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

(11) EP 0 795 596 A1

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
17.09.1997 Bulletin 1997/38

(51) Int Cl.^{6}: **C10L 1/22**, C10L 1/18,
C10L 10/00

(21) Application number: **97200775.1**

(22) Date of filing: **14.03.1997**

(84) Designated Contracting States:
BE CH DE ES FI FR GB IT LI NL

(30) Priority: **15.03.1996 EP 96301782**
15.03.1996 EP 96301781

(71) Applicant: **SHELL INTERNATIONALE RESEARCH MAATSCHAPPIJ B.V.**
2596 HR Den Haag (NL)

(72) Inventors:
- **Barratt, David John**
  Ince, Chester CH1 3SH, Cheshire (GB)
- **Kalghatgi, Gautam Tavanappa**
  Ince, Chester CH1 3SH, Cheshire (GB)
- **Lin, Jian**
  Ince, Chester CH1 3SH, Cheshire (GB)

(54) Fuel compositions

(57) This invention provides a fuel composition which comprises a major amount of a fuel boiling in the gasoline boiling range and a minor amount of an additive comprising a furan derivative containing a furyl group bearing one or more substituents comprising one or more heterocyclic and/or one or more aryl groups; an additive concentrate for addition to such fuel and a method of operating an internal combustion engine using such fuel composition. Fuels of the invention give rise to octane requirement increase control and/or octane requirement reduction effects.

Printed by Jouve, 75001 PARIS (FR)

Description

This invention relates to fuel compositions containing furan derivatives, a method of operating an internal combustion engine using such fuel compositions and to fuel additive concentrates.

It is well known in the art that internal combustion engines, more particularly spark ignition engines, tend to exhibit what is termed the octane requirement increase effect. This effect may be described as the tendency for an initially new or relatively clean engine to require higher octane quality fuel as operating time accumulates, and is coincidental with the formation of deposits in the region of the combustion chamber of the engine.

During initial operation of a new or clean engine, a gradual increase in octane requirement, i.e. fuel octane number required for knock-free operation, is observed with an increasing build up of combustion chamber deposits until a stable or equilibrium octane requirement level is reached. This level appears to correspond to a point in time when the quantity of deposit accumulation on the combustion chamber and valve surfaces no longer increases but remains relatively constant. This so-called "equilibrium value" is normally reached between 3,000 and 20,000 miles (4,000 and 32,000 km) or corresponding hours of operation. The actual equilibrium value of this increase can vary with engine design and even with individual engines of the same design; however, in almost all cases, the increase appears to be significant, with octane requirement increase values ranging from about 2 to 14 research octane numbers being commonly observed in modern engines.

Fuel additives which inhibit or prevent deposit formation in the combustion chamber may be termed octane requirement increase control (ORIC) agents; those which remove or modify formed deposits, leading to decrease in octane requirements, may be termed octane requirement reduction (ORR) agents.

US Patent No. 4,339,245 discloses the use of certain furyl compounds including furfuryl alcohol, furfuryl amine, ethylfurfurylacrylate, furfuryl acetate, furfuryl propionate, furfuryl isobutyrate, methyl furoate, ethyl furoate and compounds having alkyl groups substituted on the furyl rings as antiknock additives in gasoline. Addition of the furyl compounds described increased the RON (research octane number) of the gasoline. The RON is an intrinsic property of a gasoline, and is independent of any ORIC or ORR effect which that gasoline might, or might not, manifest in use. No ORIC or ORR activity is either described or hinted at in US Patent No. 4,339,245.

EP-A-174 123 discloses a process for the preparation of alkylfurans, and acknowledges that alkylfurans may be included in gasoline compositions as octane improving additives. As above, this relates to the RON of the gasoline, and not to any ORIC or ORR effect.

It has now surprisingly been found that fuel compositions containing certain furan derivatives exhibit octane requirement increase control and/or octane requirement reduction effects.

According to the present invention there is provided a fuel composition which comprises a major amount of a fuel boiling in the gasoline boiling range and a minor amount of an additive comprising a furan derivative containing a furyl group bearing one or more substituents comprising one or more heterocyclic and/or one or more aryl groups.

The or each heterocyclic group may be any optionally substituted saturated or unsaturated ring system, e.g. a 5 to 7 membered ring system, containing at least one heteroatom selected from oxygen, nitrogen and sulphur, 5- and 6-membered rings being preferred, e.g. a furyl, piperidinyl, pyridinyl, pyrrolyl, triazinyl, imidazolinyl or thiophenyl(thienyl) group. Especially preferred are 5-membered ring systems containing oxygen and/or nitrogen, preferably a furan or pyrrole ring.

The aryl group(s) may be any optionally substituted aryl group, preferably an optionally-substituted phenyl group. Preferred aryl groups are phenyl groups which are unsubstituted or substituted by an alkyl group.

Thus it is preferred that the heterocyclic and/or aryl groups comprise unsaturated 5-membered ring systems containing oxygen and/or nitrogen, or benzene ring systems.

Examples of substituent groups for both the heterocyclic and aryl groups include halogen atoms (e.g. chlorine atoms), nitro, hydroxyl, carboxyl, amino, cyano, alkyl, formyl, alkoxycarbonyl, alkanoyl, alkylthio, alkylsulphinyl, alkylsulphonyl, carbamoyl and alkylamido groups. As used herein, when a substituent consists of or contains an alkyl, alkoxy or alkylene moiety, this may be linear or branched and may contain up to 12, preferably up to 6, especially up to 4, carbon atoms.

