

(19)



Europäisches Patentamt

European Patent Office

Office européen des brevets



(11)

EP 1 538 192 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

08.06.2005 Bulletin 2005/23

(51) Int Cl.7: **C10L 1/06**

(21) Application number: **04106249.8**

(22) Date of filing: **02.12.2004**

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IS IT LI LT LU MC NL PL PT RO SE SI SK TR**

Designated Extension States:

AL BA HR LV MK YU

(30) Priority: **04.12.2003 EP 32576399**

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(54) **GASOLINE COMPOSITIONS**

(57) The invention provides a gasoline composition comprising a major amount of a gasoline suitable for use in a spark-ignition engine, which gasoline comprises a blend of at least two hydrocarbon refinery components boiling within the gasoline boiling range, at least one of which hydrocarbon refinery components has been treated with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, and a minor amount of a nitro-

gen-containing detergent containing a hydrocarbyl group having a number average molecular weight (Mn) in the range 750 to 6000; a process for the preparation of such compositions; and the use of such compositions in operation of a spark-ignition engine to give engine cleanliness benefits.

EP 1 538 192 A1

Description

[0001] This invention relates to gasoline compositions, more particularly to gasoline compositions containing a nitrogen-containing detergent, to processes for their preparation, and to their use in operation of spark-ignition engines.

[0002] It is known to treat hydrocarbons such as gasoline by passing them in the gaseous phase through filtering or absorbing material such as fullers earth or charcoal, e.g. as disclosed in US Patent 2,090,007, US Patent 2,338,142, or UK Patent 614,636.

[0003] UK Patent 437, 023 discloses a process for refining cracked hydrocarbons of substantially gasoline boiling range by the treatment with a solid active adsorbent such as fullers earth, clay or other suitable adsorptive catalysts, under conditions of elevated temperature and superatmospheric pressure adequate to maintain said hydrocarbons in substantially liquid phase, which comprises first removing from said hydrocarbons relatively unstable low boiling constituents, namely dissolved gases, propane, part or all of the butanes and their corresponding unsaturates, and reducing the vapour pressure of said hydrocarbons by submitting them to a stabilising fractionation and thereupon subjecting the stabilised hydrocarbons, whilst still hot, to said refining treatment.

[0004] US Patent 3,529,944 discloses a method for clarifying and stabilizing hydrocarbon liquids which are subject to oxidative deterioration, particularly jet fuels, which includes adding to the fuel a material which accelerates the oxidative deterioration of the fuel, such as a polyphenyl substituted lower alkane or lower alkylene, an alkanol ester of citric acid or acetoxymethyl monobutylether; passing the hydrocarbon liquid through the solid, particulate, adsorbent media to remove microimpurities and the products of oxidative deterioration; and thereafter adding additional amounts of a stabilizing material to stabilize the hydrocarbon liquid against further oxidative deterioration. Suitable adsorbent materials (Col 5 lines 22 to 25) include various types of natural or synthetic clays, either treated or untreated, fullers earth, attapulgite, silica gel and adsorbent catalysts. In the examples, jet fuels are treated by filtration through attapulgite clay. It is specifically taught (Column 6, lines 27 to 32) that the effectiveness of the filtration process can be greatly improved and the life of the filter substantially prolonged if certain promoting agents which apparently promote oxidation and speed up certain types of degradation are added prior to filtration. In Table V, an antioxidant in the form of 2,6-di-tert-butyl paracresol is added to some jet fuels together with a mixed polyamine product known as "jet fuel additive 5" "JFA5" prior to adsorptive filtration.

