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FUEL COMPOSITION

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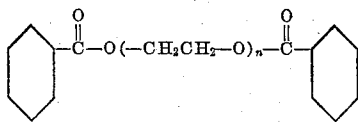
No Drawing. Filed Oct. 19, 1956, Ser. No. 616,915

3 Claims. (Cl. 44—70)

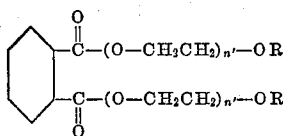
This invention relates to a novel fuel composition. More particularly, this invention relates to a motor fuel composition which has excellent engine cleanliness properties.

The need for superior deposit inhibitor additives for motor fuels is continually increasing due to advances in engine design. All engines in continuous operation eventually suffer from the effect of engine deposits. However, engines which are run at low temperatures usually develop deposits more quickly than those engines run at high temperatures. Low temperature deposits are of particular concern to automotive owners and operators who run their automobile engines for short periods of time. For instance, taxicabs and autos used for short delivery runs, particularly in the winter season in colder climates, are subject to low temperature deposits on the engine parts. Engine deposits which find their origin in the fuel are primarily responsible for surface ignition phenomena, such as preignition and octane requirement increase (ORI) which is the tendency of spark ignition engines in service to require higher octane fuels for proper performance. As a consequence, gasoline manufacturers have resorted to various additives either to reduce the amount of deposits or to minimize their effects.

In accordance with the present invention an improved motor fuel composition which suppresses the formation of engine deposits comprises a major portion of a hydrocarbon motor fuel and a minor portion sufficient to suppress deposits in the engine of an aromatic carboxylic acid diester selected from the group consisting of a dibenzoate of a polyethylene glycol having the following general formula:



where n ranges from 2 to 12, preferably 4 to 8, and an alkoxyalkyl phthalate having the following general formula:



where n' ranges from 1 to 5, preferably 1 to 2, R is an alkyl group having from 1 to 6 carbon atoms and the carbon to oxygen weight ratio of the phthalate compound does not exceed 2.25, preferably 2.0. In order to maintain the carbon to oxygen weight ratio below 2.25, longer chain terminal radicals are combined with a larger number of repeating ethylene oxide units while lower molecular weight terminal aliphatic radicals are combined with a smaller number of repeating ethylene oxide radicals.

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Examples of the alkoxyalkyl phthalates which are useful in accordance with this invention include bis(diethoxyethyl) phthalate more commonly called di-Carbitol phthalate, bis(ethoxyethyl) phthalate commonly called di-Cellosolve phthalate, bis(methoxyethyl) phthalate, bis(methoxy tri-ethoxy ethyl) phthalate and bis(penta-ethoxyethyl) phthalate. The preferred phthalates are di-Carbitol phthalate and bis(methoxyethyl) phthalate.

The major application of the additive of the invention is in gasoline for automotive engines wherein fuel-derived engine deposits have become a particularly vexing problem. The deposit-forming properties of both regular and premium gasolines, both of the leaded and of the non-leaded type, are improved by the addition of the aromatic carboxylic acid diesters of polyalkylene ethers of this invention. The application of the additive to other fuels including diesel, jet, and gas turbine fuels improves their deposit-suppressing properties also. In diesel fuels the presence of the additive maintains the injection system and combustion zone in a clean condition. This is particularly important with the increasing use of the so-called "economy" diesel fuels, that is fuels having a high sulfur content or containing cracked or residual stocks. A jet fuel containing aromatic carboxylic acid diesters of polyethylene glycols of the type prescribed in this invention is an excellent heat exchange medium since it is relatively free from deposits in the cooling system and burner nozzle where deposits cannot be tolerated.

The fuel compositions of this invention have been found to be effective in additive amounts of 0.01 volume percent and continue to be effective in amounts over 1.0 volume percent, however, additive amounts in a fuel of over 1.0 volume percent cease to be economic. The preferred additive amount of the polyglycol esters in the fuel composition of this invention ranges from 0.05 to 0.5 volume percent.