The or each heterocyclic group and/or aryl group is connected to the furyl group directly or by means of a bridging optionally substituted hydrocarbyl (preferably alkylene), carbonyl, dicarbonyl, amido, alkyleneamido, alkyleneoxyalkyl or alkoxycarbonyl group. One or more additional heterocyclic and aryl groups may also be connected to a heterocyclic or aryl group which is connected to the furyl group, directly or via such a bridging group.

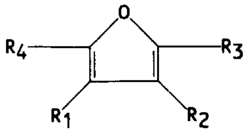
Preferably connections between furyl groups and heterocyclic or aryl groups as defined above or between heterocyclic or aryl groups and additional heterocyclic or aryl group are either direct connections or are bridging groups selected from C_{1-4} alkylene (preferably $-CH_2-$), $-CH_2NHCO-$, $-NHCO-$, $-CO-CO-$, $-CH_2-O-CO-$ and $-CH_2OCH_2-$ groups.

Preferably the furyl group bears a single substituent which comprises one or more heterocyclic and/or one or more aryl groups.

For example, the number of heterocyclic and/or aryl groups present in addition in the furyl group may advantageously range from 1 to 5, preferably from 1 to 4.

The molecular weight of the furan derivative is preferably in the range from 100 to 5000, more preferably in the range 100 to 500 and most preferably 145 to 500. When the furan derivative is a single compound having a discrete chemical structure, the molecular weight corresponds to the formula weight of the compound. When, however, the furan derivative has a range of structures, the molecular weight is number average molecular weight, as determined by gel permeation chromatography (GPC), using polystyrene calibration standards.

By way of example, suitable furan derivatives to be used in accordance with the present invention include those having the following general formula:



(I)

wherein R1, R2, R3 and R4 each independently represent hydrogen, a heterocyclic group or an aryl group connected to the furyl group directly or by means of a bridging group as defined hereinbefore provided that at least one of R^1, R^2, R^3 and R^4 is such a heterocyclic group or an aryl group. Preferably, one or both of R3 and R4 represent an optionally substituted saturated or unsaturated ring system containing at least one heteroatom selected from oxygen, nitrogen and sulphur, connected to the furyl group as defined above.

A particularly preferred furan derivative for use in fuel compositions of the present invention is a furfuryl alcohol resin or a derivative thereof.

In the context of the present invention a furfuryl alcohol resin is defined as a polymer product obtained by condensation of optionally substituted furfuryl alcohol monomers (e.g. 2-furanmethanol monomers), or a distillation product thereof containing at least two furan rings. Preferably, the furfuryl alcohol resin has a number average molecular weight in the range of 145 (i.e. from about 150) to 5000, more preferably in the range of from 145 (about 150) to 500, as measured by gel permeation chromatography (GPC) using polystyrene calibration standards.

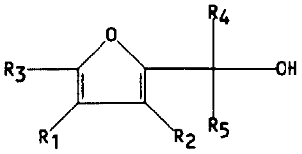
It will be understood that the furfuryl alcohol resin or derivative thereof comprises in addition to the furyl group a number of further furyl groups which are connected to the neighbouring furyl groups by means of an optionally substituted hydrocarbyl (preferably alkylene), alkyleneoxyalkyl or alkoxycarbyl group, e.g. a $-CH_2-$ or $-CH_2-O-CH_2-$ group.

Preferably, the furfuryl alcohol resin comprises the condensation product of non-substituted 2-furanmethanol monomers.

It will be understood that in the latter condensation product the additional furyl groups are connected to the neighbouring furyl groups by means of a methylene group, or in some cases a $-CH_2-O-CH_2-$group.

The preparation of furfuryl alcohol resins is well known in the art. In this respect reference is for instance made to Journal of Applied Polymer Science, Vol. 15, pp. 1079-1090 (1971), which document is hereby incorporated by reference.

Suitable monomers include those having the following general formula:

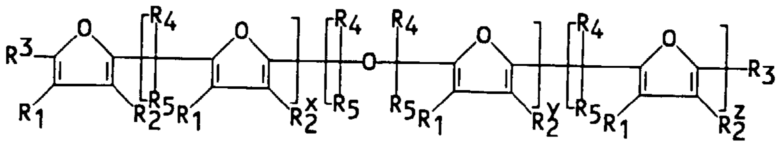


(II)

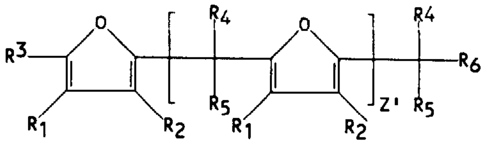
wherein R1, R2, R4 and R5 each independently represent hydrogen, a hydrocarbyl group, a nitrogen-containing, an oxygen-containing or a sulphur-containing hydrocarbyl group and R3 represents hydrogen. The hydrocarbyl group may conveniently comprise an aryl, alkyl, alkenyl or cycloalkyl group. Advantageously, the hydrocarbyl group contains 2 to 50 carbon atoms, preferably 2 to 20 carbon atoms and more preferably 2 to 10 carbon atoms.

Suitable furfuryl alcohol resins or derivatives thereof include those obtained by polycondensation of different types of monomers (II).

