoline and 90 percent rusting in water.

The additives of the invention also are beneficial with respect to improvement in the type of sulfur corrosion detected ordinarily by the copper strip corrosion test. For example, the monomethyl ester of octadecyl phosphonic acid was dissolved in the above described regular grade gasoline in a concentration of 5 pounds per 1,000 barrels by blending with xylene solution containing the additive in a cencentration of 0.1 gram per 100 cc. The additive of the invention imparted perfect corrosion protection to the gasoline under the conditions of the copper strip corrosion test described by J. A. Bolt in the Oil and Gas Journal of August 9, 1947. Under the conditions of a more severe test, the Philadelphia copper strip test, wherein the copper strip is placed in a flask and an ASTM distillation is run, it was the only material of a representative group of commercially available additives tested that appeared to give significant protection in desirably small quantities.

As an example of the use of a free phosphonic acid in gasoline, a solution of 0.0015 percent of octadecyl phosphonic acid in benzene is added to gasoline in an amount producing a final blend having a concentration of 0.00015 weight percent. Octadecyl phosphonic acid forms extremely rigid tenacious film as shown by testing a solution of 6 milligrams of the acid in 40 grams of benzene on a Langmuir-Adam-Harkins film balance. The solution was prepared by warming the flask for one minute in a water bath held at a temperature of 210° F. The collapse pressure of a mono-molecular film deposited from this solution was 53 dynes per centimeter, compared to a value of 40 dynes per centimeter which may be considered an acceptable standard for anti-rust agents of the film forming type.

I claim:

1. A non-viscous liquid hydrocarbon composition consisting essentially of a non-viscous distillate hydrocarbon fraction boiling in the gasoline to diesel fuel range and from about 0.00001% to about 0.1% by weight of a phosphonic acid additive selected from the group consisting of phosphonic acids and mono-alkyl esters thereof in which the acid contains a long chain hydrocarbon group comprising an essentially straight aliphatic chain of at least 10 carbon atoms attached to the phosphorus atom and in which the alkyl radical of the ester group contains less than 10 carbon atoms.

2. The composition of claim 1 in which the composition contains from about 0.002 to 0.004% by weight of the phosphonic acid additive.

3. A non-viscous liquid hydrocarbon composition consisting essentially of a non-viscous distillate hydrocarbon fraction boiling in the gasoline to diesel fuel range and from about 0.00001 percent to about 0.1 percent by weight of a phosphonic acid containing a long chain hydrocarbon group comprising an essentially straight aliphatic chain of at least 10 carbon atoms attached to the phosphorus atom.

4. The composition of claim 3 in which the hydrocarbon fraction is gasoline.

5. The composition of claim 4 in which the phosphonic acid has been incorporated in the form of a solution in an aromatic hydrocarbon.

6. A non-viscous liquid hydrocarbon composition consisting essentially of a non-viscous distillate hydrocarbon fraction boiling in the gasoline to diesel fuel range and from about 0.00001 percent to about 0.1 percent of a monoalkyl ester of a phosphonic acid which contains a long chain hydrocarbon group comprising an essentially straight aliphatic chain of at least 10 carbon atoms attached to the phosphorus atom and in which the alkyl radical of the ester group contains less than 10 carbon atoms.

7. The composition of claim 6 in which the hydrocarbon fraction is gasoline.

8. The composition of claim 6 in which the ester is a monoalkyl ester of octadecyl phosphonic acid.

9. The composition of claim 6 in which the ester is a monomethyl ester of the phosphonic acid.

10. The composition of claim 9 in which the ester is the monomethyl ester of octadecyl phosphonic acid.

11. The composition of claim 9 in which the ester is the monomethyl ester of dodecyl phosphonic acid.

12. The composition of claim 9 in which the ester is the monomethyl ester of hexadecyl phosphonic acid.

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