The superior low deposit forming properties of some of the fuel compositions of the present invention have been demonstrated in the Modified Chevrolet Deposits Test—CRC FL-2-650 (Chevrolet S-II Test). This test is well known in the art and consists of using the test fuel to run a standard 1942-52 Chevrolet engine (216.5 cu. in.) having tin plated, cast iron pistons, under the following conditions:

- (1) Speed, r.p.m.; 2500 ± 25
- (2) Load, B.H.P.; 45 ± 1 (uncorrected)
- (3) Fuel flow rate; 30 lb./hr.¹
- (4) Jacket temp., in; $85 \pm 2^\circ \text{F.}$
- (5) Jacket temp., out; $95 \pm 5^\circ \text{F.}$
- (6) Oil temp., sump; $155 \pm 5^\circ \text{F.}$
- (7) Oil temp., gallery; 160°F.^1
- (8) Int. man. vac.; 7.0" hg.¹
- (9) Exh. back press.; 4" hg.¹
- (10) Ckce. vent.; 1 c.f.m.
- (11) Spark advance; $38 \pm 3^\circ \text{B.T.C.}$
- (12) A/F ratio; $14.5 \pm 0.5:1$
- (13) Oil pressure; 12 p.s.i.
- (14) Duration; 40 hours
- (15) Break-in; none (½ hr. warm-up)
- (16) Two four hour shutdown periods

¹ Typical values—not controlled.

These conditions are intended to impose a more severe test by simulating low temperature conditions wherein deposit formation is most pronounced. After the termination of each run, the engine is disassembled and its parts are evaluated by a merit system adapted from the CRC-L-4-1252 Test. This merit system involves visual examination of the engine part in question and their rating according to deposits by comparison with standards which have assigned ratings. For example, a rating of

10 on a piston skirt designates a perfectly clean piston while a rating of zero represents the worst condition. Similarly, a rating of 100 on total engine deposits represents a perfectly clean engine, etc.

The following table shows the results obtained with several of the fuel compositions of this invention in the above-described test. The base fuel used was a high quality regular grade gasoline comprising a mixture of thermal cracked stock, fluid catalytically cracked stock and straight run gasoline. This regular base fuel had an 87.0 ASTM research octane rating, containing 2.90 ml. of TEL per gallon, had an API gravity of 58.0 and a boiling range between 106° F. and 396° F.; the base fuel was negative in the copper corrosion test and had an oxidation stability in the ASTM test of 530 minutes minimum. The reference fuel also contained minor amounts of gasoline inhibitors, namely N,N'-di-secondary butyl phenylene diamine, lecithin, and N,N'-disalicylidene 1,2-diaminopropane. In all the runs in Table I, the laboratory engines in the Chevrolet S-II test were lubricated with Advanced Custom Made Havoline, a heavy duty type oil meeting Supplement I requirements and manufactured by the Texas Company.

TABLE I
Chevrolet S-II test results

	Piston Skirt Rating	Total Engine Rating
Base fuel.....	5.8	80.8
Base fuel + 0.1 vol. percent additive:		
PEG-300-dibenzoate.....	8.8	88.8
PEG-200-dibenzoate.....	9.0	88.5
DEB-dibenzoate.....	6.7	81.8

PEG 300 and 200=polyethylene glycols having average molecular weights of about 300 and 200, respectively.
DEB=diethylene glycol.

The polyethylene glycol dibenzoate additives lend unusually high cleanliness characteristics to the base fuel as seen in the above table. The fuel containing diethylene glycol dibenzoate wherein the polyglycol molecular weight is about 104 showed a comparatively small improvement signifying that the molecular weight of the polyglycol portion should not be less than 104 and therefore that *n* in the polyethylene glycol dibenzoate general formula should be at least 2.

Reduced octane requirement increase was demonstrated in the laboratory for the additive-containing motor fuel of this invention in comparison with the reference fuel by the following procedure:

LAUSON H-2 ORI TEST PROCEDURE

Test operation.—The engine was operated under the following standard operating conditions and the data recorded was outlined in the following table:

TABLE II

Variable:	Condition
Test hours.....	To equilibrium O.R.=200 hr.
Wattmeter retarding..	1500–1600.
Fuel flow, lbs. per hr.	1.6±.04.
Coolant temp., ° F. ...	210±5.
Oil temp., ° F.	175±5.
Oil level.....	Check once each day.
Maintain intake manifold press.	0 inch (each hour).
Orifice press. drop....	Record each hour.

Octane requirement of the engine was determined approximately every 24 hours. Before taking octane requirement the oil level was checked and necessary addi-

tions made and the following items determined and recorded:

- Compression pressure at operating throttle position
Air temperature, ° F.
Barometer reading, in Hg
Spark advance, ° B. T. D. C. (should be 20 degrees)
Amount of oil added

Equilibrium octane requirement was reached when the engine had operated for 50 hours with a change in ORI of 2 numbers or less.