Suitably the furfuryl alcohol resins or derivatives thereof to be applied in accordance with the present invention include those having the following general formulae (III) or (IV):

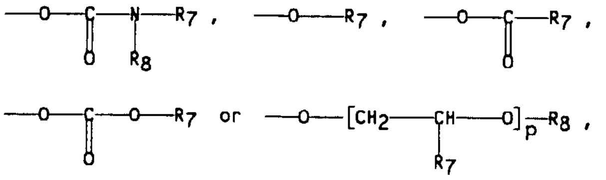


(III)



(IV)

wherein R_1, R_2, R_3, R_4 and R_5 have the meanings as defined hereinabove for formula II, R_6 represents hydrogen, OH,



$$-O-C(=O)-N(R_8)-R_7,\quad -O-R_7,\quad -O-C(=O)-R_7,\quad -O-C(=O)-O-R_7 \text{ or } -O-[CH_2-CH(R_7)-O]_p-R_8,$$

and R_7 and R_8 represent an optionally nitrogen-containing, oxygen-containing or sulphur-containing hydrocarbyl group, x is in the range from 0 to 60, preferably from 0 to 30 and more preferably from 0 to 10, y is 0 or 1, z is in the range from 0 to 60, preferably from 0 to 30 and more preferably from 0 to 10, each of (x + z) and Z' ranges from 1 to 60, preferably 1 to 30 and more preferably from 1 to 10, and p is in the range from 1 to 80, preferably ranging from 5 to 25.

It will be understood that the furfuryl alcohol resin or derivatives thereof will usually comprise a mixture of any of the polymer products III and IV described above, and of course any unreacted 2-furanmethanol or derivative thereof.

The furfuryl alcohol resins may contain unreacted hydroxy groups which may subsequently be derivatised, e.g. esterified, in known manner. A preferred derivative is an alkylsuccinic acid ester of a furfuryl resin, which may be prepared by reaction of the furfuryl resin with an olefin-succinic anhydride, e.g. a C_{15-19} internal olefin-succinic anhydride.

A particularly preferred fuel composition according to the present invention is one wherein the furan derivative is selected from the group consisting of N-furfuryl-2-furamide, 2-amino-1-(2-furanylmethyl)-4,5-difuryl-3-pyrrolecarbonitrile, N-phenyl furamide, 1-furfurylpyrrole, furil, furfuryl benzoate, furfuryl resins having number average molecular weights in the range 145 to 500 and alkylsuccinic acid esters of furfuryl resins having number average molecular weights in said range.

The additive comprising the furan derivative is preferably present in the fuel composition in an octane requirement reducing amount.

The fuel is present in a major amount (i.e. more than 50%w), and the additive comprising the furan derivative is present in a minor amount, preferably from 0.005 to 10%w, more preferably from 0.01 to 5%w, and most preferably from 0.02 to 1%w, based on the weight of the fuel composition.

The invention further provides an additive concentrate suitable for addition to fuel for an internal combustion engine which comprises a fuel-compatible diluent and an additive comprising a furan derivative as defined above, preferably in an amount of from 5 to 75%w calculated on the diluent.

Further in accordance with the present invention there is provided a method of operating an internal combustion engine which comprises introducing into the combustion chambers of said engine a fuel composition as defined above according to the invention.

The fuel boiling in the gasoline boiling range may consist substantially of hydrocarbons or it may contain blending components. Alternatively, e.g. in countries such as Brazil, the fuel may consist substantially of ethanol.

Suitable liquid hydrocarbon fuels of the gasoline boiling range are mixtures of hydrocarbon boiling in the temperature range from about 25°C to about 232°C, and comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline mixtures having a saturated hydrocarbon content ranging from about 40% to about 80% by volume, an olefinic hydrocarbon content from 0% to about 30% by volume and an aromatic hydrocarbon content from about 10% to about 60% by volume. The base fuel is derived from straight run gasoline, polymer gasoline, natural gasoline, dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of these. The hydrocarbon composition and octane level of the base fuel are not critical. The octane level, (R+M)/2, will generally be above about 85 (where R is Research Octane Number and M is Motor Octane Number).

Any conventional base gasoline can be employed in the practice of the present invention. For example, hydrocarbons in the gasoline can be replaced by up to a substantial amount of conventional alcohols or ethers, conventionally known for use in fuels. The base gasolines are desirably substantially free of water since water could impede a smooth combustion.

Normally, the gasolines to which the invention is applied may be leaded or unleaded, although are preferably substantially lead-free, and may contain minor amounts of one or more blending agents such as methanol, ethanol, tertiary butanol, ethyl tertiary butyl ether, methyl tertiary butyl ether, and the like, at from about 0.1% by volume to about 25% by volume of the base fuel, although larger amounts (e.g. up to 40%v) may be utilised.

The gasolines may further suitably contain a nonionic surfactant, such as an alkylphenol or an alkyl alkoxylate. Suitable examples of such surfactants include C_4-C_{18}-alkylphenol and C_2-C_6-alkylethoxylate or C_2-C_6-alkylpropoxylate or mixtures thereof. The amount of the surfactant is advantageously from 10 to 1000 ppmw.

The gasoline can also contain other conventional additives including antioxidants such as phenolics, e.g. 2,6-di-tert-butylphenol or phenylenediamines, e.g. N,N'-di-sec-butyl-p-phenylenediamine, dyes, metal deactivators, dehazers such as polyester-type ethoxylated alkylphenol-formaldehyde resins. Corrosion inhibitors, such as that commercially sold by Rhein Chemie, Mannheim, Germany as "RC 4801", or a polyhydric alcohol ester of a succinic acid derivative having on at least one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 500 carbon atoms, for example, pentaerythritol diester of polyisobutylene-substituted succinic acid, the polyisobutylene group having an average molecular weight of about 950, in an amount from about 1 ppmw to about 1000 ppmw, may also be present. The fuels can also contain antiknock compounds such as methyl cyclopentadienylmanganese tricarbonyl, tetraethyl lead or other lead-containing compounds, and ortho-azodiphenol as well as co-antiknock compounds such as benzoyl acetone.

