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FUEL COMPOSITION

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This invention relates to hydrocarbon compositions. More particularly this invention relates to oxidation inhibited motor fuel compositions.

The increasing refinements of motor fuels required by engines of improved design and operating efficiency require of petroleum refiners continuous improvement in gasoline quality. These improvements are evidenced by continuously increasing octane values, increased heat stability, lower carbon deposit, lower impurity content, improved color stabilization, improved low temperature operating efficiency, and increased oxidation inhibiting characteristics.

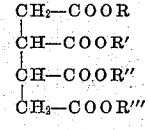
It is with this latter property of motor fuel compositions that this invention is particularly concerned.

It has been accepted practice in the petroleum industry for many years to add to motor fuel compositions a small amount of a corrosion inhibiting additive to minimize the corrosiveness of the fuel composition. These additives must be comparatively inexpensive, and simultaneously inhibit corrosion without adversely affecting the burning qualities of the motor fuel.

It is accordingly an object of the present invention to provide a motor fuel composition having improved oxidation inhibiting characteristics.

It is another object of the present invention to provide an improved gasoline composition of reduced corrosive characteristics.

The foregoing objects are attained according to the present invention by incorporating in the fuel composition as a corrosion inhibitor alkyl esters of 1,2,3,4 butane tetracarboxylic acid. These esters can be conveniently represented by the following formula:



wherein R, R', R'', and R''' represent alkyl radicals having from 1 to 8 carbon atoms in a straight or branched chain configuration. These groups are preferably saturated, and include such radicals as methyl, ethyl, propyl, isopropyl, butyl, isobutyl, amyl, 2-ethyl hexyl, and

2-ethyl butyl. In the foregoing generic structure, it is, of course, understood that a mixed alkyl tetraester is contemplated in which the various radicals may be of like or unlike configuration, depending on the source of the acid.

The additives of the present invention may be prepared in any suitable manner. For example, the tetra alkyl esters may be prepared according to the method described in U. S. 2,687,429 in which 1 mol of a dialkyl fumarate is combined with 1 mol of a dialkyl succinate. When prepared according to this method, it is relatively easy to obtain a mixed tetraester.

The tetraesters of the present invention may also be prepared by the direct esterification of 1,2,3,4 butane tetracarboxylic acid. According to this method of preparation, 1 mol of the butane acid is dissolved in 6 mols of the selected alcohol, with a sufficient amount of an azeotrope forming solvent being added to permit removal of the water of esterification from the reaction zone. Suitable solvents for this purpose are benzene, toluene and xylene.

When carrying out this preparation, reflux of the reactant mixture is conducted at a suitable temperature, depending on the particular solvent used, for a period of from 4 to 8 hours. Generally speaking, for the solvents heretofore mentioned, reflux will be conducted at temperatures ranging from about 80° C. to about 140° C.

After the theoretical amount of water has been collected, indicating completion of the esterification reaction, the solvent is distilled from the reaction zone, leaving a crude ester product which in itself can be satisfactorily used as an additive for the purposes of this invention. It is preferred, however, to obtain a purified product. Accordingly, the crude ester product is washed and further distilled.

The tetraesters prepared according to the foregoing reaction are the unique property of providing anti-oxidant characteristics for motor fuel composition when used in comparatively small amounts.

The following is an example of the preparation of a typical tetraalkyl ester utilized in the present invention.

In a 1 liter three-neck flask fitted with a water trap, stirrer and condenser, ½ mol of butane tetracarboxylic acid (117 grams dry) was dissolved in 3 mols of 2-ethyl butyl alcohol in the presence of 100 ml. of toluene. This reactant mixture was refluxed for a period of 7 hours, after which the volume of azeotrope water collected was between 62 and 65 ml. The theoretical amount of water (including the water present in the acid) should have been 62.8 ml. Recovery data and significant physical and chemical properties of the reaction product are shown in Table I which follows. The product of the foregoing example is identified as D in the table. Included in the table, in addition to the 2-ethyl butyl tetraester, is a series of esters prepared in a similar manner to that previously described.