[0005] In US Patent 4,225,319, in order to suppress carburettor deposit formation, adsorbent-treated cat cracked gasoline is blended into a fuel composition for use in an internal combustion engine. In Column 2, lines 57 to 62, it is stated that adsorbents which are useful "for treating the cat cracked gasoline include many of the well known adsorbents such as silica, alumina, silica-alumina, charcoal, carbon black, magnesium silicate, aluminium silicate, zeolites, clay, fuller's earth, magnesia and the like". In the examples, the adsorbent used is silica-gel. Interestingly, in Example IV it is stated that "carburettor deposit tests were run as in Example 1 with the same base fuel and with the addition of each of a primary and a secondary amine. Triplicate values of 11.6, 13.8 and 16.6 mg (Average = 14.0 mg) carburettor deposits are given for "Base fuel" and values of 32.0 mg and 14.6 mg respectively are given for "Base fuel + 0.05 vol% p-n-butaniline" and "Base fuel + 0.05 vol% N-methylaniline".

[0006] US Patent 5,951,851 relates to a process for removing elemental sulphur from fluids, particularly fuels such as gasoline, jet fuel, diesel, kerosene and fuel additives such as ethers. The process involves contacting the sulphur contaminated fluid with layered double hydroxide (or hydrotalcite) $Mg_2Al(OH)_6$; mH_2O or $Mg_3Al(OH)_6$; mH_2O , where m is the number of waters of hydration. In Example 1, it is shown that Attapulgus clay, molecular sieve 5 Angstrom, silica gel, alumina, bayerite, tetraphenylphosphonium-montmorillonite, Kao-EG. 9.4 Angstrom, Kao-tetraethylene glycol, Al_3 pillared montmorillonite, tetramethylammonium-montmorillonite, palygorskite-PF1-s, Kaolinite KGa-1, Kao-cellosolve and Iron (III) montmorillonite are ineffective in removing elemental sulphur, whilst the hydrotalcites Al_2LiCl , $Mg_2Al(OH)_6$, $Mg_2Fe(OH)_6$, $Mg_3Fe(OH)_6$ and $Mg_3Al(OH)_6$ are particularly effective in removing elemental sulphur.

[0007] The New Encyclopaedia Britannica, Macropaedia, Volume 4, 15th Edition, 1984, ISBN 0-85229-413-1, Pages 700 to 706 classifies clay minerals on the basis of variations of atomic structure and chemical composition into 9 groups, viz (1) allophane, (2) kaolinite, (3) halloysite, (4) smectite, (5) illite, (6) chlorite, (7) vermiculite, (8) sepiolite, attapulgite and palygorskite and (9) mixed layer clay minerals.

[0008] Group (8), sepiolite, attapulgite and palygorskite, are described as fibrous clay minerals, and these have, as an important structural element, the amphibole double silica chain which is oriented parallel to the c axis.

[0009] It has now surprisingly been found that when a gasoline has been treated with a particular class of fibrous clay minerals, it can give surprising engine cleanliness when used together with a nitrogen-containing detergent.

[0010] According to the present invention therefore there is provided a gasoline composition comprising a major amount of a gasoline suitable for use in a spark-ignition engine, which gasoline comprises a blend of at least two hydrocarbon refinery components boiling within the gasoline boiling range, at least one of which hydrocarbon refinery components has been treated with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, and a minor amount of a nitrogen-containing detergent containing a hydrocarbyl group having a number average molecular weight (Mn) in the range 750 to 6000.

[0011] Preferably, the blend of at least two refinery components has been treated with the fibrous clay mineral.

[0012] The nitrogen-containing detergent containing a hydrocarbyl group having a number average molecular weight (M_n) in the range 750 to 6000 may be an amine, e.g. a polyisobutylene mono-amine or polyamine, such as a polyisobutylene ethylene diamine, or N-polyisobutenyl-N',N'-dimethyl-1,3-diaminopropane, or amides, e.g. a polyisobutenyl succinimide, and are variously described, for example, in US Patent 5,855,629 and WO 0132812.

[0013] Preferably the nitrogen-containing detergent is a polyisobutylene monoamine or polyamine or a polyisobutenyl succinimide.

[0014] A particularly preferred nitrogen-containing detergent is hydrocarbyl amine of formula R^1-NH_2 and R^1 represents a group R^2 or a group R^2-CH_2- and R^2 represents a hydrocarbyl group having a number average molecular weight in the range 750 to 6000, preferably in the range 900 to 3000, more preferably 950 to 2000, and most preferably in the range 950 to 1350, e.g. a polybutenyl or polyisobutenyl group having a number average molecular weight in the range 950 to 1050.

