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LIQUEFIED PETROLEUM GAS FUEL COMPOSITION

Herbert E. Vermillion, Wappingers Falls, and James J. O'Loughlin, Tuckahoe, N.Y., assignors to Texaco Inc., New York, N.Y.

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ABSTRACT OF THE DISCLOSURE

Motor fuel composition comprising a liquefied petroleum gas containing from about 0.0001 to 0.1 volume percent of (1) a polymer of a C_2 to C_6 unsaturated hydrocarbon, (2) a copolymer of a C_2 to C_6 unsaturated hydrocarbon, or (3) the corresponding hydrogenated polymer or copolymer, said polymer or copolymer having a molecular weight in the range from about 500 to 3500 and a method for operating an internal combustion gasoline engine.

BACKGROUND OF THE INVENTION

Field of invention

Internal combustion engines, particularly of the overhead valve design, are subject to a substantial build-up of hard, tenacious deposits on the intake valves and ports of the engine. These deposits seriously interfere with the operation of the engine. As the deposits level grows, the engine exhibits loss of power, rough idling, and, occasionally, valve burning. When the deposits become excessive, portions break off and are drawn into the combustion chamber. Instances of mechanical damage to the piston and piston rings caused by these deposits have been observed.

Considerable work has been conducted to determine the nature and cause of the intake valve deposits. The deposits themselves are composed essentially of the by-products of fuel combustion and lubricating oil deterioration. Analysis of the deposits indicates that the viscosity index improvers contained in the lubricating oil act as binders for the deposits. Polymethacrylate viscosity index improvers, as an example, are one class of materials which appear to contribute materially to the deposits build-up.

The reason lubricating oil deterioration can contribute to deposits in the fuel-air intake system is seen from a study of engine operation. A spark-ignited internal combustion engine contains a reservoir of lubricating oil in the crankcase. When the engine is running, the primary lubrication is effected by the crankcase oil being splashed up on the operating parts of the engine and on the cylinder walls. A portion of this oil is pumped to the upper parts of the engine to lubricate the working parts therein. In an overhead valve engine, a small stream of the oil pumped to the upper section of the engine is constantly run down the intake and exhaust valve stems to insure that they are constantly lubricated in their guides during operation. The oil trickling down the intake valve stem, the intake valve head and around the intake port is apparently pyrolyzed under the temperatures prevailing, thereby contributing to the formation and build-up of the above-noted deposits.

This deposits problem is not encountered to any material extent in or around the exhaust ports or valves. This is believed to be due to the high temperatures existing at the exhaust valve during the exhaust cycle and to the action of the expelled exhaust gases which do not permit a laydown of deposits or continually burns, evaporates or carries off any potential deposits.

With the advent of strict measures to reduce or prevent atmospheric air pollution caused by the exhaust from internal combustion engines, numerous changes are being adopted or proposed to solve the serious problem noted. These changes are directed not only at the engine design involving the crankcase ventilation system, evaporative controls, catalytic mufflers and the like but they are also being directed to changes in the gasoline fuel composition. Among the changes proposed are use of a less volatile gasoline mixture, removal of tetraalkyl lead anti-knock compounds from gasoline and the incorporation of combustion promoters in gasoline.

DESCRIPTION OF THE PRIOR ART

It is not known to provide an additive-containing liquefied petroleum gas motor fuel composition which prevents or inhibits the formation of deposits on the intake valves and ports of a spark-ignited, internal combustion engine.

SUMMARY OF THE INVENTION

The fuel composition of the invention comprises a liquefied petroleum gas containing a minor amount of a polymer, copolymer or hydrogenated polymer or copolymer of a C_2 to C_6 unsaturated hydrocarbon. More specifically, the fuel composition of the invention contains from about 0.001 to 0.1 percent of (1) a polymer of a C_2 to C_6 unsaturated hydrocarbon, (2) a copolymer of a C_2 to C_6 unsaturated hydrocarbon, or (3) the corresponding hydrogenated polymer or copolymer, said polymer, copolymer or hydrogenated derivative having a molecular weight in the range from about 500 to 3500. The method of the invention comprises supplying to and burning in a spark-ignited internal combustion gasoline engine the above-described liquefied petroleum gas fuel composition.

The provision of an improved petroleum gas motor fuel composition effective for preventing or inhibiting intake valve and port deposits in an internal combustion engine is most surprising since additive-containing petroleum gas fuel compositions of this type have not been known heretofore.

