United States Patent Office

3,574,574
Patented Apr. 13, 1971

3,574,574
MOTOR FUEL COMPOSITION

Fred W. Moore, Fishkill, and Herbert E. Vermillion, Wappingers Falls, N.Y., assignors to Texaco Inc., New York, N.Y.

No Drawing. Filed June 12, 1968, Ser. No. 738,376
Int. Cl. C10l 1/18
U.S. Cl. 44—66 16 Claims

ABSTRACT OF THE DISCLOSURE

A motor fuel composition which promotes reduced intake valve and port deposits containing from 0.005 to 0.1 volume percent of a polyester of a polymerized carboxylic acid.

This invention relates to a motor fuel composition for a four-cycle, spark-ignited internal combustion engine. More particularly, the invention relates to a motor fuel composition containing a polyester of polymerized carboxylic acids as an additive in an amount effective to reduce or eliminate harmful deposits on the intake valves and around the ports of an internal combustion engine. The invention also relates to a method for inhibiting the formation of such deposits.

Internal combustion engines of current manufacture are subject to a substantial build-up of tenacious deposits on the intake valves and around the ports of the engine, overhead valve engines being particularly prone to this condition. The deposits seriously interfere with the proper functioning of the fuel intake system. As the level of deposits builds up, the engine will exhibit a substantial loss of power, rough idling and even valve burning. On further deposit build-up, portions will break off and be drawn into the combustion chamber where they can cause scoring of the combustion cylinder walls and other mechanical damage.

The intake valve and port deposits are composed of the by-products of fuel combustion and lubricating oil deterioration. Research has shown that the viscosity index improvers contained in the lubricating oil act as binders for the deposits and that certain types of VI improvers appear to be worse than others. Polymethacrylate viscosity index improvers are one class of materials which appear to contribute materially to the deposit build-up.

A description of engine operation illustrates how lubricating oil deterioration can contribute to deposits in the intake manifold. Spark-ignited internal combustion engines contain a reservoir of lubricating oil in the crankcase. When the engine is in operation, the greater part of this oil is forced and splashed up on the pistons and cylinder walls for cooling and lubricating. However, some 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 over both the intake and exhaust valve stems to insure that they are constantly lubricated in their guides during operation. The oil trickling over the intake valve stem and other portions of the valve head is apparently pyrolyzed under the temperatures experienced resulting in the laydown and build-up of deposits with the viscosity index improver acting as a binder.

This particular problem is not encountered to any material extent in the exhaust manifold or around the exhaust valves. This is believed to be due to the high temperatures existing in the exhaust manifold which either do not permit the laydown of deposits or continually burns off any such deposits that may be laid down.

It has now been discovered that a minor amount of a polyester of a polymerized carboxylic acid when dissolved in a motor fuel is effective for removing or preventing the formation of deposits on the intake valves and ports of a four-cycle, spark-ignited, internal combustion engine. More specifically, a motor fuel composition comprising a mixture of hydrocarbons boiling in the gasoline boiling range broadly containing from about 0.005 to 0.1 volume percent of a fully esterified ester of a polymerized carboxylic acid is effective for removing the aforesaid deposits. The method of the invention involves running the four-cycle, spark-ignited internal combustion engine on a motor fuel composition containing the additive of the invention.

The base fuel in the composition of the invention comprises a mixture of hydrocarbons boiling in the gasoline boiling range. This base fuel may consist of straight chain or branched chain paraffins, cyclo-paraffins, olefins and aromatic hydrocarbons or any mixture of these. The fuel can be derived from straight run naphtha, polymer gasoline, natural gasoline or from catalytically cracked or thermally cracked hydrocarbons and catalytically reformed stocks. The composition or hydrocarbon components of the base fuel is not critical nor does the octane level of the base fuel have any material effect on the invention. Thus, any conventional motor fuel base can be employed in the practice of this invention. In addition, the base fuel can contain any of the additives normally employed in a motor fuel. For example, the base fuel can contain an anti-knock compound, such as a tetraalkyl lead compound including tetraethyl lead, tetramethyl lead, tetrabutyl lead, mixtures thereof and the like. The tetraethyl lead mixture commercially available for automotive use contains an ethylene chloride-ethylene bromide mixture as a scavenger for removing lead from the combustion chamber in the form of a volatile lead halide. The motor fuel may also contain any of the conventional anti-icing additives, corrosion inhibitors, dyes, upper cylinder lubricating oils and the like.

