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(54) Title: A FUEL ADDITIVE FORMULATION WITH IMPROVED HANDLING AND SOLUBILITY COMPRISING A METALLOCENE

(57) Abstract: The invention provides a fuel additive formulation with improved handling and solubility comprising a metallocene, preferably ferrocene (dicyclopentadienyl iron) or a derivative thereof, a fuel soluble solvent to the metallocene, and an organic gelling agent in an amount sufficient to cause the formulation to gel.



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Description

A fuel additive formulation with improved handling and solubility comprising a metallocene

Technical Field

[0001] The current invention concerns a fuel additive formulation with improved handling and solubility comprising a metallocene. It also concerns the use of the additive, thus boosting the performance of an internal combustion engine (or Stirling engine, which is an engine that may rely on external combustion as heat source) and providing cars relying on the spiked fuel to obtain more mileage.

Background Art

- [0002] The use of metallocene and ferrocene in particular, as fuel additive, is known. From Wikipedia, the free encyclopedia, it is known that Ferrocene is a chemical compound with the formula $\text{Fe}(\text{C}_5\text{H}_5)_2$. Ferrocene is the prototypical metallocene, a type of organometallic chemical compound consisting of two cyclopentadienyl rings bound on opposite sides of a central metal atom. Such organometallic compounds are also known as sandwich compounds. Ferrocene and its derivatives are antiknock agents used in the fuel for petrol engines; they are considered to be safer than tetraethyl lead, previously used.
- [0003] It is possible to buy at Halfords in the UK, a petrol additive solution which contains ferrocene which can be added to unleaded petrol to enable it to be used in vintage cars which were designed to run on leaded petrol. The iron containing deposits formed from ferrocene can form a conductive coating on the spark plug surfaces. In diesel-fuelled engines, ferrocene reduces the production of soot.
- [0004] In **GB 1477806** and **GB 1477807** additive formulations are known for improving diesel fuel or gasoline that comprise 1-3 parts by weight dicyclopentadienyl iron or a mole equivalent amount based on the dicyclopentadienyl iron nucleus, of a diesel-fuel-soluble or gasoline-soluble dicyclopentadienyl iron derivative having a dicyclopentadienyl iron nucleus, 0,1 to 10 parts by weight of a diesel fuel or gasoline antioxidant and from 2-20 parts by weight of a diesel fuel or gasoline sludge

dispersant which are dissolved in from 27 to 100 [parts by weight of an inert organic solvent. Suitable dicyclopentadienyl iron derivatives, anti-oxidants and dispersants are listed in the parent application. Solvents include diesel fuel, benzene, xylene, chlorobenzene, mineral spirits, ethers, polyethers, chlorinated hydrocarbons, aliphatic hydrocarbons and kerosene.

- [0005] **US 3353938** provides antiknock compositions and motor fuels containing them based on ferrocene.
- [0006] **WO 2004/101717** concerns a lubricant composition comprising a base oil and one or more additives, wherein the composition has an elevated pressure auto ignition temperature of at least about 500 K. This invention also includes a lubricant composition comprising a base oil and one or more additives, wherein the composition has an octane number $((R+M)/2)$ of at least about 80. This invention also includes a lubricant composition for reducing the propensity of end gas knock in a flame propagation engine, comprising: a base oil and one or more additives, wherein the composition has an average boiling point in excess of 200 DEG C.
- [0007] **US 6881235** concerns a method of reducing smoke and particulate emissions from an exhaust gas from a spark-ignited reciprocating engine by adding a fuel additive which contains an oil-soluble iron compound and an over-based magnesium compound to liquid petroleum fuel.
- [0008] **US 6488725** relates to the use of fuel additives in the regeneration of particulate filter traps, e.g. diesel particulate filter traps. The invention further relates to fuel additives suitable for use in such a process.
- [0009] Ferrocene may be dissolved in organic solvents such as benzene, diethyl ether, methanol, ethyl alcohol, gasoline, diesel oil, and kerosene, but not in aqueous. It is chemically steady and not poisonous, it does not react with acid, alkali and ultraviolet. It doesn't decompose easily. Mixed with ferrocene, a diesel fuel can be preserved for a long use.
- [0010] In 1984, Eagle Company introduced Maxi-mizer™ on the market, a ferrocene based formulation that has proven to provide a 10% increase in fuel economy and a 40% increase in engine life.