The polymer which is employed in this fuel composition is a polymer prepared from an unsaturated hydrocarbon, i.e. a monoolefin, diolefin or copolymer of either having an average molecular weight in the range of about 500 to 3500. Mixtures of olefin polymers with an average molecular weight falling within the foregoing range are also effective. Olefins which can be employed to prepare the polyolefin polymers include ethylene, propylene, 1-butene, 2-butene, isobutylene, amylene, hexylene, butadiene, and isoprene. In general, the olefin monomers from which the polyolefins are prepared are unsaturated hydrocarbons having from two to six carbon atoms. The polyolefin polymers from C_3 and C_4 olefins, such as polypropene, polyisobutylene and polybutene-1, are particularly preferred for the practice of this invention. Other polyolefins which can be employed are those prepared by cracking polyolefin polymers or copolymers of high molecular weight to a polymer in the above-noted molecular weight range. Derivatives of the noted polymers obtained by saturating the polymers by hydrogenation are also effective and are a part of this invention. The word "polymers" is intended to include the polyolefin polymers and their corresponding hydrogenated derivatives.

The molecular weight of the polymer or polymer derivative component is important in preparing an effective fuel composition according to this invention. Effective fuel compositions of the invention require a polymer or hydrogenated polymer derivative having an average molecular weight broadly in the range of 500 to 3500 as determined by an osmometer method. More desirable fuel

compositions are obtained with polymers and derivatives having molecular weights in the range from 650 to 2600. Particularly effective fuel compositions can be prepared from relatively low molecular weight polymers, such as polypropylenes, polybutenes and copolymers of same having average molecular weights in the range of 850 to 1200.

The method of preparation of the olefin polymer, copolymers, and hydrogenated polymers or copolymers is well known in the art and is not part of the present invention. The average molecular weight determination for the polymers is determined by the ASTM Osmometer Method identified as ASTM D-2503-67. Examples of specific polymers which are effective in the fuel composition of the invention together with their average molecular weight are as follows: polypropylene 800, polypropylene 850, polypropylene 975, polypropylene 1120, polypropylene 1150, polypropylene 1370, polypropylene 2560, polybutene-1 800, polybutene-1 1200, polybutene-2, 1100, polyisobutylene 850, polyisobutylene 1000, polyisobutylene 1200, polyisobutylene 1575, hydrogenated polybutene 1100, 1 to 1 C₃-C₄ copolymer 1010 and ethylene-butylene copolymer 810.

The base fuel of the invention is liquefied petroleum gas or liquefied gas commonly referred to as LPG, LP gas and LNG. It comprises the compounds or mixtures of compounds produced with or derived from petroleum which are gases at room temperature and atmospheric pressure and which are compressed or liquefied in use. As used herein, the term liquefied petroleum gas refers to both the compressed and liquefied petroleum gases. These liquefied gases or mixtures thereof may be natural gases or they can be derived or manufactured from light or heavy petroleum oils by cracking or reforming or from other hydrocarbon sources, such as coal, kerogen and asphalt. The important natural gases (LNG) are methane and ethane. The important LPG gases are propane and normal- and isobutanes, having 3 and 4 carbon atoms respectively. Minor amounts of ethane and ethylene and other C₃ and C₄ hydrocarbon gases, such as propylene, isobutylene, butene-1 and butene-2 are commonly present in the LPG gas base fuel. Minor amounts of low-boiling normally liquid hydrocarbons, such as a pentane, can also be present in the liquefied petroleum gas. The Natural Gas Processors Association has published standards for propane, commercial propane, commercial butane and butane-propane mixtures which appear in the Second edition of "Encyclopedia of Chemical Technology" by Kirk-Othmer, vol. 12, pages 470-471. The petroleum gases are normally stored under superatmospheric pressure and/or at subatmospheric temperature sufficient to compress most if not all of the gas into liquid form, hence the name liquefied petroleum gas. Methods for handling liquefied petroleum gas fuels have been described in papers presented at meetings of the Society of Automotive Engineers. Paper No. 700078 by McJones and Corbeil entitled "Natural Gas Fueled Vehicles Exhaust Emissions and Operational Characteristics" presented at the Automotive Engineering Congress held at Detroit, Mich. on Jan. 12-16, 1970 and Paper No. 680529 by Baxter, Leck and Mizelle entitled "Total Emissions Control Possible With LP-Gas Vehicle" presented at the West Coast Meeting at San Francisco, Calif. on Aug. 12-15, 1968 describe these methods. It is contemplated that the polymer can be added to the petroleum gas fuel feed stream going to the engine preferably with the aid of a carrier, such as a liquefied petroleum gas.

