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Declarations under Rule 4.17:

— *as to applicant's entitlement to apply for and be granted a patent (Rule 4.17(H))*

— *of inventorship (Rule 4.17(iv))*

Published:

— *with international search report (Art. 21(3))*

WO 2016/014028 A1

(54) Title: FUEL BLEND WITH NANODIAMONDS

(57) Abstract: A fuel and nanodiamond mixture includes a fuel for combustion and a fuel additive in the form of nanodiamonds mixed into the fuel to be dispersed throughout the fuel.

FUEL BLEND WITH NANODIAMONDS

TECHNICAL FIELD

The field of this invention relates to improved fuel blend with nanodiamonds in suspension.

BACKGROUND OF THE DISCLOSURE

Fuel efficiency has long been a high priority among industry and governments. Many modifications to engine technology are purely driven by fuel efficiency. These technical improvements include tighter manufacturing tolerances in the piston and cylinder, better materials for piston rings, hardened valves, better timing of the valve train and better recirculation of exhaust gases.

Fuel has also been improved for better fuel efficiency. Better blends and compositions of fuel have been developed. For over a hundred years petroleum has been cracked, distilled and blended to provide better octane ratings and improve combustion burn. Many of these improvements involve blending different gasoline grades and fuel additives. The fuel additives have been added for several different purposes, including changing the octane rating, removing old deposits and reducing new deposits from internal engine components, promoting longer life of the valves and for stabilizing the gasoline for longer storage. Some of these additives such as tetraethyl lead have since fallen out of favor due in part to the detrimental toxic effects of accumulating amounts of tetraethyl lead in the environment. The adoption of catalytic converters which are incompatible with lead has also greatly further diminished the use of lead as an additive. Hardened valve seats and upgraded exhaust valve materials have

been introduced to compensate for the elimination of lead as an additive.

There is great development in nanodiamond materials technology. The applications for nanodiamonds have been applied as additives to oils for lubrication purposes, dry lubricants in the metal industry, reinforcing fillers for plastic and rubber, and as an additive to electroplating electrolytes. Nanodiamonds have also been used for lapping and polishing. The use of nanodiamonds as an additive to engine lubricant, i.e. oil or a synthetic, introduces the nanodiamonds into the engine via the path of the engine lubricant to the crankshaft side of the piston and piston rings. Some thin lubricant films containing nanodiamonds may then pass by the piston rings into the combustion chamber. While nanodiamonds primary crystals are produced under 10 nm in size, they tend to agglomerate after formation to particle exceeding 10 nm.

What is needed is a fuel additive having nanodiamonds that increases fuel mileage, improves fuel ignition and combustion burn, cleans valve trains and decreases wear and tear on engine parts while it reduces the toxic effects of additives on the environment. What is also needed is nonagglomerated nanodiamonds that are introduced into an engine as a fuel additive through the fuel system, for example, a fuel injector or carburetor and into the combustion chamber from an origin on the combustion side of the piston.

SUMMARY OF THE DISCLOSURE

In accordance with one aspect of the invention, a fuel and nanodiamond mixture is made from a fuel and a fuel additive in the form of nanodiamonds mixed into the fuel to be dispersed throughout the fuel. Preferably, the nanodiamonds are less than lOnm in size and preferably between 2-10 nm in size.

The concentration of nanodiamonds to fuel is preferably between .0001% and .001% by volume relative to the fuel. The nanodiamonds are preferably detonation synthesis nanodiamonds. In one embodiment the nanodiamonds are graphenated, however, it is acceptable to use graphenated nanodiamonds or a blend of graphenated and ungraphenated nanodiamonds. The fuel is preferably one of diesel or gasoline, even though it is foreseen that kerosene, bio-diesel and all types of jet fuels are suitable. Because of the extremely small amount of additive needed and the small particle size, it is also foreseen that the nanodiamonds will also be suitable to be added to gaseous fuels; for example propane, CNG, CPG, butane, methane and hexane among others.

