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MOTOR FUEL ADDITIVE AND FUEL CONTAINING SAME

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12 Claims. (Cl. 44—56)

This invention relates to a motor fuel additive capable of inhibiting the formation of deposit in the carburetor and intake manifold of an internal combustion engine as well as to liquid hydrocarbon motor fuels containing minor concentrations of such an additive.

Fuels derived from petroleum, and particularly cracked gasoline fuels, normally contain from 10 to 60% olefins which tend to polymerize upon standing to form "potential" gum. This gum is readily decomposed during combustion of the fuel in the engine to form adhering deposits on the valves and in the intake system.

Gum deposits may be the cause of serious operational difficulties, for the accumulation of deposits in the intake passageway diminishes its size and therefore the maximum air flow which the passage is capable of delivering to the engine. The effects of such deposits on engine performance are, therefore, manifested whenever the engine is operated at or near full throttle as a reduction in power output due directly to the reduction in air flow.

The art has been aware that if there were incorporated in the fuel an additive which has a high solvent power for the gummy residue and which is also a non-volatile liquid at combustion temperatures, it would remain with the residue on the metal parts, such as valve stems, dissolve the gum, and then drain from the parts. Thus it would remove and prevent deposition of residue on such parts. Numerous materials of this type, such as torch oil, have therefore previously been blended with motor fuels. In addition to having a high solvent power for the gummy residue and substantial non-volatility, however, such substances must also be relatively stable to oxidation and decompose into volatile decomposition products. Those materials used heretofore have been deficient in one or more of these properties.

It has now been found that the formation of fuel gum deposits can be inhibited with surprising effectiveness through the utilization of a fuel additive which comprises a solution of boric acid in a solvent mixture consisting essentially of a lower alcohol and an oil-soluble polyoxyalkylene compound.

The solvent mixture of alcohol and polyoxyalkylene is preferably one containing from 20% to 80% alcohol by volume. The additive is preferably prepared by first dissolving as much boric acid as possible in the alcohol and then adding the polyoxyalkylene compound to the solution.

The alcohol component of the solvent mixture may be any lower alcohol, such as methyl-, ethyl-, isopropyl-, butyl-, or an amyl-alcohol, that is soluble in the motor fuel and is capable of dissolving boric acid. Methyl alcohol is preferred.

The oil-soluble polyoxyalkylene compounds forming a component of the solvent mixture in the additive of the invention are old compounds, well known to those skilled in the art, and therefore form no part per se of the present invention. They are characterized by having the following general formula:

$$R-O-\left[(CHR')_n-O\right]_y-R''$$

in which R and R'' are selected from the group consisting of hydrogen, alkyl and acyl groups having from four to about twenty carbon atoms, R' is hydrogen or an alkyl group having from one to about five carbon atoms, n is a variable small whole number from one to about four, preferably two or three, and may vary in this range even in a single long chain molecule, and y represents the number of repeating units in the chain, and may be a whole number from about five to several hundred, depending on the molecular weight.

For the purposes of the invention the character of R and R'', i. e., of the end groups of the chain, is not critical. Gum solvency properties of these compounds are attributed primarily to the oxyalkylene units which form the chain, and not to the end groups. However, although quite a wide variety of these compounds have gum solvency properties, only those with viscosities in the range of 200 to 1000 SSU at 100° F. have the necessary involatility and gasoline solubility characteristics.

These compounds are prepared by condensation of the corresponding oxides, or oxide mixtures, such as ethylene or 1,2-propylene oxide, or mixtures thereof, as is set forth more fully in U. S. Patents Nos. 2,425,755 to Roberts et al., issued August 19, 1947; 2,425,845 to Toussaint et. al., issued August 19, 1947; 2,448,664 to Fife et al., issued September 7, 1948, and 2,457,139 to Fife et al., issued December 28, 1948. If R or R'' is alkyl, an aliphatic alcohol is incorporated in the reaction mixture, and if R or R'' is acyl, an aliphatic carboxylic acid is incorporated in the reaction mixture.

