(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) Publication number: **0 127 316**
A2

(12) # EUROPEAN PATENT APPLICATION

(21) Application number: **84302782.2**

(51) Int. Cl.³: **C 10 L 1/02**

(22) Date of filing: **25.04.84**

(30) Priority: **29.04.83 US 489735**

(43) Date of publication of application:
05.12.84 Bulletin 84/49

(84) Designated Contracting States:
BE DE FR GB IT NL SE

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(54) **Flame luminosity improvers for methanol.**

(57) A methanol fuel composition with improved flame luminosity comprising methanol and a petroleum hydrocarbon mixture which includes selected aromatic and saturate/olefin fractions and forms an azeotropic mixture with all of the methanol and has a select boiling range.

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This invention relates to a methanol fuel composition.

The composition of this invention has improved flame luminosity and comprises methanol and a select petroleum hydrocarbon mixture. More particularly, this invention is directed to the improved flame luminosity of methanol which results by combining methanol with a petroleum hydrocarbon mixture comprising selected aromatic and saturate/olefin fractions to form an azeotropic mixture and which combination has a select boiling range.

The use of methanol as a fuel for various needs, such as in spark ignition engines, is becoming more and more of interest because of the varying availability of different petroleum fuels and the change in costs of such fuels. One of the problems that exists with the use of methanol is that it burns with a light blue flame that is almost invisible under normal light conditions such as daylight or a lighted room. Because it burns with such a nonluminous flame, the use of methanol presents a special safety hazard, especially when used as a fuel. Thus, a methanol spill could be very dangerous since its ignition might not be visible to people in the near vicinity.

The use of co-fuels such as volatile hydrocarbons has been shown to enhance flame luminosity and visibility as disclosed in "Use of Co-Fuels to Increase the Luminosity of Methanol Pool Fires: Some Preliminary Findings" by J. E. Anderson and W. O. Siegl, presented to Division of Petroleum Chemistry, Inc., A.C.S., Kansas City Meeting, September, 1982. As

generally shown in this article, such combinations of methanol with a co-fuel did not provide flame luminosity over the entire burning cycle.

Other teachings showed that flame luminosity could be improved by adding gasoline, toluene or reformate to methanol containing 5 and 10 vol. % pentane. By adding 5% toluene to the pentane containing methanol fuel, the flame was visible until about 50 to 70% of the methanol was consumed. By using 15% gasoline in methanol, a visible light persisted until all the liquid was consumed. See "Environmental Implication of the Use of Alcohol-Fuel Highway Vehicles" by E. E. Ecklund, T. J. Timbario and P. W. McCallum, presented to the 75th Annual Meeting of Air Pollution Control Association, New Orleans, June 20-25, 1982 and "Methanol Fuel Modification for Highway Vehicle Use" by J. L. Keller, G. M. Nakaguchi and J. C. Ware, Final Report, U. S. Dept. of Energy EY-76-C-04-3683, published as NTIS document HCP/W3683-18, 1978. While such methanol fuel combinations containing fairly large amounts of gasoline do provide flame luminosity, problems due to water sensitivity have developed.

Accordingly, there is the need to develop a methanol fuel system which burns with a luminous flame throughout its burning cycle and additionally does not have any problems related to water contamination and water sensitivity.

Now in accordance with this invention, it has been found that a methanol fuel composition which combines methanol with a select petroleum hydrocarbon

mixture has improved flame luminosity and is relatively water insensitive.

More particularly, this invention is directed to a methanol fuel composition with improved flame luminosity which comprises methanol and a petroleum hydrocarbon mixture of:

a) at least about 2 volume % based on the total volume of the composition of an aromatic hydrocarbon fraction, said fraction including at least about 1 volume % based on the total volume of the composition of aromatic hydrocarbons which distil substantially uniformly over a wide boiling range having an initial boiling point of less than about 240°F and a final boiling point of greater than about 375°F, and

b) at least about 1 volume % based on the total volume of the composition of a saturate/olefin hydrocarbon fraction,

said petroleum hydrocarbon mixture having an initial boiling point of less than about 150°F and a final boiling point of greater than about 375°F and combines with the methanol to form an azeotropic mixture which includes all of the methanol, said composition being capable of burning with a luminous flame throughout its burning cycle and is effectively water insensitive when small amounts of water are present.

Another embodiment of this invention relates to the method of operating a spark ignition engine comprising the use of the methanol fuel

composition of this invention which contains a particular petroleum hydrocarbon mixture and which burns with a luminous flame throughout its burning cycle.