The esters employed in this invention are prepared from dimer and trimer acids which are produced by the condensation of unsaturated aliphatic monocarboxylic acids having between about 16 and 18 carbon atoms per molecule. For example, linoleic acid can be polymerized or condensed to form essentially the dimer of linoleic acid, a dicarboxylic acid and also can be polymerized to form essentially the trimer of linoleic acid, a tricarboxylic acid. Similarly, other C_{16} and C_{18} unsaturated aliphatic monocarboxylic acids, including ricinoleic and linolenic acid, can be polymerized to dimer and trimer acids. The preparation of such dimer and trimer acids is described in U.S. 2,632,695.

The polyesters are prepared by reacting a suitable amount of an aliphatic alcohol with the polycarboxylic acid to esterify essentially all of the carboxyl groups in the acid. Esterification is conducted according to conventional, known methods. Alcohols which are suitable for this purpose are the aliphatic alcohols, preferably saturated aliphatic alcohols, having from about 2 to 20 carbon atoms. Representative effective alcohols include n-butyl alcohol, isobutyl alcohol, n-propyl alcohol, ethyl alcohol, hexyl alcohol, 2-ethylhexyl alcohol, decyl alcohol, dodecyl alcohol, tridecyl alcohol, lauryl alcohol, stearyl alcohol, hexadecyl alcohol and nondecyl alcohol. For the purposes of this invention ester and/or polyester refers to the essentially fully esterified polycarboxylic acid to distinguish from partially esterified acids having some free carboxylic acid in the ester.

The preparation of a typical polyester employed in the fuel of the invention was as follows:

870 grams (1.0 mole) of commercial "Trimer Acid" consisting of about 90 percent of the trimer of linoleic acid and 5 percent of the dimer of linoleic acid and 5 percent of linoleic acid was combined with 620 grams (>3.0 moles) of tridecyl alcohol in a hydrocarbon solvent and esterification conducted at a temperature from 80 to 150° C. for about 6 hours.

The following table lists the polyesters prepared for this invention in accordance with the above method.

TABLE I

Example:		
1	Tri(tridecyl)	Ester of the trimer of linoleic acid.
2	Tri(n-butyl)	Do.
3	Di(tridecyl)	Ester of the dimer of linoleic acid.
4	Tri(isodecyl)	Ester of the trimer of linoleic acid.
5	Tri(n-decyl)	Do.
6	Tri(isodecyl)	Do.
7	Tri(n-butyl)	Do.
8	Tri(isobutyl)	Do.
9	Tri(sec. butyl)	Do.

The novel fuel composition of the invention is prepared by adding a polyester of a polymerized carboxylic acid to the base fuel. Broadly, the additive can be employed in a range from about 0.005 to 0.1 volume percent. A preferred additive range for the fuel composition is from about 0.015 to 0.075 volume percent. A still more particularly preferred range for the additive is from about 0.02 to 0.05 volume percent, this range corresponding to about 60 and 150 p.t.b. (pounds of additive per thousand barrels of gasoline).

The Buick Induction System Deposits Test is conducted using a 1964 Buick 425 CID V–8 engine operated in a cyclic manner to simulate usual motor car usage. The details for this test are given in a co-pending application S.N. 546,212 and now U.S. 3,502,451.

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. The rating 10 is a perfectly clean valve. The rating 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 base fuel employed in the following examples was a typical premium grade gasoline containing 3 cc. of TEL per gallon. This fuel consisted of 25.0 percent aromatics, 14.5 percent olefins and 60.5 percent aliphatic hydrocarbons as determined by FIA analysis. This fuel had an ASTM distillation I.B.P. of 95° F., and E.P. of 380° F. and a research octane number of 101.3. The results of the tests are set out in the table below.