A modified Model H-2 Lauson engine, which is a single cylinder, liquid cooled, four stroke spark ignition engine with a bore of 2 $\frac{3}{8}$ inches and a stroke of 2 $\frac{3}{4}$ inches giving a displacement of 14.89 cubic inches, was used. Power output was rated at 4.3 H.P. at 2400 r.p.m. Compression ratio of the engine was 6.5:1 using a modified head. The original flywheel magneto was replaced with a Bendix-scintella magneto, Type CBR-4R and coupled to the forward end of the engine crankshaft to provide ignition. The engine was operated under the following conditions:

- Engine speed..... 1800 r.p.m.
Engine load..... 1600 watts.
Spark advance..... 20° B.T.C.
Fuel flow rate..... 1.6#/hr.
Air-fuel ratio..... 13.5:1.
Coolant temperature..... 210° F.
Carburetor air temp. 100° F.
Oil temperature..... 175° F.
Test duration..... App. 200 hr. to equilibrium octane requirement.

The octane requirement of the engine was determined with primary reference fuels on the clean engine and after each period of operation until equilibrium octane requirement was attained. The difference between the initial (clean) octane requirement and the equilibrium octane requirement is known as the octane requirement increase or ORI.

The premium reference fuel used in this test was a high quality premium grade fuel comprising mainly fluid catalytically cracked stock and straight run gasoline. The fuel had a 95 ASTM research octane rating, contained 2.74 ml. of tetraethyl lead per gallon, had a ° API gravity of 60 to 65 and a boiling point range between 100 and 398° F. It was negative in the copper corrosion test and had an oxidation stability in the ASTM test of 240 minutes minimum. The reference fuel also contained minor amounts of conventional gasoline inhibitors, for example, approximately 6 pounds of N,N'-di-secondary butyl-p-phenylenediamine, a gum inhibitor, per thousand barrels of gasoline, about 1.2 pounds of N,N'-disalicylidene-1,2-diaminopropane, a metal deactivator, per thousand barrels of gasoline, and about 1.1 pounds of lecithin, a tetraethyl lead stabilizer, per thousand barrels of gasoline. The following table presents the results of the Lauson test.

TABLE III

	Octane requirement increase
Fuel:	
Base fuel	10
Base fuel + 0.1 vol. percent of polyethylene glycol (200) dibenzoate	6

The preceding Table III obviously demonstrates the superiority of the fuel composition of this invention with respect to lowering the ORI in an internal combustion engine.

The following table demonstrates the usefulness of the phthalate additives of this invention as determined by the previously described Chevrolet S-II test. The base fuel and engine lubricant are those previously described for the tests shown in Table II.

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TABLE IV
Chevrolet S-II test results

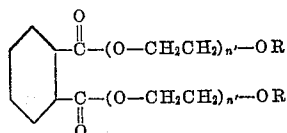
	Piston Skirt Rating	Total Engine Rating	Carbon to Oxygen Weight Ratio of Additive
Base fuel	5.8	80.8	
Base fuel + 0.1 vol. percent additive:			
Di-Carbitol phthalate	9.2	85.2	1.87
Bis(methoxyethyl) phthalate	8.5	86.5	1.75
Di-Cellosolve phthalate	7.7	84.7	2.0
Bis(butoxyethyl) phthalate	4.8	77.8	2.5
Di-2-ethylhexyl phthalate	5.3	75.3	4.5
Di-allyl phthalate	5.2	82.2	2.6

As previously stated, the carbon to oxygen weight ratio of the compounds in order to be useful must be below 2.25 and preferably below 2.0. The above table amply demonstrates this fact along with the great benefit obtained by employing the preferred phthalates, such as di-Carbitol phthalate and bis(methoxyethyl) phthalate, as a fuel additive.

Obviously, many modifications and variations of the invention, as hereinbefore set forth, may be made without departing from the spirit and scope thereof, and therefore only such limitations should be imposed as are indicated in the appended claims.

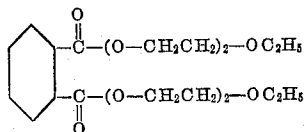
We claim:

1. A hydrocarbon motor fuel boiling within the gasoline to diesel fuel range containing an alkoxyalkyl phthalate having the following formula:



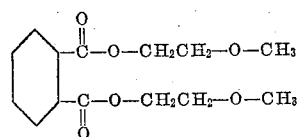
wherein n' ranges from 1 to 5, R is an alkyl group having from 1 to 6 carbon atoms and the carbon-to-oxygen weight ratio is less than 2.25, said alkoxyalkyl phthalate being present in an amount sufficient to suppress engine deposits.

2. A hydrocarbon motor fuel boiling within the gasoline to diesel fuel range containing an alkoxyalkyl phthalate having the following formula:



in an amount ranging from 0.05 to 0.5 percent by volume.

3. A hydrocarbon motor fuel boiling within the gasoline to diesel fuel range containing an alkoxyalkyl phthalate having the following formula:



in an amount ranging from 0.05 to 0.5 percent by volume.

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