In accordance with another aspect of the invention, a method of making a fuel and nanodiamond mixture includes the steps of producing nanodiamonds via a detonation synthesis technology or any other method that allows the nanodiamonds to obtain a primary crystal size of 2-10 nm and to disperse in liquid media with the aim to reduce their agglomeration; refining the nanodiamonds to separate it from non-diamond material; e.g. soot; maintaining the nanodiamonds in a moist state to reduce possibility of agglomeration; and introducing the nanodiamonds into one of a petroleum based carrier, partially synthetic partially petroleum lubricant, a fully synthetic lubricant, and a petroleum based fuel.

In accordance with another aspect of the invention, a method of introducing nanodiamonds into an internal combustion engine along with fuel for the combustion cycle includes the steps of providing a moist nanodiamond mixed with a petroleum based carrier; injecting the carrier with the nanodiamond into a combustion chamber of the engine from an origin on a combustion side of a piston along with fuel before ignition to provide a mixture of nanodiamonds and fuel in the combustion chamber; and igniting the fuel and nanodiamond mixture in the combustion chamber for a power stroke. Preferably, the carrier is the fuel and nanodiamonds are introduced into the combustion chamber with the fuel from a fuel injector system or carburetor.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

Significant improvement in fuel economy and environmental performance of internal combustion engines have been achieved by introducing between .0001% and .001% by volume of nanodiamonds to fuel for example, gasoline, diesel, liquefied natural gas, propane, kerosene or any hydrocarbon based fuel system. The nanodiamonds have average sizes of 2-10 nm and more preferably 4-6 nm.

Detonation synthesis or any other method which allows the nanodiamonds to obtain a particle size of 2-10 nm to be dispersed in liquid media to reduce their agglomeration is used to manufacture nanodiamonds. Detonation synthesis technology employs charges of explosive substances which are detonated in a high strength, hermetically sealed chamber. Diamond particles of nanometer size are formed from the free carbon of the molecules of the explosives. The initial detonation process creates a diamond blend that contains on average 40-50% diamonds which are then refined to a higher percentage. A refinement process may be used to extract both graphenated and ungraphenated forms of these nanodiamonds from the non-diamond material, e.g. soot.

The nanodiamonds are maintained in the refinement output moist state, i.e., it contains some amount of liquid to reduce the possibility of agglomeration and produce a stable additive product with minimal nanodiamond settling in the finished product and resulting in extended shelf life. For example, the liquid may be water, acid or urea. Reduction of agglomeration is important to maintain the size under 10 nm and preferably 4-6 nm.

The nanodiamonds can be introduced into the fuel at the refinery or downstream thereof. When added directly to the fuel, the nanodiamond concentration is between .0001% and .001% by volume to the fuel. In one embodiment, the fuel is in the form of

diesel or gasoline suitable for internal combustion engines. The nanodiamonds can easily pass from a fuel tank to an engine and through fuel filters for automotive use because fuel filters are not designed to filter particles smaller than a few microns in size.

When used as an aftermarket additive, the fuel additive can have the nanodiamonds mixed into a carrier based on petroleum based lubricant, partially synthetic partially petroleum based lubricant or a fully synthetic lubricant. The preferred method of mixing the nanodiamond is by introducing the moist state nanodiamonds into the carrier using ultrasonic and mechanical mixing to reduce settling out of the nanodiamonds in the carrier. The nanodiamond mix in the carrier is preferably between 0.5% and 4% by weight. The optimal ratio of additive in the form of the carrier to the fuel is 10-30 ml of carrier per 50 liters of fuel. Other ranges outside of this are possible but with decreasing results. When the nanodiamonds are introduced as an aftermarket additive, it is preferred to add the additive first to the fuel tank and then add the gasoline, diesel or other fuel to the fuel tank to promote complete blending and suspension of the nanodiamonds in the fuel.