A preferred gasoline composition of the invention may additionally contain a minor amount of at least one additional additive compound selected from the group consisting of polyalkenyl amines, Mannich amines, polyalkenyl succinimide, poly(oxyalkylene)amines, poly(oxyalkylene)carbamates, and poly(alkenyl)-N-substituted carbamates.

An effective amount of the additive comprising the furan derivative is introduced into the combustion zone of the engine in a variety of ways to prevent build-up of deposits or to accomplish the modification of existing deposits that are related to octane requirement. A preferred method is to add a minor amount of a furan derivative as defined above to the gasoline. For example, one or more furan derivatives as defined above are added directly to the gasoline or are blended with one or more carriers and/or one or more hydrocarbon-soluble alkali metal or alkaline earth metal salts and/or one or more additional detergents before being added to the gasoline.

The amount of furan derivative used will depend on the particular furan derivative used, the fuel, and the presence or absence of carriers, detergents and diluents.

The carrier, when utilised, may conveniently have an average molecular weight from about 250 to about 5000. Suitable carriers, when utilised, include hydrocarbon based materials such as polyisobutylenes (PIB's), polypropylenes (PP's) and polyalphaolefins (PAO's), all of which may be hydrogenated or unhydrogenated but are preferably hydrogenated; polyether based materials such as polybutylene oxides (poly BO's), polypropylene oxides (poly PO's), polyhexadecene oxides (poly HO's) and mixtures thereof (i.e. both (poly BO) + (poly PO) and poly-BO-PO)); and mineral oils such as those sold by member companies of the Royal Dutch/Shell group under the designations "HVI" and "XHVI" (trade mark), Exxon Naphthenic 900 sus mineral oil and high viscosity index oils in general. The carrier is preferably selected from PIB's, poly BO's and poly PO's with poly PO's being the most preferred.

A particularly prepared carrier fluid comprises a combination of a polyalphaolefin having a viscosity at 100°C in the range 2×10^{-6} to 2×10^{-5} m^2/s (2 to 20 centistokes) being a hydrogenated oligomer containing 18 to 80 carbon atoms derived from at least one alphaolefinic monomer containing from 8 to 16 carbon atoms, and a polyoxyalkylene compound selected from glycols, mono- and diethers thereof, having number average molecular weight (M_n) in the range 400 to 3000, the weight ratio polyalphaolefin: polyoxyalkylene compound being in the range 1:10 to 10:1.

The polyalphaolefins are primarily trimers, tetramers and pentamers, and synthesis of such materials is outlined in Campen *et al.*, "Growing use of synlubes", Hydrocarbon Processing, February 1982, pages 75 to 82. The polyalphaolefin is preferably derived from an alphaolefinic monomer containing from 8 to 12 carbon atoms. Polyalphaolefins derived from decene-1 have been found to be very effective. The polyalphaolefin preferably has viscosity at 100°C in the range of 6×10^{-6} to 1×10^{-5} m^2/s (6 to 10 centistokes). Polyalphaolefin having a viscosity at 100°C of 8×10^{-6} m^2/s (8 centistokes) has been found to be very effective.

Preferred polyoxyalkylene compounds for use in combination with these polyalphaolefins are described in EP-A-588429 (Applicants reference T 5677).

The carrier concentration in the final fuel composition is up to about 1000 ppm weight. When a carrier is present, the preferred concentration is from about 50 ppm by weight to about 400 ppm by weight, based on the total weight of the fuel composition. Once the carrier is blended with the furan derivative and any other desired components, the blend is added directly to the fuel or packaged for future use.

The hydrocarbon-soluble alkali metal or alkaline earth metal salt, when utilised, may be one of those described in WO 87/01126, and the compounds of formula I are particularly suitable for incorporation, as additional component, in fuel compositions as described in WO 87/01126. Preferred hydrocarbon-soluble alkali metal or alkaline earth metal salts are, however, alkali metal or alkaline earth metal salts of a succinic acid derivative. Such a salt of a succinic acid derivative, when utilised, will have as a substituent on one of its alpha-carbon atoms an unsubstituted or substituted aliphatic hydrocarbon group having from 20 to 200 carbon atoms.

Alternatively, the succinic acid derivative will have as a substituent on one of its alpha-carbon atoms an unsubstituted or substituted hydrocarbon group having from 20 to 200 carbon atoms which is connected to the other alpha-carbon atom by means of a hydrocarbon moiety having from 1 to 6 carbon atoms, forming a ring structure. Suitable such salts are described for example in EP-A-207560 and in EP-A-491439.

The salts of the succinic acid derivative can be monobasic or dibasic. Monobasic salts in which the remaining carboxylic acid group has been transformed into an amide or ester group may also be used. Suitable alkali metal salts of a partial ester of an alkyl polyether alcohol with a succinic acid derivative are described in EP-A-491439.

Suitable metal salts include lithium, sodium, potassium, rubidium, caesium and calcium salts. Particularly preferred salts are described in EP-A-207560.

The aliphatic hydrocarbon substituent(s) of the succinic acid derivative is suitably derived from a polyolefin, the monomers of which have 2 to 6 carbon atoms. Thus, convenient substituents include polyethylene, polypropylene, polybutylenes, polypentenes, polyhexenes or mixed polymers. Particularly preferred is an aliphatic hydrocarbon group which is derived from polyisobutylene.