The novel additive-containing fuel composition of the invention is conveniently prepared and stored under pressure in the liquid form with the above-described polymer dissolved therein. In general, this liquefied fuel composition contains from about 0.0001 to 0.1 volume percent of the polymer additive based on the liquid volume of the gas fuel. A more effective concentration of the additive is from about 0.001 to 0.075 volume percent with the preferred concentration being from about 0.01 to 0.05 percent.

The fuel composition is tested in the Buick Induction System Deposits Test which uses a 1964 Buick 425 CID V-8 engine modified to run on a liquefied petroleum gas fuel. The fuel is evaluated basis deposit ratings of the intake valves and ports of the engine as more fully described below.

The test is conducted using the noted engine equipped with PCV (Positive Crankcase Ventilation) valve and installed on a dynamometer test stand with supporting equipment to control speed, load and engine temperatures. The engine is run on the test fuel for approximately 96 hours as described below.

Prior to each run, the cylinder heads are completely reconditioned and new intake valves installed. Special care must be taken to insure that the inlet valve-to-valve guide clearance be maintained between 0.0035 to 0.0045 inch. In addition, the valve seat widths are maintained between $\frac{3}{4}$ and $\frac{5}{4}$ inch. The engine block is completely overhauled in accordance with the procedures stated in the 1964 Buick Service Manual when blow-by or oil consumption become excessive.

The engine is charged with four quarts of oil and flushed for 15 minutes at 1500 r.p.m. Following an oil drain, four quarts of new oil are added and the fuel tests begun. The engine is operated on a four-stage six-hour cycle for a total of 16 cycles or 96 hours as follows:

	Cycle time	Hours	Operation
State:			
1-----	0-1	1	Idle;
2-----	1-4	3	Road load;
3-----	4-5	1	Heavy load.
4-----	5-6	1	Rest.

Operation	Idle stage	Road load stage	Heavy load stage
Speed, r.p.m.-----	1,000±15	2,250±15	2,250±15
Load, b.h.p.-----	0	30±1.5	75±1.5
Air-fuel ratio-----	11.5±0.5	12.2±0.4	12.2±0.4
Spark advance*, BTDC-----	30	40	34
Exhaust back press., in. Hg.-----	0.2	1.0±0.1	3.5
Intake air temp., ° F.-----	140±2	140±2	140±2
Jacket-out temp., ° F.-----	200±2	200±2	200±2
Ck's oil temp., ° F.-----	200	234±2	234±2

* Approximate values—spark advance set 6° BTDC at 600 r.p.m.

Upon completion of a run, the cylinder heads and valves are removed and the valves visually rated for the extent of deposit build-up on the valve tulip surface. The intake valve deposits are rated according to a merit rating scale running from 10 to 1. A rating of 10 indicates a perfectly clean valve while the rating of 1 is applied to an extremely heavily coated valve. Deposits around the port opening are rated T-trace, L-light, M-medium and H-heavy.

The following examples illustrate the practice of this invention.

Base Fuel A is commercial propane meeting the NGPA (Natural Gas Processors Association) specifications having a maximum vapor pressure in p.s.i.g. at 100° F. of 200 and a maximum 95% boiling point at 760 mm. Hg. of -37° F. Base Fuel B is a butane-propane mixture having a maximum vapor pressure of 200 and a 95% boiling point of 36° F. Base Fuel C is commercial butane having a maximum vapor pressure at 100° F. of 70 p.s.i.g. and a maximum 95% boiling point at 760 mm. of pressure of 36° F.

In rating an additive-containing liquefied petroleum gas fuel composition an improvement in the valve rating of about 0.5 unit above the base fuel and an acceptable port rating, Trace or Light, is considered an important improvement. An improvement of about 1.0 unit or more over the base fuel and a passing port rating is considered a very significant improvement in engine cleanliness for the additive-containing fuel composition.

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EXAMPLE I

The fuel composition of the example consists of commercial propane, Base Fuel A, liquefied under superatmospheric pressure containing about 0.05 volume percent based on the liquidified volume of the propane of polypropene 850.

This additive-containing fuel composition provides a substantial improvement in engine cleanliness as determined in the Buick Induction System Deposits Test over the performance of the non-additive Base Fuel A.

EXAMPLE II

A fuel composition is prepared consisting of liquefied commercial propane, Base Fuel A, and about 0.075 volume percent of polypropene 975. This additive-containing liquefied petroleum gas gives a substantial improvement in engine cleanliness in the Buick Induction System Deposits Test over what is obtained using non-additive Base Fuel A alone.