The results of several tests showed an increase of up to 10% in fuel efficiency depending on engine load. Furthermore, reduction of both carbon monoxide and other hydrocarbons results were as follows:

TESTING

Gasoline Engine with Catalytic Converter

Test 1

Options	At Idle		Revving		
	No Nanodiamonds	With Nanodiamond Additive	Without Nanodiamonds	With Nanodiamond Additive	Improvement With Nanodiamonds
CO, %	0.12	0.08	0.3	0.15	42.3 1%
HCppm	167	129	42	32	18%

Diesel Engine Without Catalytic Converter

Test 2

Options	At Idle			Revving			
	No Nanodiamonds	With Nanodiamond Additive		Without Nanodiamonds	With Nanodiamond Additive		Improvement With Nanodiamonds
CO, %	7.7	8.4	7.82	1.2	0.7	1.05	27.08%
HCppm	396	425	351	127	95	111	18.9%

It is believed that the nanodiamond blended additive to the fuel improves environment performance of engines due a more uniform and therefore complete combustion. There is a general reduction of NOx, soot, carbon monoxide and hydrocarbons. The nanodiamond additive cleans combustion chamber, and increases the efficiency and engine power. Duration is also improved by decreasing wear as shown in the test results below:

PIN AND V TEST DATA SUMMARY AND COMPARISON			
	PSI Load	Wear Scar	Coefficient of Friction
Oil Only, No Break-in	81,605	0.225	0.116
Nanodiamond, 48-Hour Break-in	95,709	0.190	0.101
Improvement	17.3%	15.6%	12.9%

In general, an increase by approximately 1.5 points in octane is obtained by adding nanodiamonds to the fuel.

The additive further reduces the load on afterburning catalysts and diesel particulate filters. The elimination of metals as an additive reduces the content of harmful impurities including carcinogens in the exhaust gases. The additive apparently improves flammability of the fuel mixture and the combustion process at different loads of the engine. The nanodiamonds are believed to create more uniform points of ignition to slow the oxidation of the fuel during the compression stroke of the air-fuel mixture

and to intensify the combustion process after ignition of the fuel by its high thermal conductivity which creates a more uniform flame front during the detonation down-stroke. As such, improved combustion efficiency increases the proportion of energy consumption going to perform useful work.

There is a noticeable reduction of spark plug fouling due to soot. There is improved lubrication of fuel injectors and valves, cleaner combustion chamber and restored mobility of the piston rings in the grooves of the piston during operation of an engine on the gasoline blended with the nanodiamonds. There is less soot deposited in the exhaust path which reduces the soot load on the catalysts and diesel particulate filters thereby increasing these components useful life. The engine has reduced sensitivity to fuel quality because of the increase combustion efficiency. The improved engine combustion provides reduced engine vibration and engine noise.

By adding the nanodiamond to the fuel, it is assured that a sufficient quantity is introduced into the combustion chamber from above the piston in more consistent quantities rather than via a lubricant from below the piston. The small percentage of nanodiamonds to fuel provides for an economically viable additive.

It is foreseen to use the nanodiamonds in fuels for other purposes, i.e. alcohol, liquefied natural gas or propane based fuel as well as solid or gel based fuels for applications other than internal combustion engines.

Variations and modifications are possible without departing from the scope and spirit of the present invention as defined by the appended claims.

CLAIMS

The embodiments in which an exclusive property or privilege is claimed are defined as follows:

1. A fuel and nanodiamond mixture comprising:

a fuel for providing combustion; and

a fuel additive in the form of nanodiamonds mixed into the fuel to be dispersed throughout said fuel.

2. A fuel and nanodiamond mixture comprising:

said nanodiamonds being less than 10nm in size.

3. A fuel and nanodiamond mixture as defined in claim 2 further comprising:

said nanodiamonds being 2-10 nm in size.

4. A fuel and nanodiamond mixture as defined in claim 3 further comprising:

said nanodiamonds being between .0001% and .001% by volume relative to the fuel.

5. A fuel and nanodiamond mixture as defined in claim 4 further comprising:

said nanodiamonds being formed by a method that allows the nanodiamonds to obtain a primary crystal size of 2-10 nm and to be dispersed in liquid media to

reduce their agglomeration.

6. A fuel and nanodiamond mixture as defined in claim 5 further comprising:

said nanodiamonds being detonation synthesis nanodiamonds.

7. A fuel and nanodiamond mixture as defined in claim 5 further comprising:

said nanodiamonds being a blend of graphenated and ungraphenated nanodiamonds.

8. A fuel and nanodiamond mixture as defined in claim 7 further comprising:

said fuel being one of diesel fuel or gasoline.

9. A fuel and nanodiamond mixture as defined in claim 2 further comprising:

said nanodiamonds being between .0001% and .001% by volume relative to the fuel.