TABLE I

Yields and properties of butane tetracarboxylic acid esters

Alcohol Uses in Esterification	A n-propyl	B n-butyl	C n-amyl	D 2-ethyl-butyl	E 2 ethyl-hexyl
Percent Yield of Crude Ester	78	80	85	89	89.
Appearance and Color of Distilled Ester.	Lt. br. Syrup.	Lt. br. Oil.	Brown Oil.	Lt. br. Oil.	Lt. br. Oil.
Neut. No. Distilled Ester	198	126	122	161	107.
Sap. No. (ASTM) Distilled Ester	685	587	545	440	410.
Sap. No. (Diethylene Glycol-Phenetole Method) of Distilled Ester.	700	587	540	415	
Ester No. of Distilled Ester	502	461	418	279	
Ester No. (Theor.) of Pure Tetraesters.	556	489	436	393	

As described above, the tetra alkyl esters of 1,2,3,4 butane carboxylic acid find particular application as oxidation inhibitors for gasoline compositions. Generally speaking, the alkyl esters of the present invention may be used for the oxidation inhibition of any gasoline composition. Specifically, they may be used in unsaturated gasoline, polymerized gasoline, reformed gasoline, cracked gasoline and aviation gasoline. In addition to the specific gasoline compositions mentioned, these additives may also be used in other hydrocarbon fuel compositions such as fuel oil and diesel oil.

The additive of the present invention is generally added to the fuel composition in an amount of less than 1% by weight, and more generally in the range of from about 0.0001% to about 1% by weight, and preferably from about 0.001% to about 0.1%.

The additives of the present invention may be used if desired along with other additives such as metal deactivators, dyes, anti-knock agents, upper cylinder lubricants, heat stabilizers, gum inhibitors, and the like.

To demonstrate the effectiveness of the corrosion inhibitors of the present invention in reducing the oxidation or corrosion tendencies of gasoline compositions, a series of tests were carried out in which gasoline compositions were prepared with varying weight amounts of the additives previously described. In carrying out these tests, a gasoline generally referred to is regular grade. This gasoline had the following properties and characteristics:

Research octane (F–1) min	90.0
Motor octane (F–2) min	82.0
Distillation:	
10% evap. temp. ° F. max	140
50% evap. temp. ° F. max	245
90% evap. temp. ° F. max	380
End point ° F. max	425
Residue percent max	2.0
R. V. P. at 100° F. max	10.0
Gum A. S. T. M. max	4.0
Gum F. S. B. 330.1 max	20.0
Sulfur wt. percent max	0.10

The test used in determining the effectiveness of these agents as oxidation inhibitors in a fuel composition was the modified A. S. T. M. turbine oil test D665–52T modified to room temperature on a four hour cycle using synthetic sea water prepared according to Army Specification 2–126. The test equipment included a series of 400 ml. beakers provided with a plastic cover and a stirrer inserted therein. The test was carried out on metal test strips 4" x 1" x ⅛" of cold rolled open hearth 1018 steel polished with a final grit size of 180. In carrying out a test the panel or test strip is cleaned with acid and weighed after polishing and emerged in the solution being tested. About three inches of the test strip is placed in the solution. The stirrers are run at about 50 R. P. M. during the period of test. Samples of gasoline containing the specified amount of additive as shown in the tables which follow were added to the beakers to provide a total test sample of about 300 ml. of the gasoline composition.

After immersion in the gasoline solution for about four hours, the panels are removed, cleaned, and weighed to determine weight loss. The weight loss in grams expressed in the tables which follow and the exposed area of the panel are used in calculating the corrosion rate in inches per year according to the following formula:

$$\frac{\text{Wt. loss (g.)}}{\text{Area (sq. in.)}} \times (0.683) = \text{corrosion rate, inches/year}$$

(Navy Department Specification 51–I–11, May 15, 1945)

In applying the above formula, the area is determined by measuring from the bottom of the test strip to the corrosion line formed at the interface of the liquid and vapor phases. The area is then calculated in square inches, with proper consideration being given to the sides and edges of the test strip.

In Table II below, results are provided measuring the oxidation characteristics of a gasoline containing the normal butyl tetraester of butane carboxylic acid. The test was carried out in the manner described above.

TABLE II

Ester (B)	P. p. m.	Wt. Change of Panel (gm.)	Corrosion rate, inches/year
Crude	50	−.0035	.00035
Distilled	50	−.0018	.00021
Crude	20	−.0052	.00067
Distilled	20	−.0053	.00064
Crude	10	−.0112	.00113
Distilled	10	−.0097	.00098
Blank		−.0126	.00122

In the results reported in Table II, it will be noted that substantial reduction in the corrosive effect of the gasoline composition was obtained by including in the gasoline a small amount of ester B. It will be evident that the additives of the present invention provided a considerable reduction in the corrosive characteristics of the gasoline.