- [0011] Clearly ferrocene and its analogs and derivatives are very suitable as fuel additive, in particular in the present day environment where fuel prices are on the increase and concerns about the environment are becoming more and more important. On the other hand, adding ferrocene and such as powder to the fuel is not customer-friendly, whereas liquid concentrations of ferrocene, dissolved in fuel or a similar solvent, are difficult to dose. In this respect it should be noted that there is some concern about using too much of the metallocene to the fuel, which can cause damage to the spark plug in conventional gasoline-based internal combustion engines.
- [0012] **WO 96/07717** relates to a pumpable paste as an additive for liquid fuels with fuel-soluble additives bonded into the paste and an addition process. It is thereby possible to insert the additive for any fuel not during its production or delivery nor even when it is finally supplied, but only directly into the inlet pipe to the combustion chamber or engine in easily and properly metered quantities. The paste is formed using bentonite or a similar inorganic product. Aside from solubility issues, such inorganic products may cause damage to parts of the engine.
- [0013] For these fuel additives to be truly successful, a different formulation should be found that allows easy dosage, allows easy dissolution into the fuel without any downsides such as components that do not burn cleanly and or cause damage to the engine. Moreover, economics are important; consumers are worried about mileage, but about fuel prices too. The inventor has solved this problem.

Disclosure of Invention

- [0014] Accordingly, the invention provides a fuel additive formulation with improved handling and solubility comprising a metallocene, preferably ferrocene (dicyclopentadienyl iron) or a derivative thereof, a fuel soluble solvent to the metallocene, and an organic gelling agent in an amount sufficient to cause the formulation to gel.

Mode(s) for Carrying Out the Invention

- [0015] Although plain ferrocene is the preferred additive, other metallocenes and organometallic compounds having a sandwich structure may be used too. Examples include the metallocenes of the formula $M(C_5H_5)_2$ where $M = Cr$,

Fe, Co, Ni, Zr, Ti, V, Mo, W, Zn. These species are also called bis(cyclopentadienyl)metal complexes. Replacement of one ring in a metallocene gives rise to a still larger family of "half sandwich" compounds. An example of such a compound is methylcyclopentadienyl manganese tricarbonyl. Such species are occasionally referred to "piano stool" compounds, at least when there are three diatomic ligands in addition to the hydrocarbon "seat" of the piano stool. Such compounds may be used in the additive formulation too.

[0016] Moreover, it is known to prepare derivatives of the above metallocenes, using "ordinary" substitution chemistry and the like. Examples of such derivatives include, for instance,

1. acetyl ferrocene
2. propiolyl ferrocene
3. butyryl ferrocene
4. pentanoyl ferrocene
5. hexanoyl ferrocene
6. octanoyl ferrocene
7. benzoyl ferrocene
8. 1,1'-diacetyl ferrocene
9. 1,1'-dibutyryl ferrocene
10. 1,1'-dihexanoyl ferrocene
11. ethyl ferrocene
12. propyl ferrocene
13. n-butyl ferrocene
14. pentyl ferrocene
15. hexyl ferrocene
16. 1,1'-diethyl ferrocene
17. 1,1'-dipropyl ferrocene
18. 1,1'-dibutyl ferrocene
19. 1,1'-dihexyl ferrocene
20. cyclopentenyl ferrocene
21. cyclohexenyl ferrocene
22. 3-ferrocenoyl propionic acid

23. 4-ferrocenoyl butyric acid
24. 4-ferrocenylbutyric acid
25. 5-ferrocenylvaleric acid
26. 3-ferrocenoyl propionic acid esters
27. 4-ferrocenoyl butyric acid esters
28. 4-ferrocenyl butyric acid esters
29. 5-ferrocenylvaleric acid esters
30. dimethylaminomethyl ferrocene.

[0017] The above are known derivatives, of which several have been used as fuel additives. Being able to use metallocene derivatives may be important indeed once biofuels and the like (with an increase tendency in polarity, e.g., due to the presence of ethanol and the like) are being used.