EXAMPLE III

A fuel composition is prepared consisting of a liquefied butane-propane gas mixture, Base Fuel B, containing about 0.03 volume percent, based on the liquid volume of the butane-propane mixture, of polyisobutylene 1200. This additive-containing liquefied petroleum gas gives a substantial improvement in engine cleanliness in the Buick Induction System Deposits Test as compared to non-additive Base Fuel B alone.

EXAMPLE IV

A fuel composition is prepared consisting of liquefied commercial butane, Base Fuel C, containing about 0.05 volume percent, based on the liquid volume of the commercial butane, of a 1 to 1 propylene-isobutylene copolymer 1010. This additive-containing liquefied petroleum gas gives a substantial improvement in engine cleanliness in the Buick Induction System Deposits Test as compared to non-additive Base Fuel C alone.

EXAMPLE V

A fuel composition is prepared consisting of liquefied natural gas base fuel containing about 0.05 volume percent based on the fuel composition of polypropene 1150. This additive-containing liquefied petroleum gas gives a substantial improvement in engine cleanliness in the Buick Induction System Deposits Test as compared to the non-additive natural gas base fuel alone.

In general, a liquefied or compressed petroleum gas or gas mixture containing a minor intake valve and port deposit inhibiting amount of a polymer, copolymer or hydrogenated polymer or copolymer of a C_2 to C_6 olefin having an average molecular weight ranging from about 500 to 3500 provides a substantial improvement in engine cleanliness in the Buick Induction System Deposits Test as compared to the petroleum gas base fuel alone.

We claim:

1 A motor fuel composition comprising a liquefied petroleum gas containing from about 0.0001 to 0.1 volume percent of (1) a polymer of a C_2 to C_6 unsaturated hydrocarbon, (2) a copolymer of a C_2 to C_6 unsaturated hydrocarbon or (3) the corresponding hydrogenated polymer or copolymer, said polymer, copolymer or hydrogenated derivative having a molecular weight in the range from about 500 to 3500.

2. A motor fuel composition according to claim 1 in which said liquefied petroleum gas is propane.

3. A motor fuel composition according to claim 1 in which said liquefied petroleum gas is butane.

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4. A motor fuel composition according to claim 1 in which said liquefied petroleum gas is a mixture of C_3 and C_4 hydrocarbons.

5. A motor fuel composition according to claim 1 in which said liquefied petroleum gas is natural gas.

6. A motor fuel composition according to claim 1 in which said polymer has an average molecular weight in the range from 650 to 2600.

7. A motor fuel composition according to claim 1 in which said polymer of an unsaturated hydrocarbon is polypropene 850.

8. A motor fuel composition according to claim 1 in which said polymer of an unsaturated hydrocarbon is from a C_3 - C_4 olefin.

9. A motor fuel composition according to claim 1 in which said polymer of an unsaturated hydrocarbon is polypropene 975.

10. A motor fuel composition according to claim 1 in which said polymer of an unsaturated hydrocarbon is polybutene-1 1200.

11. A motor fuel composition according to claim 1 in which said polymer of an unsaturated hydrocarbon has a molecular weight from about 850 to 1200.

12. A method for preventing the build-up of intake valve and port deposits in a spark-ignited, internal combustion engine which comprises supplying to said engine a motor fuel composition comprising a liquefied petroleum gas containing from about 0.0001 to 0.1 volume percent of (1) a polymer of a C_2 to C_6 unsaturated hydrocarbon, (2) a copolymer of a C_2 to C_6 unsaturated hydrocarbon or (3) the corresponding hydrogenated polymer or copolymer, said polymer, copolymer or hydrogenated derivative having a molecular weight in the range from about 500 to 3500.

13. A method according to claim 12 in which said liquefied petroleum gas is propane.

14. A method according to claim 12 in which said liquefied petroleum gas is butane.

15. A method according to claim 12 in which said liquefied petroleum gas is a mixture of C_3 and C_4 hydrocarbons.

16. A method according to claim 12 in which said liquefied petroleum gas is natural gas.

17. A method according to claim 12 in which said polymer of an unsaturated hydrocarbon is polypropene 975.

18. A method according to claim 12 in which said polymer of an unsaturated hydrocarbon is polypropene 850.

19. A method according to claim 12 in which said polymer of an unsaturated hydrocarbon has a molecular weight from about 650 to 2600.

20. A method according to claim 12 in which said polymer of an unsaturated hydrogen is from a C_3 - C_4 olefin.

21. A method according to claim 12 in which said polymer of an unsaturated hydrocarbon is polybutene-1 1200.

References Cited

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DANIEL E. WYMAN, Primary Examiner

Y. H. SMITH, Assistant Examiner

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