[0015] The nitrogen-containing detergents are known materials and may be prepared by known methods or by methods analogous to known methods. For example, US Patent 4,832,702 describes the preparation of polybutenyl and polyisobutenyl amines from an appropriate polybutene or polyisobutene by hydroformylation and subsequent amination of the resulting oxo product under hydrogenating conditions.

[0016] Suitable hydrocarbyl amines are obtainable from BASF A.G., under the trade mark "Kerocom".

[0017] The nitrogen-containing detergent may be present in a wide range of concentrations, but is preferably present at a concentration in the range 25 to 2500 ppmw, based on total composition, more preferably 50 to 1000 ppmw, conveniently 50 to 500 ppmw and advantageously 50 to 250 ppmw.

[0018] Number average molecular weights, e.g. of hydrocarbons such as polyalkenes, may be determined by several techniques which give closely similar results. Conveniently M_n may be determined by vapour phase osmometry (VPO) (ASTM D 3592) or by modern gel permeation chromatography (GPC), e.g. as described for example in W.W. Yau, J. J. Kirkland and D.D. Bly, "Modern Size Exclusion Liquid Chromatography", John Wiley and Sons, New York, 1979. Where the formula of a compound is known, the number average molecular weight can be calculated as its formula weight.

[0019] Typical of gasolines suitable for use in spark ignition engines are mixtures of hydrocarbons having boiling points in the range from 25°C to 232°C and comprising mixtures of saturated hydrocarbons, olefinic hydrocarbons and aromatic hydrocarbons. Preferred are gasoline blends having a saturated hydrocarbon content ranging from 40 to 80 per cent volume, an olefinic hydrocarbon content ranging from 0 to 30 per cent volume and an aromatic hydrocarbon content ranging from 10 to 60 per cent volume. The gasoline can be derived from straight run gasoline, polymer gasoline, natural gasoline, dimer- or trimerised olefins, synthetically produced aromatic hydrocarbon mixtures from thermally or catalytically reformed hydrocarbons, or from catalytically cracked or thermally cracked petroleum stocks, or mixtures thereof. The hydrocarbon composition and octane level of the gasoline are not critical. The octane level, $(R+M)/2$, will generally be above 85. Any conventional gasoline can be used.

[0020] In the gasoline composition, hydrocarbons can be supplemented by up to substantial amounts of conventional alcohols or ethers conventionally known for use in gasoline.

[0021] The gasoline composition is preferably lead-free, and this may be required by law. Where permitted, lead-free anti-knock compounds and/or valve-seat recession protectant compounds (e.g. known potassium salts, sodium salts or phosphorous compounds) may be present.

[0022] Modern gasolines are inherently low-sulphur fuels, e.g. containing less than 200 ppmw sulphur.

[0023] The gasoline composition may additionally contain one or more corrosion inhibitors, anti-oxidants, dyes, de-hazers, metal deactivators, detergents other than a nitrogen-containing detergent containing a hydrocarbyl group having a number average molecular weight (M_n) in the range 750 to 6000 (e.g. a polyether amine), synthetic or mineral oil carriers e.g. a polyalphaolefin or a polyoxyalkylene compound, friction modifiers, diluents and markers.

[0024] The present invention further provides a process for the preparation of a gasoline composition of the invention, which comprises treating at least one hydrocarbon refinery component boiling within the gasoline boiling range with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, before or after blending said at least one hydrocarbon refinery component with at least one other hydrocarbon refinery component boiling within the gasoline boiling range, to form a gasoline suitable for use in a spark-ignition engine, and bringing the gasoline suitable for use in spark-ignition engine into admixture with the nitrogen-containing detergent.

[0025] In the process of the invention the treatment with fibrous clay mineral is effected with the hydrocarbons in the liquid phase, very conveniently at ambient temperature. At ambient temperature, the treatment may very conveniently be effected at atmospheric pressure.