TABLE II.—BUICK INDUCTION SYSTEM DEPOSITS TEST

Additive	Additive concentration in fuel, p.t.b.	Valve rating [1]	Port rating [2]
None (base fuel)		5.8	H
Example 1	230	9.1	T
Example 2	230	8.6	L
Example 3	230	8.5	T
Example 4	230	8.7	T
Example 5	150	7.6	T
Example 6	150	7.7	T
Example 7	150	7.9	T
Example 8	150	7.1	T
Example 9	150	7.3	T

[1] Valve rating: 10=clean.
[2] Port rating: H=heavy, M=moderate, L=light, T=trace.

In the above test, the base fuel without any deposit control additive gave a valve rating of 5.8 and a port rating of heavy. An improvement of 0.5 in the valve rating is a significant and important improvement as is a change in the port rating from one deposit condition to a lighter deposit rating. It is evident that the deposits control additive of the invention provided a remarkable improvement both in the valve rating and in the port rating.

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 motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing from about 0.005 to 0.1 percent of a polyester prepared from the reaction of a compound selected from polycarboxylic dimer and trimer acids produced by the polymerization of an unsaturated aliphatic mooncarboxylic acid having between 16 and 18 carbon atoms per molecule and an aliphatic monohydric alcohol having from about 2 to 20 carbon atoms.

2. A motor fuel composition according to claim **1** containing from about 0.02 to 0.05 of said polyester.

3. A motor fuel composition according to claim **1** containing from about 0.005 to 0.1 percent of the polyester of the reaction of the tricarboxylic acid trimer of linoleic acid and an aliphatic alcohol having from 2 to 20 carbon atoms.

4. A motor fuel composition according to claim **1** containing from about 0.005 to 0.1 percent of the polyester of the dicarboxylic acid timer of linoleic acid.

5. A motor fuel composition according to claim **1** in which said polyester is the tri(tridecyl) ester of the trimer of linoleic acid.

6. A motor fuel composition according to claim **1** in which said polyester is the tri(n-butyl) ester of the trimer of linoleic acid.

7. A motor fuel composition according to claim **1** in which said polyester is the tri(n-decyl) ester of the trimer of linoleic acid.

8. A motor fuel composition according to claim **1** in which said polyester is the tri(isodecyl) ester of the trimer of linoleic acid.

9. A motor fuel composition according to claim **1** in which said polyester is the di-(tridecyl) ester of the dimer of linoleic acid.

10. A motor fuel composition according to claim **1** in which said polyester is the tri(isobutyl) ester of the trimer of linoleic acid.

11. A motor fuel composition according to claim **1** in which said polyester is the tri(sec.butyl) ester of the trimer of linoleic acid.

12. A method of operating a spark-ignited internal combustion engine which comprises burning in said engine a motor fuel composition comprising a mixture of hydrocarbons in the gasoline boiling range containing from about 0.005 to 0.1 percent of a polyester prepared from the reaction of a compound selected from polycarboxylic dimer and trimer acids produced by the polymerization of an unsaturated aliphatic monocarboxylic acid having between about 16 and 18 carbon atoms per molcule and an aliphatic monohydric alcohol having from about 2 to 20 carbon atoms.

13. A method according to claim **12** in which said motor fuel contains from about 0.02 to 0.05 percent of said polyester.

14. A method according to claim **12** in which said polyester is prepared from the trimer of linoleic acid and an aliphatic alcohol having from about 2 to 20 carbon atoms.

15. A method according to claim **12** in which said polyester is prepared from the dimer of linoleic acid and an an aliphtic alcohol having froma bout 2 to 20 carbon atoms.

16. A motor fuel composition according to claim **1** in which said polycarboxylic dimer and trimer acid has at least 32 carbon atoms.

References Cited

UNITED STATES PATENTS

1,692,784	11/1928	Orelup et al.	44—66
3,235,494	2/1966	Piatt et al.	44—66X

FOREIGN PATENTS

932,773	7/1963	Great Britain	44—66

DANIEL E. WYMAN, Primary Examiner

W. J. SHINE, Assistant Examiner

U.S. Cl. X.R.

44—70