[0018] The solution to the aforementioned problem is the use of an organic gelling agent. The expression "organic" in this respect means a gelling agent based on hydrocarbon chemistry (as opposed to inorganic). Various gelling agents (also referred to as solidifiers) are known and commercially available and equally suitable. The amount of gelling agent and metallocene is preferably such that an additive formulation comprises on a total of 100 parts by weight from 1 to 10 parts by weight of metallocene, from 85 to 98 parts by weight of solvent and from 1 to 3 parts by weight of gelling agent. The amount of gelling agent does depend on selection of the gelling agent and the solvent, provided a formulation is obtained that behaves as a gel at temperatures in the range of from -30 degrees Centigrade (for colder climates) up to +40 degrees Centigrade (for tropical climates). Note that the formulation for arctic climates need not be the same as that for tropical climates. It is important, however, to keep the amount of gelling agent low, this will allow faster dissolving into the fuel in the fuel tank, without gelling the fuel itself.

[0019] The solvent may be any organic solvent that itself is compatible with the fuel to which the additive formulation is added. Preferably the solvent is a fuel or fuel component itself, e.g., gasoline for use in engines running on gasoline, or diesel for use in engines running on diesel. Again in terms of solvent, the person skilled in the art will know which solvent to select on

the basis of his expertise or a few simple experiments, depending on the fuel and e.g. the amount of (bio)additives typically present therein.

[0020] Styrenic block copolymers have been found to be excellent gelling agents. These block copolymers, are of the form SBS where S represents a polystyrene block, and B represents a block of conjugated diene(s). These polymers may also come as branched or multiblock copolymers and/or mixtures of block copolymers. Moreover, the block copolymers may be hydrogenated or partially hydrogenated. By changing the molecular weight of the blocks, block copolymers can be made with improved gelling behaviour. The polymers as such are known and are provided for instance by Kraton Polymers and others, Also their use in candles and oil gels is known, but not their use to provide fuel additive formulations.

[0021] Finally, the current additive formulation may be used to add further additives that improve the performance of the engine or the stability of the additive formulation. Ideally, these additional additives are not poisonous themselves, to allow customer handling.

Industrial Application

[0022] Fuel additive formulation, which may be used to improve internal combustion engines typically found in automotive applications.

Claims

1. A fuel additive formulation with improved handling and solubility comprising a metallocene, preferably ferrocene (dicyclopentadienyl iron) or a derivative thereof, a fuel soluble solvent to the metallocene, and an organic gelling agent in an amount sufficient to cause the formulation to gel, but low enough to avoid gelling the fuel to which the additive is added.
2. The additive formulation of claim 1, comprising on a total of 100 parts by weight from 1 to 10 parts by weight of metallocene, from 85 to 98 parts by weight of solvent and from 1 to 3 parts by weight of gelling agent.
3. The additive formulation of claim 1 or 2, wherein the gelling agent is a styrenic block copolymer.
4. The use of the fuel additive of claims 1 to 3, in improving the fuel economy and engine life of an automotive combustion engine.

INTERNATIONAL SEARCH REPORT

International application No

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A. CLASSIFICATION OF SUBJECT MATTER

INV. C10L1/14

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C10L

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 96/07717 A (PLUTO CHEM BETRIEBE [DE]; SVENDBORG DAMPSKIBS AS [DK]; DAMPSKIBSSELSKA) 14 March 1996 (1996-03-14) cited in the application page 4, line 23 - line 29 page 5, line 32 - line 37; claims 1,7	1-4
A	WO 2007/062330 A (FEROX INC [US]; PARISH W WESLEY [US]; THOMPSON MICHAEL D [US]) 31 May 2007 (2007-05-31) page 1, line 19 - page 2, line 20	1-4

☐ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

* Special categories of cited documents:

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INTERNATIONAL SEARCH REPORT

Information on patent family members

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Patent document cited in search report		Publication date	Patent family member(s)		Publication date
WO 9607717	A	14-03-1996	AU	3519295 A	27-03-1996
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WO 2007062330	A	31-05-2007	AU	2006318235 A1	31-05-2007
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