[0026] Whilst when it is known that a particular hydrocarbon refinery component or combination/components of a gasoline is at least predominantly responsible for deposit formation when used as fuel in a spark-ignition engine, that component or combination of components may be treated with the fibrous clay mineral before blending with at least the other hydrocarbon refinery component to form the gasoline, it is preferred to treat the fully pre-blended gasoline.

[0027] Accordingly, the process of the invention preferably comprises blending at least two hydrocarbon refinery components boiling within the gasoline boiling range and treating the resulting mixture with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, to form a gasoline suitable for use in a spark-ignition engine, and bringing the gasoline into admixture with the nitrogen-containing detergent.

[0028] The fibrous clay mineral of the sepiolite, attapulgite and palygorskite, groups must at least contain at least one mineral of the sepiolite, attapulgite and palygorskite groups. The term "fullers earth" is used in published literature on clays in a number of different ways, but in the context of the present invention "fullers earth" comprises at least one fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups. One type of fullers earth may comprise a mixture of montmorillonite and palygorskite.

[0029] Preferably the fibrous clay mineral is sepiolite, attapulgite or fullers earth, as will be illustrated in the examples which follow this description.

[0030] The mechanism by which the process of the invention is effective is not fully understood, but it is believed that the fibrous clay mineral may remove iron and/or copper ions from iron and/or copper compounds which may contaminate hydrocarbon refinery components. Those skilled in the art will understand that if spent clay contains iron and/or copper, whilst containing negligible organic contaminants, it may be susceptible for disposal as land fill, without prior incineration.

[0031] The present invention further provides a method of operating a spark-ignition engine, which comprises bringing into the combustion chambers of such engine a gasoline composition according to the invention giving improved engine cleanliness, e.g. reduced intake valve deposits.

[0032] The invention will be further understood from the following illustrative examples, in which, unless otherwise indicated, parts and percentages are by weight, and temperatures are in degrees Celsius.

[0033] Base fuel blends were prepared from 50%v of an unleaded gasoline (95 ULG) of RON 95.7, MON 84.6, and having sulphur content (ASTM D 2622-94) of 483 ppmw, saturated hydrocarbon content of 49.1% v/v, aromatics content of 29.6% v/v and olefins content of 21.3% v/v (ASTM D6623-01 (procedure C), density at 15°C (DIN 51757/V4) 735.1 kg/m³, distillation (ISO 3405/88) IBP 24°C, 10% 41°C, 50% 100°C, 90% 175°C and FBP 218°C and 50% v of a heavy catalytically cracked (HCC) gasoline (the higher boiling fraction of a refinery stream produced by catalytic cracking of heavier hydrocarbons), by mixing at ambient temperature (20°C). The HCC gasoline had distillation (ISO 3405/88) IBP 65.6°C, 10% 79.3°C, 50% 94.3°C, 90% 124°C and FBP 153.3°C, sulphur content (ASTM D 2622-94) 520 ppmw, RON 91.8 and MON 79.7.

[0034] The resulting base fuel blends had properties as follows:- density at 15°C (DIN 51757/V4) 746.6 kg/m³, distillation (ISO 3405/88) IBP 40°C, 10% 68°C, 50% 98.5°C, 90% 145°C, FBP 195.5°C, RON 93.2, and MON 81.

[0035] Glass columns of about 1 metre in height and diameter of 7.5 cm, having a tap at the bottom and a loose glass cap on top, were fitted with a glass wool layer immediately above the tap and were then loaded with 0.5 kg of dry clay, in powder form. The clay filled the column to about 40 cm above the tap, and the glass wool layer prevented clay from falling into the tap.