The hydrocarbon group may include an alkyl and/or an alkenyl moiety and may contain substituents. One or more hydrogen atoms may be replaced by another atom, for example halogen, or by a non-aliphatic organic group, e.g. an (un)substituted phenyl group, a hydroxy, ether, ketone, aldehyde or ester. A very suitable substituent in the hydrocarbon group is at least one other metal succinate group, yielding a hydrocarbon group having two or more succinate moieties.

The aliphatic hydrocarbon group should contain 20 to 200, preferably 35-150, carbon atoms. When a polyolefin is used as substituent the chain length is conveniently expressed as the number average molecular weight. The number average molecular weight of the substituent, e.g. determined by osmometry, is advantageously from 400 to 2000.

The succinic acid derivative may have more than one C_{20-200} aliphatic hydrocarbon group attached to one or both alpha-carbon atoms, but preferably it has one C_{20-200} aliphatic hydrocarbon group on one of its alpha-carbon atoms and on the other alpha-carbon atom either no substituent or a hydrocarbon of only a short chain length, e.g. C_{1-6} group. The latter group can be linked with the C_{20-200} hydrocarbon group forming a ring structure.

The gasoline compositions of the present invention may also contain one or more detergents. When detergents are utilised, the gasoline composition will comprise a mixture of a major amount of fuel boiling in the gasoline boiling range as described hereinbefore, a minor amount of the furan derivative as defined above and a minor amount of an detergent selected from polyalkenyl amines, e.g. polybutyleneamines, such as "KEROCOM" polyisobutyleneamine, available ex BASF, Mannich amines, polyalkenyl succinimides, poly(oxyalkylene)amines, poly(oxyalkylene) carbamates, poly(alkenyl)-N-substituted carbamates, and mixtures thereof. As noted above, a carrier as described hereinbefore may also be included. The "minor amount" of detergent is preferably less than about 10% by weight of the total fuel composition, more preferably less than about 1% by weight of the total fuel composition and yet more preferably less than about 0.1% by weight of the total fuel composition.

The polyalkenyl amine detergents utilised comprise at least one monovalent hydrocarbon group having at least

50 carbon atoms and at least one monovalent hydrocarbon group having at most five carbon atoms bound directly to separate nitrogen atoms of a diamine. Preferred polyalkenyl amines are polyisobutenyl amines. Polyisobutenyl amines are known in the art and representative examples are disclosed in various US Patents including US Patent No. 3,753,670, US Patent No. 3,756,793, US Patent No. 3,574, 576 and US Patent No. 3,438,757. Particularly preferred polyisobutenyl amines for use in the present fuel composition include N-polyisobutenyl-N', N'-dimethyl-1,3-diaminopropane (PIB-DAP), OGA-472 (a polyisobutenyl ethylene diamine available commercially from Oronite), N-polyisobutenyl diethylene triamine (PIB-DETA) and N-polyisobutenyl triethylene tetramine (PIB-TETA) .

The Mannich amine detergents utilised comprise a condensation product of a high molecular weight alkylsubstituted hydroxyaromatic compound, an amine which contains an amino group having at least one active hydrogen atom (preferably a polyamine), and an aldehyde. Such Mannich amines are known in the art and are disclosed in US Patent No. 4,231,759. Preferably, the Mannich amine is an alkyl substituted Mannich amine.

The polyalkenyl succinimide detergents comprise the reaction product of a dibasic acid anhydride with either a polyoxyalkylene diamine, a hydrocarbyl polyamine or mixtures of both. Typically the succinimide is substituted with the polyalkenyl group but the polyalkenyl group may be found on the polyoxyalkylene diamine or the hydrocarbyl polyamine. Polyalkenyl succinimides are also known in the art and representative examples are disclosed in various patent references including US Patent No. 3,443,918, EP-A-208560, DE-OLS 3,126,404, US Patent No. 4,234,435, US Patent No. 4,810,261, US Patent No. 4,852,993, US Patent No. 4,968,321, US Patent No. 4,985,047, US Patent No. 5,061,291 and US Patent No. 5,147,414.

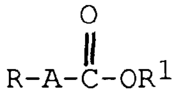
Particularly effective succinimide detergents are those obtained by reacting at least one amine, with a polyalkenyl derivative of a monoethylenically unsaturated C_{4-10} dicarboxylic acid material in which the ratio of dicarboxylic acid moieties per polyalkenyl chain is not greater than 1.2:1 and the number average molecular weight (Mn) of the polyalkenyl chain is in the range from 1600 to 5000, e.g. as described in EP-A-587250 (Applicants reference T1665).

Amines employed in the preparation of said succinimide detergents are preferably C_{1-30}, more preferably C_{1-18}, and especially C_{8-12}, amines containing 1 to 8 nitrogen atoms. Such amines may be branched or unbranched, saturated aliphatic, primary or secondary amines, containing 1 to 8 nitrogens, preferably mono- or diamines, such as ethylamine, butylamine, sec. butylamine, diethylamine and 3-dimethylamino-1-propylamine, but including higher polyamines such as alkylene polyamines, wherein pairs of nitrogen atoms are joined by alkylene groups of 2 to 4 carbon atoms.

Poly(oxyalkylene)amines are described, for example, in US Patents Nos. 4,985,047 and 4,332,595, in EP-A-440 248, EP-A-310 875, EP-A-208 978 and WO-A-85 01956. The poly(oxyalkylene) carbamate detergents comprise an amine moiety and a poly(oxyalkylene) moiety linked together through a carbamate linkage, i.e., -O-C(O)-N<.