Compounds in accordance with the above general formula are available commercially under the trade name "Ucon" from the Carbide and Carbon Chemicals Corporation. The compounds available commercially may have a hydroxyl group at one end of the chain and an alkyl ether or ester group at the other end of the chain, such as those of Patent Nos. 2,425,755, 2,448,664 and 2,457,139 but it will be understood that for the purpose of the instant invention compounds having two terminal hydroxyl groups at each end of the chain, such as those of Patent No. 2,425,845, or having two terminal alkyl ether or ester groups at each end of the chain are suitable as well. All three types of these compounds are intended to be covered by the generic term "polyoxyalkylene compound" as employed in the specification and claims.

It is essential that the polyoxyalkylene compound be oil-soluble, and have an SSU viscosity at 100° F. of from 200 to 1000. Compounds having a viscosity of less than 200 SSU are too volatile to serve as gum solvents, while those having a viscosity of over 1000 SSU are too insoluble in gasoline fuels to be suitable.

It is surprising that polyoxyalkylene compound-alcohol blends, in which the proportion of alcohol is preferably in the range of 20% to 80% by volume and which are known to inhibit to an appreciable extent the formation of gummy deposits when present in the fuel in amounts ranging from a fraction of 1% to about 5% by volume and preferably about 1% by volume, have their effectiveness increased still further when small amounts of boric acid are dissolved in the blend. It is also surprising that a given concentration of boric acid dissolved in the blend will remain dissolved in the presence of a motor fuel such as gasoline inasmuch as the same concentration of boric acid dissolved in polyoxyalkylene compound alone or in alcohol alone precipitates when the solution is added to gasoline. This is shown by a series of tests conducted to deter-

mine the solubility in gasoline, of "Ucon L–B 285," a monobutyl poly-1,2-oxypropylene glycol having a viscosity of 285 SSU at 100° F., a viscosity index of 146, a pour point of —40° F., a refractive index n_D^{20} of 1.448 and a density of 0.975 g./cc. at 100° F., methanol, and of boric acid dissolved in the Ucon compound alone, the methanol alone and in blends thereof. The results of these tests are tabulated immediately below:

Test No.	Additive in Gasoline, Percent by Volume		Boric Acid, Percent by Weight		Solubility of Boric Acid in Gasoline—Solvent Mixture
	Ucon L–B 285 [1]	Methanol	in Additive	in Gasoline	
1	5				Soluble.
2	5		0.75	0.0375	Boric Acid precipitates.
3		5	0.75	0.0375	Soluble.
4		5	1.0	0.05	Boric Acid precipitates.
5	1.25	3.75	0.75	0.0375	Soluble.
6	0.25	0.75	1.0	0.01	Do.
7	0.25	0.75	1.25	0.0125	Boric Acid precipitates.

[1] A monobutyl poly-1,2-oxypropylene glycol having a viscosity of 285 SSU at 100° F.

Test No. 2 indicates that when a stable solution of as little as 0.75% by weight boric acid in polyoxyalkylene compound is added to gasoline, the boric acid forms a precipitate. Tests Nos. 3 and 4 indicate that boric acid dissolved in methanol alone is somewhat less prone to precipitation when the solutions are added to gasoline, but not when the concentration of boric acid in methanol is as high as 1% by weight. As contrast, test No. 6 shows that the boric acid in a 1% by weight solution thereof in a blend of polyoxyalkylene compound and alcohol does not precipitate upon addition to gasoline but, unlike in tests Nos. 2 and 4, remains stable as a solute.

It has been found by further tests that surprisingly small concentrations of additive containing dissolved boric acid will have an appreciable effect in inhibiting the formation of gummy deposits in the fuel distribution system of an internal combustion engine. While it is preferred to dissolve in the additive and therefore incorporate into the fuel as much boric acid as will form a stable solution with the solvent blends, appreciable effects are also produced when the amount of boric acid in the fuel is considerably below 0.01% by weight and the amount thereof in the additive is considerably below 0.75%. Inasmuch as the maximum amount of boric acid capable of stable dissolution in the solvent blend is about 1% by weight, as shown by the data from test No. 7 in the table, the concentration of boric acid in the gasoline may range from an extremely small but effective amount, e. g., about 0.001% by weight, to about 0.05% by weight and the concentration of the additive in the gasoline may range from a significant amount, i. e., as little as about 0.1% by volume, to about 5% by volume. Balancing the amount of improvement obtained against the expense of the additive and of blending it with the gasoline, it is generally preferred that the amount of boric acid in the blend be approximately 1% by weight and that the concentration of the additive in the gasoline be approximately 1% by volume so that the concentration of boric acid in the gasoline will be approximately 0.01% by weight.