The select aromatic and saturate/olefin fractions which comprise the petroleum hydrocarbon mixture used in the composition of this invention can generally be obtained from any of the commonly available petroleum hydrocarbon mixtures or crude oils. Such petroleum materials usually comprise a mixture of paraffinic, cycloparaffinic (naphthenes), olefinic and aromatic hydrocarbons. The selected fractions are obtained from the starting petroleum materials by refining and separation techniques which are well known in the petroleum art including distillation, cracking, thermal diffusion, reforming etc.

The saturate/olefin hydrocarbon fraction of the petroleum hydrocarbon mixture will generally include paraffins, straight and branched chained, and cycloparaffins as well as some olefins. The cycloparaffins comprise not only the monocyclic compounds, but the polycyclics and the alkyl substituted derivatives thereof. While this fraction will generally be derived from petroleum mixtures and crude oils where the saturate components, i.e., paraffins and cycloparaffins comprise the larger or predominant portion, nevertheless, there may be some olefinic components

present. In fact, the fractions derived from some operations, such as a cracking process, can contain amounts of olefins which can vary up to about 20 vol.% or even higher. Typical olefins will include the mono and diolefins such as cyclopentadiene. The saturate/olefin hydrocarbon fraction will generally comprise at least about 1 volume % and preferably at least about 1.4 volume %, such volume based on the total volume of the composition.

The aromatic hydrocarbon fraction will generally comprise at least about 2% by volume and preferably at least about 2.5% by volume, based on the total volume of the composition and will contain a number of different compounds. This aromatic hydrocarbon fraction will include at least about 1 volume % based on the total volume of the composition of a mixture of aromatic hydrocarbons which distil substantially uniformly over a wide boiling range having an initial boiling point of less than about 240°F and a final boiling point of greater than about 375°F. By distilling substantially uniformly it is meant that this portion of the aromatic fraction will distil at a fairly uniform rate, i.e., a rate such that the distillation curve (temperature vs. percent distilled) is relatively smooth or even over the entire range and does not sharply increase or decrease at any particular point. In other words, this aromatic mixture will comprise a number of different hydrocarbons which distil at different temperatures throughout the desired temperature range and are present in sufficient quantities to provide distillation which is substantially uniform, i.e. the distillation rate is generally smooth or even over the temperature range. What in effect is needed to obtain a generally uniform distillation is a small amount, usually less than about 10 volume %, of a

large number of different compounds. Typical compounds found in the aromatic fraction are the alkylbenzenes such as toluene, the xylenes and p-cymene, the polycyclic aromatics such as naphthalenes, biphenyl, acenaphthene, fluorenes, phenanthrenes, mononaphthene benzenes and dinaphthene benzenes. It is understood that branched or substituted ring components are also included in the defined aromatic fraction.

Generally, both the aromatic and saturate/olefin fractions will comprise a mixture of compounds containing about 5 to about 12 carbon atoms per molecule. Each fraction will generally contain a variety of branched substituents and may contain small amounts of sulfur and nitrogen content. In determining or defining the aromatic and saturate/olefin fractions as used in this invention, the procedure "Hydrocarbon Types by FIA," ASTM D-1319 is used. A further description of petroleum hydrocarbon fractions of this type and typical compounds in such petroleum compositions is given in Kirk-Othmer, "Encyclopedia of Chemical Technology," 2nd Edition, Vol. 14, pp. 845-855, 1967.

The petroleum hydrocarbon mixture comprising the aromatic and saturate/olefin fractions as defined herein will generally comprise at least about 3 volume % and preferably at least about 4 volume % of the total composition; however greater amounts can be used with cost efficiency being a prime factor in determining the upper limit for the amounts to be used. The important thing about this added petroleum hydrocarbon mixture is that it form an azeotropic mixture which includes all of the methanol. While the azeotrope could comprise part of the petroleum hydrocarbon mixture itself, it must include all of the methanol. This makes it possible for the petroleum mixture or luminosity component

to be co-distilled with the methanol and to impart luminosity as long as a flame exists. As noted earlier, the select wide boiling aromatic component which makes up part of the aromatic fraction, must distil substantially uniformly over a range having an initial boiling point of less than about 240°F and a final boiling point of greater than about 375°F. The petroleum hydrocarbon mixture, i.e. combined aromatic and saturate/olefin fractions must have an initial boiling point of less than about 150°F and a final boiling point of greater than about 375°F. In determining the boiling points of various components, ASTM D-86 is a procedure that is generally followed.