In a similar manner, the normal amyl ester of butane tetracarboxylic acid (compound C, Table I) was tested by being added to gasoline in the amount specified. The results of this test are noted in Table III, below.

TABLE III

Ester (C)	P. p. m.	Wt. Change of Panel (gm.)	Corrosion rate, inches/year
Crude	50	−.0001	.00001
Distilled	50	−.0001	.00001
Commercial	50	−.0004	.00004
Crude	20	−.0054	.00054
Crude	20	−.0035	.00010
Distilled	20	−.0048	.00049
Distilled	20	−.0009	.00009
Crude	10	−.0132	.00143
Distilled	10	−.0004	.00004
Commercial	10	−.0004	.00004
Blank		−.0130	.00131

In the foregoing table, results of the corrosion inhibiting properties of a commercially available additive are compared with the results obtained with the normal amyl tetraester of butane carboxylic acid. It will be noted that at 50 p. p. m. the crude or distilled ester of the present invention was more effective than the commercial additive. In all respects, with the possible exception of the crude ester in the amount of 10 p. p. m., substantial improvement in corrosion inhibition was obtained by the presence of the additives of the present invention.

In a manner similar to the test method described in connection with Tables II and III above, the 2-ethyl butyl ester of butane tetracarboxylic acid (compound D, Table I) was added to a cracked gasoline in the amount stated. The corrosion test results for gasolines with and without this additive are reported in Table IV.

TABLE IV

Ester (D)	P. p. m.	Wt. Change of Panel (gm.)	Corrosion rate, inches/year
Distilled	20	−.0073	.00094
	20	−.0013	.00012
	10	−.0137	.00138
Dist. (Cut 2)	50	−.0007	.00008
	20	−.0041	.00045
	20	−.0014	.00014
	10	−.0083	.00080
Dist. (Cut 3)	20	−.0031	.00039
	20	−.0033	.00033
	10	−.0108	.00105
Commercial A	10	−.0046	.00053
Commercial C	10	−.0002	.00002
Blank		−.0132	.00145

Here again it will be noted, as with Tables II and III, that the inhibitors of the present invention provide substantial protection of the metal strips in gasoline compositions, particularly when compared with the blank, or in this case with commercially available corrosion inhibiting additives identified as A and C.

A further test was carried out with the 2-ethyl hexyl ester of butane tetracarboxylic acid in which 50 p. p. m. of the additive were added to a cracked gasoline having the properties previously described. The results of this test are as follows:

Ester (E)	P. p. m.	Wt. Change of Panel (gm.)	Corrosion rate, inches/year
Distilled	50	0.00009	0.00009
Commerical Additive (Bryton Calcium Sulfate)	50	0.00049	0.00049

The results noted above, in which ester E was compared with commercial Bryton calcium sulfate additive at 50 p. p. m., clearly show the superiority of the additives of this invention over the commercially available and presently used additives.

Although the present invention has been described in conjunction with certain preferred embodiments thereof, those skilled in the art will recognize that certain variations and modifications can be made hereto. Such modifications are to be considered within the scope of this specification and the claims appended hereto.

What I claim as my invention and desire to secure by Letters Patent of the United States is:

1. A gasoline fuel containing from 0.002 to about 1.0% based on the weight of the gasoline fuel of an alkyl tetraester having the formula

$$\begin{array}{l} CH_2\text{—}COOR \\ | \\ CH\text{—}COOR' \\ | \\ CH\text{—}COOR'' \\ | \\ CH_2\text{—}COOR''' \end{array}$$

wherein R, R', R'', and R''' represent alkyl substituents having from 1 to 6 carbon atoms.

2. A gasoline fuel as claimed in claim 1, wherein R, R', R'', and R''' have a like number of carbon atoms.

3. A gasoline fuel as claimed in claim 1, wherein R, R', R'', and R''' have a differing number of carbon atoms.

4. A gasoline as claimed in claim 1, wherein R, R', R'', and R''' are n-butyl substituents.

5. A gasoline as claimed in claim 1, wherein R, R', R'', and R''' are n-amyl substituents.

6. A gasoline as claimed in claim 1, wherein R, R', R'', and R''' are 2-ethyl hexyl substituents.

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