These poly(oxyalkylene) carbamates are known in the art and representative examples are disclosed for example in US Patent No. 4,191,537, US Patent No. 4,160,648, US Patent No. 4,236,020, US Patent No. 4,270,930, US Patent No. 4,288,612 and US Patent No. 4,881,945. Particularly preferred poly(oxyalkylene) carbamates for use in the present fuel composition include OGA-480 (a poly(oxyalkylene) carbamate which is available commercially from Oronite).

The poly(alkenyl)-N-substituted carbamate detergents utilised are of the formula:



$$R-A-\overset{\displaystyle O}{\overset{\|}{C}}-OR^1$$

in which R is a poly(alkenyl) chain; R^1 is a hydrocarbyl or substituted hydrocarbyl group; and A is an N-substituted amino group. Poly(alkenyl)-N-substituted carbamates are known in the art and are disclosed in US Patent No. 4,936,868.

The one or more detergents are added directly to the fuel boiling in the gasoline boiling range, blended with the furan derivative as defined above, or blended with the furan derivative and one or more carriers before being added to the fuel.

The concentration of the one or more detergents in the final fuel composition is generally up to about 1000 ppmw for each detergent. When one or more detergents are utilised, the preferred concentration for each detergent is from about 10 ppmw to about 400 ppmw, based on the total weight of the fuel composition, even more preferably from about 25 ppmw to about 250 ppmw, based on the total weight of the fuel composition.

Additive components can be added separately to the fuel boiling in the gasoline boiling range or can be blended with one or more diluents, forming an additive concentrate, and added to the fuel together. Suitable gasoline-compatible diluents are hydrocarbons and mixtures of hydrocarbons with alcohols or ethers, such as methanol, ethanol, propanol, 2-butoxyethanol, methyl tert-butyl ether, or higher alcohols such as "Dobanol 91", (Trade Mark) available from member companies of the Royal Dutch/Shell group.

Preferably the diluent is an aromatic hydrocarbon solvent such as toluene, xylene, mixtures thereof or mixtures of toluene or xylene with an alcohol. Additionally preferred diluents include "Shellsol AB", "Shellsol R", (Trade Marks) and low aromatic white spirit (LAWS), which are available from member companies of the Royal Dutch/Shell group.

Use in fuels of the preferred furan derivatives of the present invention, especially preferred furfuryl alcohol resins, in concentrations within the preferred ranges has been found to bring about considerable reduction in combustion chamber deposit weights. From observations, it is believed that this is achieved by promotion of deposit flaking in combustion chambers.

The present invention will be further understood from the following illustrative examples, in which the test materials were as follows:-

Test Material 1 - N-furfuryl-2-furamide

N-furfuryl-2-furamide was prepared by adding dropwise to a mixture of furfurylamine (7.44 g; 76 mmol; ex Aldrich) and triethylamine (35.6 g; 352 mmol) in dichloromethane 2-furoyl chloride (23 g; 176 mmol) at a temperature of 0 to 5 °C. The product obtained was washed with water, dried with magnesium sulphate and evaporated. Subsequently, the product so obtained was purified by flash chromatography (silica, hexane/ethyl acetate as eluant) and 14 g (97 % yield) of the product was recovered.

Test Material 2 - 2-amino-1-(2-furanylmethyl)-4,5-difuryl-3-pyrrolecarbonitrile

2-amino-1-(2-furanylmethyl)-4,5-difuryl-3-pyrrolecarbonitrile was prepared as follows: 300 g (1.56 mol) of furoin (ex Aldrich) was reacted with 151.6 g (1.56 mol) of furfurylamine in the presence of 1.5 g of p-toluenesulphonic acid in toluene under stirring at reflux temperature. Water produced by the reaction was removed via a Dean Stark trap. When formation of water had ceased (31 ml removed), 103.1 g (1.56 mol) of malononitrile was added as a dispersion in 100 ml toluene, reflux was continued. When again formation of water had ceased (26 ml removed via the Dean Stark trap), the reaction mixture was cooled and the toluene was removed by evaporation. In this way 498 g of a black solid product was obtained. Subsequently, 100 g of this product was purified by flash chromatography (silica, hexane/ethyl acetate as eluant) and 24 g of the product was recovered.

Test Material 3 - N-phenyl furamide

N-phenyl furamide was prepared by adding to a mixture of aniline (23.3 g; 250 mmol) and triethylamine (25.3 g; 250 mmol) in dichloromethane slowly 32.6 g (250 mmol) of 2-furoyl chloride, while maintaining the temperature at -10°C. The product obtained was washed with diluted hydrochloric acid and water, dried with magnesium sulphate and evaporated. The product so obtained was than triturated with hexane and filtered. 39.3 g (84 % yield) of product was recovered.

Test Material 4 - 1-furfurylpyrrole (ex Aldrich)

Test Material 5 - furil (ex Aldrich)

Test Material 6 - furfuryl benzoate (ex Aldrich)

Test Material 7 - furfuryl alcohol resin, Mn 175

10.6 g of a furfuryl alcohol resin of the present invention (Mn 175) was obtained by distilling 100 g of "QuaCorr 1300" furfuryl alcohol resin (Trade Mark) (ex QO Chemicals) (Mn 425) under reduced pressure at a temperature from 42°C (2.24 10^{-3} atm) (224 to 92°C (6.58 10^{-5} atm) (6.58 Pa)

Test Material 8 - furfuryl alcohol resin, Mn 156

123 g of a furfuryl alcohol resin of the present invention (Mn 156) was obtained by distilling 1,014 g of "QuaCorr 1300" resin (ex QO Chemicals) under reduced pressure at a temperature from 42 °C (7.24 10^{-4} atm) (72.4 Pa) to 120 °C (1.97 10^{-3} atm) (197 Pa).