The utility of the additive and motor fuel blend of the invention will become further apparent from the following example:

Example

Two fuels were subjected to comparative tests to determine the relative amounts of deposits in the engine fuel induction system. One of these fuels was a motor gasoline containing 1.5 cc./gal. tetraethyl lead and 1% by volume of an additive consisting of 25% by volume "Ucon L–B 285" and 75% by volume "methanol." The other fuel was a sample of the same gasoline containing

the same amount of the same additive in which, however, 1% by weight, based on the additive, of boric acid had been dissolved prior to addition of the additive to the gasoline. The first fuel therefore contained no boric acid and the second fuel contained 0.01% by weight boric acid.

The procedure used in the tests was as follows: The equipment consisted of a Waukesha single cylinder knock testing engine equipped with a special glass intake manifold. This manifold system incorporated 16¾ inch long Pyrex tube (22 mm. outside diameter) between the carburetor and the intake port where it was held by two special flanges. A Nichrome coil of 10 ohms resistance was wrapped around the glass manifold about 3 inches from the carburetor end so that the heated area was about 3½ inches long. This heating element was controlled by a 110 volt Variac and supplied localized heating to the special manifold. The temperature of the manifold was measured by a surface contact thermocouple located about ½ inch beyond the end of the coil, and the temperature was taken directly from a potentiometer. The intake air was drawn into the carburetor through a preheater consisting of a glow coil heater in the induction system surge. The heater was controlled from the engine panel board. The engine was operated for 10 hours, with the fuel being tested under the following conditions:

R. P. M	600.
Coolant temperature	210° F.
Oil temperature	Approximately 150° F.
Air temperature:	
Intake at carburetor	95° 5.
½ beyond the coil	170° 5.
Approximate fuel consumption	1.2 lbs./hr. (1.8 gal./10 hrs.).

The glass manifold was weighed both before and after each test run. It was found that whereas the test with the gasoline containing no boric acid deposited an average of 0.0180 gram in the glass manifold after 10 hours of operation, the gasoline containing 0.01% by weight of boric acid deposited an average of only 0.0088 gram under the same conditions, i. e., less than half the amount of gum deposited in the other test. These results show the remarkable effectiveness of the small concentrations of boric acid in a polyoxyalkylene compound alcohol blend.

It is to be understood that many modifications and alterations will occur to those skilled in the art upon reading this description. All such modifications and alterations are intended to be included within the scope of the invention as defined in the appended claims.

I claim:

1. An additive for use with a gasoline motor fuel which comprises a solution of boric acid in a solvent mixture consisting essentially of a lower alcohol and an oil-soluble polyoxyalkylene compound having the formula

$$R{-}O{-}\left[(CHR')_n{-}O\right]_y{-}R''$$

where R and R'' are selected from the group consisting of hydrogen and alkyl and acyl groups having from four to about twenty carbon atoms, R' is selected from the group consisting of hydrogen and alkyl groups having from one to about five carbon atoms, n is a small whole number having a value within the range from one to about four, and y is a number representing the number of repeating units within the chain to give a viscosity of between 200 and 1000 SSU at 100° F., the amount of alcohol in said solvent mixture ranging from 20% to 80% by volume and the amount of boric acid ranging from an effective amount up to 1% by weight of said solvent mixture.

2. The additive defined in claim 1 wherein the amount

of boric acid is about 1% by weight of the solvent mixture.

3. The additive defined in claim 1 wherein the oil-soluble polyoxyalkylene compound has a viscosity of 285 SSU at 100° F.