[0036] Base fuel at ambient temperature (20°C) was poured into the column, to a depth of 25 to 30 cm above the clay. Flow rate was adjusted to 1 litre/hour, and the column was regularly topped up with fuel. Total volume of 50 litres was passed through each column. The first litre of permeate was discarded, and subsequently 5 litre samples were collected. The 2nd, 4th, 6th, 8th and final samples were tested for Fe and Cu content. The final samples were also subjected to testing in an intake valve deposit simulator test, using a multiple inclined hot plate (MIHPT) rig, in comparison both with untreated base fuel and with portions of both untreated base fuel and of final samples into which were incorporated (by mixing at ambient temperature (20°C)) a standard detergent additive package ("DP"), at a concentration of 380 ppmw.

[0037] Details of the additive package are as follows:-

"DP" - this was a standard commercial gasoline additive package, containing a polyisobutyleneamine detergent, a synthetic carrier oil and a conventional corrosion inhibitor, corresponding closely to additive package PI of Example 3 of DE-A-10055651. The polyisobutyleneamine detergent was a polyisobutylene monoamine (PIBA) ex BASF, in which the polyisobutylene (PIB) chain has a number average molecular weight of approximately 1000. The synthetic carrier oil was a polyether carrier being a polyoxypropylene glycol hemiether, containing 50 to 30 propylene oxide units prepared using a mixture of alkanols in the C₅₋₁₅ range as initiators, and having Mn in the range 1000 to 2000. The additive package contained about 68% of non-volatile matter, about 27 %w of the package being the PIBA and 40 %w of the package being carrier fluid.

[0038] The clays which were employed were as follows:-

Example 1	Attapulgite 30-60, ex Wilfrid Smith Limited (manufactured by Millwhite)
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(continued)

Example 2	Fullers Earth 30-60, ex Aldrich
Example 3	Sepiolite, ex Steetly Bentonite & Absorbents Ltd.
Comparative A	Talc, ex Aldrich
Comparative B	Kaolin, ex Aldrich
Comparative C	Vermiculite, ex Aldrich
Comparative D	Calcined Kaolin 22-60, ex Imerys.
Comparative E	Bentonite, ex Wilfrid Smith Limited (Manufactured by Cymbar)
Comparative F	Diatomaceous earth, ex Steetly Bentonite & Absorbents Ltd.

Intake Valve Deposit Simulator Test - Inclined Hot Plate Rig

[0039] This simulator test corresponds closely to that described in SAE Paper 890215, Daneshgari *et al.*, "The Influence of Temperature upon Gasoline Deposit Build-Up on the Intake Valves", Detroit, USA, 27 February to 3 March 1989. The test rig utilises four inclined plates in parallel. The plates are strips of sandblasted aluminium 50 cm long and 2.5 cm wide, having a central groove along their lengths 3 mm wide and 1 mm deep, mounted in the rig at an angle of 3 degrees relative to the horizontal. The temperature at the top end of each plate is maintained at 400°C and at the middle of each plate is maintained at 250°C.

[0040] Gasoline samples, containing test materials at a concentration of non-volatile matter of 100 parts per million by weight (ppmw) in base fuel, are prepared, and 100 ml portions of the gasoline samples are delivered at a rate of 0.6 ml/minute from glass syringes fitted with 20 gauge steel hypodermic Luer lock needles into the groove at the top end of each plate. Once delivery is complete, after about 2 hours and 40 minutes, the plates are allowed to cool to ambient temperature (20°C) and are washed with n-heptane until the run-off liquid is clear, and are then left to dry before assessment of any deposit present.

[0041] Assessment is made using a "SEESCAN" (trade mark) Marker Image analyser with 512*512 image memory coupled to a "SONY"/"SEESCAN" (trade marks) CCD camera equipped with NIKON (trade mark) f55 Macro lens. Lighting of the plate being assessed is by two 12v Tungsten lamps mounted at a linear distance of 22 cm from the point on the plate upon which the camera is focused and at angles of 33 degrees and 147 degrees relative to the plate.

[0042] A clear portion of the plate is moved under the camera and an image thereof captured. The section of the plate containing deposit is then moved beneath the camera and an image thereof is captured. The image analyser divides, pixel by corresponding pixel, the deposit image by the clean image and automatically measures the area and optical density of deposit at the pixels contained within overall measuring frame, and calculates an integrated optical density for the image, the numerical value of which is recorded as a test rating.