10. A fuel and nanodiamond mixture as defined in claim 8 further comprising:

said nanodiamonds being formed by a method that allows the nanodiamonds to obtain a primary crystal size of 2-10 nm and to be dispersed in liquid media to

reduce their agglomeration.

11. A fuel and nanodiamond mixture as defined in claim 9 further comprising:

said nanodiamonds being detonation synthesis nanodiamonds.

12. A fuel and nanodiamond mixture as defined in claim 10 further comprising:

said nanodiamonds being a blend of graphenated and ungrapehnated nanodiamonds.

13. A fuel and nanodiamond mixture as defined in claim 12 further comprising:

said fuel being one of diesel fuel or gasoline.

14. A fuel and nanodiamond mixture as defined in claim 1 further comprising:

said nanodiamonds being between .0001% and .001% by volume relative to the fuel.

15. A fuel and nanodiamond mixture as defined in claim 1 further comprising:

said fuel being one of diesel fuel or gasoline.

16. A fuel and nanodiamond mixture as defined in claim 1 further comprising:

said fuel being a gaseous fuel.

17. A method of making a fuel and nanodiamond mixture comprising:

producing nanodiamonds via a method that allows the nanodiamonds to obtain a primary crystal size of 2-10 nm to be dispersed in liquid media to of reduce their agglomeration;

refining said nanodiamonds from non-diamond material;

maintaining said nanodiamonds in a moist state to reduce agglomeration; and

introducing said nanodiamonds into one of a petroleum based carrier; partially synthetic partially petroleum lubricant, a fully synthetic lubricant, and a petroleum based fuel.

18. A method as defined in claim 17 further comprising:

said nanodiamonds being produced by detonation synthesis technology.

19. A method of introducing nanodiamonds along with fuel for the combustion cycle into an internal combustion engine having a combustion chamber with a piston, said method comprising:

mixing moist nanodiamonds with a petroleum based carrier;

injecting said carrier with said nanodiamonds therein into said combustion chamber from an origin source on the combustion side of said piston along with fuel before ignition to provide a mixture of nanodiamonds and fuel; and

igniting said mixture of nanodiamonds and fuel in said combustion chamber for producing a power stroke.

20. A method as defined in claim 19 further comprising:

said carrier being said fuel and nanodiamonds being introduced into said combustion chamber with said fuel from a fuel injector.

21. A method as defined in claim 20 further comprising:

said nanodiamonds being between .0001% and .001% by volume relative to said fuel.

22. A method as defined in claim 21 further comprising:

said nanodiamonds being 2-10 nm in size.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 14/47555

A. CLASSIFICATION OF SUBJECT MATTER
IPC(8) - C10L 1/10 (2015.01)
CPC - C10L 1/326; C10L 1/322; C10L 1/32
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)
IPC(8)- C10L 1/10 (2015.01)
CPC- C10L 1/326; C10L 1/322; C10L 1/32

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
USPC: 44/280
Patents and NPL (classification, keyword; search terms below)

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
Databases: Google Scholar, Google Patent, PatBase
Search terms used: nanodiamond, fuel, diesel, gasoline, blend, suspension

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 201 1/011714 A1 (Ivanov et al.) 27 January 201 1 (27.01.201 1) para [0015]-[0016], [0019], [0063], [01 12], [0127M0128].	1-16
Y	US 2010/0028675 A1 (Gogotsi et al.) 04 February 2010 (04.02.2010) para [0013], [0030],	1-16
Y	US 2012/0304545 A1 (Park et al.) 06 December 2012 (06.12.2012) para [0010]-[0029],	1-16

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

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed
"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
15 April 2015 (15.04.2015)	14 MAY 2015

Name and mailing address of the ISA/US	Authorized officer:
Mail Stop PCT, Attn: ISA/US, Commissioner for Patents P.O. Box 1450, Alexandria, Virginia 22313-1450 Facsimile No. 571-273-8300	Lee W. Young PCT Helpdesk: 571-272-4300 PCT OSP: 571-272-7774

Form PCT/ISA/210 (second sheet) (January 201 5)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US 14/47555

Box No. II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This international search report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:
because they relate to subject matter not required to be searched by this Authority, namely:

2. ☐ Claims Nos.:
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:

3. ☐ Claims Nos.:
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

Box No. III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:
—please see supplemental DOX —

1. ☐ As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.