Another important advantage of using the particular composition of this invention is that it is relatively water insensitive to small amounts of water. In using certain hydrocarbon components, such as gasoline, other problems can develop when water is present. Thus problems such as phase separation or increased volatility can develop in such compositions when fairly small amounts of water are present. The composition of this invention has been found to be water insensitive even when amounts of water of up to about 3 volume % are present and still retains its ability to maintain flame luminosity. By the term "flame luminosity" as used throughout this application is meant that the flame is clearly visible and distinguishable.

The composition of this invention may be used in several applications but is particularly useful as a fuel for operating a spark ignition engine.

Generally, the methanol will comprise the major amount of this composition, i.e., at least about

50 volume % and preferably at least about 80 volume % based on the total volume of the composition.

A primer such as dimethyl ether is a particularly useful additive to the fuel composition of this invention in certain applications since it provides good volatility at low temperatures to help in cold starting. The amount of primer will depend on ambient temperatures and the particular engine being used. Typically about 2 to about 7 volume % based on the total volume of the composition will be used.

Minor amounts of other additives generally used with fuel compositions of this type may be included in the composition of this invention, e.g. corrosion and rust inhibitors, antioxidants, etc. Typically, the total amount of other additives, i.e., besides the petroleum hydrocarbon mixture and primer, will be less than about 1 volume % based on the total volume of the composition.

Further details and illustrations of this invention will be found in the following examples.

Example 1

A fuel composition comprising methanol and optionally dimethyl ether primer was tested for flame luminosity after adding a number of petroleum hydrocarbon mixtures with the following results as shown in the table below.

These results clearly show that composition containing the amounts and the saturate/olefin and aromatic fractions in accordance with this invention as

shown by the use of the mixed hydroformate or combinations of toluene and light cat naphtha provide flame luminosity over 100% of the entire burning cycle. In contrast to this, other additive mixtures did not give the desired flame luminosity at least not over the entire burning cycle. Additionally, the compositions in accordance with this invention were found to hold more than 3 volume % water without phase separation or a change in volatility.

COMPOSITION OF FUEL % BY VOLUME

Methanol	Dimethyl Ether	Toluene	Mixed Hydroformate[1]	Light Cat Naphtha[2]	Isopentane	% Burning Cycle with Luminous Flame
100						0
94	6					0
90.4	5.6	4				90
88	6	6				89
91.1	4.9		4			100
92	4		2	2		42
96			4			100
92				4		23
88.3	5.7			6		43
90.2	3.8	2		4		100
88	6	2		4		100
94					6	0

[1]This is a hydroformate containing 66% aromatics which uniformly distil in the range of 230 to 430°F and the rest saturates/olefins and the total component boiling in range 130 to 430°F.

[2]Contains 28% aromatics which uniformly distil in the range of 230 to 436°F and the rest saturates/olefins and the total component boiling in the range of 98 to 430°F.

CLAIMS:

1. A methanol fuel composition with improved flame luminosity which comprises methanol and a petroleum hydrocarbon mixture of:

(a) at least about 2 volume % based on the total volume of the composition of an aromatic hydrocarbon fraction, said fraction including at least about 1 volume % based on the total volume of the composition of aromatic hydrocarbons which distil substantially uniformly over a wide boiling range having an initial boiling point of less than about 240°F and a final boiling point of greater than about 375°F and

(b) at least about 1 volume % based on the total volume of the composition of a saturate/olefin hydrocarbon fraction,

said petroleum hydrocarbon mixture having an initial boiling point of less than about 150°F and a final boiling point of greater than about 375°F and combines with the methanol to form an azeotropic mixture which includes all of the methanol, said composition being capable of burning with a luminous flame throughout its burning cycle and is water insensitive to small amounts of water.

2. A composition according to claim 1 wherein an effective priming amount of dimethyl ether is present.

3. A composition according to either of claims 1 and 2 wherein at least about 2.5 volume % of said aromatic fraction is present.

4. A composition according to any one of the preceding claims wherein at least about 1.4 volume % of said saturate/olefin fraction is present.

5. A composition according to any one of the preceding claims wherein both the aromatic and saturate/olefin fractions comprise a mixture of compounds containing 5 to 12 carbon atoms per molecule.

6. A composition according to any one of the preceding claims wherein the petroleum hydrocarbon mixture comprising the aromatic and saturate/olefin fractions comprises at least 3 volume %, preferably at least 4 volume %, of the total composition.

7. A composition according to any one of the preceding claims wherein the methanol comprises at least 50 volume %, preferably at least 80 volume % based on the total volume of the composition.

8. A method of operating a spark ignition engine which comprises using the composition according to any one of the preceding claims as the fuel to provide a luminous flame throughout the burning cycle.