4. The additive defined in claim 1 wherein lower alcohol is methanol.

5. The additive defined in claim 1 wherein lower alcohol is isopropanol.

6. A gasoline motor fuel containing a minor amount within the limits of solubility in the gasoline of an additive comprising a solution of boric acid in a solvent mixture consisting essentially of a lower alcohol and an oil-soluble polyoxyalkylene compound having the formula

$$R-O-\left[(CHR')_n-O\right]_y-R''$$

where R and R'' are selected from the group consisting of hydrogen and alkyl and acyl groups having from four to about twenty carbon atoms, R' is selected from the group consisting of hydrogen and alkyl groups having from one to about five carbon atoms, n is a small whole number having a value within the range from one to about four, and y is a number representing the number of repeating units within the chain to give a viscosity of between 200 and 1000 SSU at 100° F., the concentration by volume of the additive in the fuel ranging from a significant amount up to about 5% and the amount of boric acid ranging from an effective amount to about 1% by weight of said solvent mixture.

7. The motor fuel defined in claim 5 wherein the amount of boric acid present in the fuel is about 0.01% by weight.

8. The motor fuel defined in claim 5 wherein the oil-soluble polyoxyalkylene compound has a viscosity of 285 SSU at 100° F.

9. The motor fuel defined in claim 5 wherein lower alcohol is methanol.

10. The motor fuel defined in claim 5 wherein lower alcohol is isopropanol.

11. An additive for use with a gasoline motor fuel which comprises a solution of boric acid in a solvent mixture consisting essentially of a lower alcohol and an oil-soluble polyoxyalkylene compound having the formula

$$R-O-\left[(CHR')_n-O\right]_y-R''$$

where R and R'' are selected from the group consisting of hydrogen and alkyl and acyl groups having from four to about twenty carbon atoms, R' is selected from the group consisting of hydrogen and alkyl groups having from one to about five carbon atoms, n is a small whole number having a value within the range from one to about four, and y is a number representing the number of repeating units within the chain to give a viscosity of between 200 and 1000 SSU at 100° F., the amount of alcohol in said solvent mixture ranging from 20% to 80% by volume and the amount of boric acid ranging from an effective amount up to a minor amount within the limits of solubility of boric acid in the solvent mixture.

12. A gasoline motor fuel containing a minor amount within the limits of solubility in the gasoline of an additive comprising a solution of boric acid in a solvent mixture consisting essentially of a lower alcohol and an oil-soluble polyoxyalkylene compound having the formula

$$R-O-\left[(CHR')_n-O\right]_y-R''$$

where R and R'' are selected from the group consisting of hydrogen and alkyl and acyl groups having from four to about twenty carbon atoms, R' is selected from the group consisting of hydrogen and alkyl groups having from one to about five carbon atoms, n is a small whole number having a value within the range from one to about four, and y is a number representing the number of repeating units within the chain to give a viscosity of between 200 and 1000 SSU at 100° F., the concentration by volume of the additive in the fuel ranging from a significant amount up to about 5% and the amount of boric acid ranging from an effective amount up to a minor amount within the limits of solubility of boric acid in the solvent mixture.

References Cited in the file of this patent

UNITED STATES PATENTS

2,151,432	Lyons	Mar. 21, 1939
2,460,700	Lyons	Feb. 1, 1949
2,563,101	Colwell	Aug. 7, 1951
2,614,985	Cook	Oct. 21, 1952

UNITED STATES PATENT OFFICE

CERTIFICATE OF CORRECTION

Patent No. 2,800,400 July 23, 1957

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It is hereby certified that error appears in the printed specification of the above numbered patent requiring correction and that the said Letters Patent should read as corrected below.

Column 3, line 33, for "As contrast" read -- In contrast --; column 4, line 32, for "$\frac{1}{2}$ beyond the coil" read -- $\frac{1}{2}$" beyond the coil --; column 5, lines 17 and 49, and column 6, line 22, after the closing bracket in the formulae, insert sub "y", in each occurrence.

Signed and sealed this 10th day of September 1957.

(SEAL)

Attest:

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