2. ☐ As all searchable claims could be searched without effort justifying additional fees, this Authority did not invite payment of additional fees.

3. ☐ As only some of the required additional search fees were timely paid by the applicant, this international search report covers ordy those claims for which fees were paid, specifically claims Nos.:

4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:
1-16

Remark on Protest

☐ The additional search fees were accompanied by the applicant's protest and, where applicable, the payment of a protest fee.

☐ The additional search fees were accompanied by the applicant's protest but the applicable protest fee was not paid within the time limit specified in the invitation.

☐ No protest accompanied the payment of additional search fees.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US 14/47555

Box III: lack of unity

This application contains the following inventions or groups of inventions which are not so linked as to form a single general inventive concept under PCT Rule 13.1. In order for all inventions to be examined, the appropriate additional examination fees must be paid.

Group I: Claims 1-16, directed to a fuel and nanodiamond mixture

Group II: claims 17-18, directed to a method of making a fuel and nanodiamond mixture comprising to obtain a primary crystal size of 2-10 nm to be dispersed in liquid media to of reduce their agglomeration: refining said nanodlamonds from non-diamond material; maintaining said nanodlamonds in a moist state to reduce agglomeration

Group III: claims 19-22, directed to a method of introducing nanodlamonds along with fuel for the combustion cycle into an internal combustion engine having a combustion chamber with a piston comprising injecting said carrier with said nanodlamonds therein into said combustion chamber from an origin source on the combustion side of said piston along with fuel before ignition to provide a mixture of nanodlamonds and fuel.

The inventions listed as Group I-III do not relate to a single special technical feature under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons:

Special Technical Feature:

Groups I and III do not require a method of making a fuel and nanodiamond mixture comprising to obtain a primary crystal size of 2-10 nm to be dispersed in liquid media to of reduce their agglomeration; refining said nanodlamonds from non-diamond material; maintaining said nanodlamonds in a moist state to reduce agglomeration, as required by Group II.

Groups I and II do not require a method of introducing nanodiamonds along with fuel for the combustion cycle into an internal combustion engine having a combustion chamber with a piston comprising injecting said carrier with said nanodiamonds therein into said combustion chamber from an origin source on the combustion side of said piston along with fuel before ignition to provide a mixture of nanodiamonds and fuel, as required by Group III

Common Technical Features:

Groups I-II share the common technical feature of fuel and nanodiamond mixture comprising: a fuel for providing combustion; and a fuel additive in the form of nanodiamonds mixed into the fuel to be dispersed throughout said fuel and said nanodiamonds being less than 10 nm in size

Groups II and III share the technical feature of introducing nanodiamonds with a petroleum based carrier

Groups I and III share the technical feature of fuel for providing combustion;

However, these shared technical features do not represent a contribution over prior art, because the shared technical feature is being obvious over US 2012/0122743 A1 to Ivanov et al. (hereinafter 'Ivanov'). Ivanov discloses a fuel and nanodiamond mixture comprising a fuel for providing combustion; and a fuel additive in the form of nanodiamonds mixed into the fuel to be dispersed throughout said fuel (para [0017] diamond nano-particles (and/or OLC) are dispersed in a base oil; para [0157] The lubricant additive in certain embodiments is comprised of: from 65.0 wt. % to 94.9 wt. % of the base oil; from 0.1 wt. % to 5.0 wt. % of nanocarbon particles; para [0158] The lubricant additive in certain embodiments can be diluted with motor oil typically used in a crankcase of an internal combustion engine), but does not teach the nanodiamond particle size is less than 10 nm. It would have been obvious to one of skill in the art to identify optimum nanodiamond particle by routine experimentation. Ivanov further teaches introducing nanodiamonds with a petroleum based carrier (para [0023], ?Diamond particles can be modified to enhance the stability of their dispersions in a suitable carrier or liquid) and fuel for providing combustion (para [0158], typically used in internal combustion engine)

As the shared technical features were known in the art at the time of the invention, they cannot be considered common technical features that would otherwise unify the groups. Therefore, Groups I-III lack unity under PCT Rule 13.