Test Material 9 - Furfuryl alcohol resin, Mn 228

150 g of a furfuryl alcohol resin of the present invention (Mn 228) was prepared by mixing 500 g (5.1 mol) of furfuryl alcohol (ex Aldrich) with 500 g of water and 1.15 g (11.5 mmol) of concentrated sulphuric acid and heating the mixture for 2 hours at a temperature of 50 °C. The mixture so obtained, which separated into two phases, was then neutralised with a saturated sodium bicarbonate solution. The organic phase containing the furfuryl alcohol resin produced was extracted into ether, washed with water, dried with magnesium sulphate and evaporated under reduced pressure.

Test Material 10 - furfuryl alcohol resin, Mn 272

117 g of a furfuryl alcohol resin of the present invention (Mn 272) was prepared in a manner similar to that described for Test Material 9 except that 400 g (4.1 mol) of the furfuryl alcohol was mixed with 400 g water and 0.092 g (0.92 mmol) of concentrated sulphuric acid, and the mixture was heated for 6 hours at a temperature of from 70 °C to 90°C.

Test Material 11 - furfuryl alcohol resin, Mn 388

255 g of a furfuryl alcohol resin of the present invention (Mn 388) was prepared in a manner similar to that described for Test Material 10 except that the heating was carried out for 24 hours at a temperature of 50°C, and ten times the amount of concentrated sulphuric acid was used (0.92 g, 9.2 mmol).

Test Material 12 - esterified furfuryl alcohol resin

321 g of an esterified furfuryl alcohol resin of the present invention was prepared by reacting 150 g (0.42 mol) of Test Material 10 with 176 g (0.42 mol) of C_{15}-C_{19} internal olefin-succinic anhydride (ex Shell Chemicals) in toluene under reflux for 6 hours, after which the toluene was evaporated.

Test Material 13 - "Quacorr 1300" furfuryl alcohol resin (ex QO Chemicals, Sheffield, UK) (Mn 425)

Comparative Test Material A - 2 - furaldehyde diethyl-(Comp. A) acetal (ex Aldrich)

Comparative Test Material B - 2-furaldehyde dimethyl-(Comp. B) hydrazone (ex Aldrich)

Comparative Test Material C - furfuryl alcohol (ex (Comp. C) Aldrich)

In each of the examples which follow, samples of the test materials were dissolved in unleaded gasoline and the resulting fuels (gasoline compositions) were tested as will be described.

EXAMPLES 1 to 5

The beneficial effect on octane requirement of gasoline additives comprising furan derivatives in accordance with the present invention was demonstrated by the following procedure.

A single cylinder Hydra engine was used, manufactured by Ricardo Co., Shoreham, Sussex, UK, having bore/stroke 86 mm/86 mm and compression ratio 9.5:1, and fitted with a flat-topped piston and flat-topped cylinder head having two valves. A fuel injector was employed, targeted onto the back of the inlet valve and arranged for injection whilst the valve is closed.

Deposits were built up at 1000 rpm with wide open throttle (WOT) and high load during 200 hours with an unleaded gasoline containing 0.5 wt% fluoranthene. Cylinder pressure signals were monitored to detect the high rate of change in cylinder pressure during autoignition and Knock Limited Spark Advance (KLSA) was determined under 1000 rpm and WOT conditions. Calibration tests with reference fuels showed that the engine responded to the Research Octane Number (RON) of the fuel and that the KLSA changed by approximately one crank angle degree (cad) per octane number. Starting from clean combustion chamber conditions, the KLSA of the Hydra engine was reduced by between 8 and 10 cad (DKLSA between -8 and -10) over the first 200 hours operation as combustion chamber deposits built up, after which it reached equilibrium. Each additive was tested over a period of continued running, after which the engine was reconditioned on base fuel.

The various properties of the additives, conditions applied and results of the experiments are shown in Table 1. It will be clear from these results that the use of the test materials 1 to 13 in accordance with the present invention (Examples 1 to 15) brings about a surprisingly high reduction in the octane requirement of the engine when compared with the comparative test materials A, B and C falling outside the scope of the present invention (Comparative Examples A, B and C).

TABLE 1

Example	Test Material	Molecular Weight	Mw/Mn	Dose (g/l)	DKLSA	Time (hours)
1	1	191.18	-	4	0.7	1
2	2	319.30	-	0.15	0.7	1
3	3	187.19	-	1	0.8	1
4	4	147.18 +	-	1	2.0	1.5
5	5	190.15 +	-	0.3	1.3	1
6	6	202.21 +	-	1	1	1
7	7	175	1.0	0.3	1.3	24
8	8	156	1.1	0.3	1	1
9	9	228	1.2	4	1	1
10	10	272	1.5	4	1.2	1
11	10	272	1.5	0.3	0.8	1
12	11	388	1.5	4	0.7	1
13	12	*	*	0.6	1.1	1
14	13	425	2.5	3	2.0	12
15	13	425	2.5	0.3	1.6	1
Comp. A	Comp. A	170.21 +	-	1	0	1
Comp. B	Comp. B	138.17 +	-	1	-1	1
Comp. C	Comp. C	98.10 +	-	1	0.5	1

* not determined

\+ data ex Aldrich

The "molecular weight" values for Test Materials 7 to 13 inclusive are number average molecular weight (Mn) values determined by gel permeation chromatography (GPC), using polystyrene calibration standards.