[0043] Results of this test are given in Table 1 as follows:-

Table 1

Example	MIHPT Rating	
	Fuel without additive	Fuel with additive package
Base fuel blend	508 [#]	567 [#]
1	287	185
1a	360*	211*
2	244	115
3	116	84
Comparative A	454	624
Comparative B	493	ND
Comparative C	489	578
Comparative D	646	514
Comparative E	234	691
Comparative F	242	417

[#] average of 7 runs ND not done

* in processing, flow rate through column was 2 l/hour, instead of 1 l/hour

[0044] In Table 1, the lower the rating, the better. Accordingly, it can readily be seen that the results for all of the test

materials of Examples 1 to 3 are surprisingly superior both to the results for the comparative examples and for the base fuel. In particular, it should be noted that for fuels of Examples 1 to 3, fuel with additive package performs better than fuel without additive package, whereas the reverse is true for the base fuel blend and for the comparative examples. Even in the case of Comparative Examples E and F, where treated fuel without additive package is significantly better in test than untreated base fuel without additive package, the ratings for treated fuel with additive package are poor, in addition to being worse than for the fuel without additive package.

Claims

1. A gasoline composition comprising a major amount of a gasoline suitable for use in a spark-ignition engine, which gasoline comprises a blend of at least two hydrocarbon refinery components boiling within the gasoline boiling range, at least one of which hydrocarbon refinery components has been treated with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, and a minor amount of a nitrogen-containing detergent containing a hydrocarbyl group having a number average molecular weight (Mn) in the range 750 to 6000.
2. A gasoline composition according to Claim 1 wherein the blend of at least two hydrocarbon refinery components has been treated with the fibrous clay mineral.
3. A gasoline composition according to Claim 1 or 2 wherein the nitrogen-containing detergent is a polyisobutylene monoamine or polyamine or a polyisobutenyl succinimide.
4. A gasoline composition according to any one of Claims 1 to 3 wherein the nitrogen-containing detergent is a hydrocarbyl amine of formula R^1-NH_2 wherein R^1 represents a group R^2 or a group R^2-CH_2- and R^2 represents a hydrocarbyl group having a number average molecular weight in the range of 900 to 3000.
5. A gasoline composition according to Claims 4 wherein R^2 represents a hydrocarbyl group having a number average molecular weight in the range 950 to 1350.
6. A gasoline composition according to any one of Claims 1 to 5 wherein the nitrogen-containing detergent is present in an amount in the range 25 to 2500 ppmw, based on total composition.
7. A process for the preparation of a gasoline composition according to any one of Claims 1 to 6 which comprises treating at least one hydrocarbon refinery component boiling within the gasoline boiling range with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, before or after blending said at least one hydrocarbon refinery component with at least one other hydrocarbon refinery component boiling within the gasoline boiling range, to form a gasoline suitable for use in a spark-ignition engine, and bringing the gasoline suitable for use in spark-ignition engine into admixture with the nitrogen-containing detergent.
8. A process according to Claim 7 which comprises blending at least two hydrocarbon refinery components boiling within the gasoline boiling range and treating the resulting mixture with a fibrous clay mineral of the sepiolite, attapulgite and palygorskite groups, to form a gasoline suitable for use in a spark-ignition engine, and bringing the gasoline into admixture with the nitrogen-containing detergent.
9. A process according to Claim 7 or Claim 8 wherein the fibrous clay mineral is sepiolite, attapulgite or fullers earth.
10. A method of operating a spark-ignition internal combustion engine, which comprises bringing into the combustion chambers of such engine a gasoline composition according to any one of Claims 1 to 6.



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EUROPEAN SEARCH REPORT

Application Number
EP 04 10 6249

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The present search report has been drawn up for all claims			
Place of search		Date of completion of the search	Examiner
The Hague		21 March 2005	Bertin-van Bomme1, S
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			

2
EPO FORM 1503 03.82 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 04 10 6249

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
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