Examples 16 and 17

In two further experiments a VW engine (1.8 1) modified for research was operated at a speed of 1500 rpm. The deposits were built up at 2250 rpm and a load of 30 Nm. The engine was knock rated by measuring Knock Limited Spark Advance (KLSA) at 1500 rpm and a load of 80 Nm at frequent intervals during the test. Combustion chamber deposit (CCD) weight was monitored by stopping the engine and removing two plugs from the combustion chamber.

In Example 16, the engine was run for 120 hours using an unleaded gasoline. The engine was then switched to the same gasoline which in addition contained 0.75 g/l of "QuaCorr 1300" furfuryl alcohol resin (ex QO Chemicals) which was dissloved in methylpropanol (0.5% by volume of the gasoline). An increase in KLSA was observed of 2.5 crank angle degrees, after 45 hours when a reference fuel of 85 octane number was used for knock rating. Over the same period of time the CCD weight was reduced from 41.5 mg to 26.6 mg. In other words use of the present additive package established a 36% reduction in CCD weight.

In Example 17, the engine was run for 43 hours using an unleaded gasoline containing 0.5% by volume of methylpropanol. The engine was then switched to the same gasoline which in addition contained 0.35 g/l of "QuaCorr 1300" furfuryl alcohol resin. An almost immediate increase was observed in KLSA of 3 crank angle degrees, whereas after 43 hours an increase was observed of 1.5 crank angle degrees. Over the same period of time the CCD weight was reduced from 29 mg to 24.5 mg. In other words the use of the present additive established a 16% reduction in CCD weight.

Claims

1. A fuel composition which comprises a major amount of a fuel boiling in the gasoline boiling range and a minor amount of an additive comprising a furan derivative containing a furyl group bearing one or more substituents comprising one or more heterocyclic and/or one or more aryl groups.

2. A fuel composition according to Claim 1 wherein the heterocyclic and/or aryl groups comprise unsaturated 5-membered ring systems containing oxygen and/or nitrogen or benzene ring systems.

3. A fuel composition according to claim 1, wherein the furyl group bears a single substituent which comprises one or more heterocyclic and/or one or more aryl groups.

4. A fuel composition according to claim 1, 2 or 3, wherein the molecular weight of the furan derivative is in the range from 100 to 5000.

5. A fuel composition according to any one of claims 1 to 4 wherein the furan derivative is a furfuryl alcohol resin having a number average molecular weight in the range from 145 to 5000.

6. A fuel composition according to any one of Claims 1 to 5, wherein the furan derivative has a molecular weight in the range of 145 to 500.

7. A fuel composition according to any one of Claims 1 to 4 wherein the furan derivative is selected from the group consisting of N-furfuryl-2-furamide, 2-amino-1-(2-furanylmethyl)-4,5-difuryl-3-pyrrolecarbonitrile, N-phenyl furamide, 1-furfurylpyrrole, furil, furfuryl benzoate, furfuryl resins having number average molecular weights in the range 145 to 500 and alkylsuccinic acid esters of furfuryl resins having number average molecular weights in said range.

8. A fuel composition according to any one of Claims 1 to 7 wherein the furan derivative is present in an octane requirement reducing amount.

9. An additive concentrate suitable for addition to fuel for an internal combustion engine which comprises a fuel-compatible diluent and an additive comprising a furan derivative as defined in any one of claims 1 to 8.

10. A method of operating an internal combustion engine which comprises introducing into the combustion chambers of said engine a fuel composition according to any one of claims 1 to 8.

European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 0775

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X	DE 575 147 C (ETHYL) * page 1, line 30 - line 31 * ---	1-4,8-10	C10L1/22 C10L1/18 C10L10/00
X	GB 392 998 A (ETHYL) * page 1, line 67 - line 68 * ---	1-4,8-10	
X	US 2 535 058 A (GLEIM ET AL.) * the whole document * ---	1-10	
X	US 2 554 687 A (THOMPSON ET AL.) * the whole document * ---	1-10	
P,X	GB 2 293 177 A (THE ASSOCIATED OCTEL) * claims 1,6,8,10 * ---	1-4,6, 8-10	
X	DE 671 891 C (ORELUP) * the whole document * ---	1-4,6, 8-10	
X	FR 1 284 977 A (SHELL) * page 4, column 2 * ---	1-4,6, 8-10	**TECHNICAL FIELDS SEARCHED (Int.Cl.6)** C10L
X	GB 795 067 A (SHELL) * page 2, line 30 - line 31 * ---	1-4,8-10	
X	US 5 196 035 A (JOHNSON) * column 2, line 33 * ---	1-4,8-10	
X A	GB 1 116 227 A (ROHM & HAAS) * claims 1,13,14 * ---	9 1-4	
X A	GB 802 589 A (CALIFORNIA RES.) * page 2, column 1 * * page 9, line 45 * ---	9 1-3	

-/--

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 July 1997	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons
& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

European Patent Office

EUROPEAN SEARCH REPORT

Application Number
EP 97 20 0775

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int.Cl.6)
X A	US 3 277 056 A (COLEMAN) * column 5, line 13 - line 14 * -----	9 1-4	
			TECHNICAL FIELDS SEARCHED (Int.Cl.6)

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
THE HAGUE	24 July 1997	De La Morinerie, B

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)