

(19)



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11)

EP 1 198 542 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication and mention
of the grant of the patent:
30.07.2003 Bulletin 2003/31

(51) Int Cl.7: **C10L 1/00**, C10L 1/06,
C10L 10/02

(21) Application number: **00938707.7**

(86) International application number:
PCT/EP00/04912

(22) Date of filing: **25.05.2000**

(87) International publication number:
WO 00/073403 (07.12.2000 Gazette 2000/49)

(54) **GASOLINE COMPOSITION**
BENZINZUSAMMENSETZUNG
COMPOSITION D'ESSENCE

(84) Designated Contracting States:
**AT BE CH CY DE DK ES FI FR GB GR IE IT LI LU
MC NL PT SE**

(72) Inventor: **MCDONALD, Clive Richard**
Cheshire CH1 3SH (GB)

(30) Priority: **26.05.1999 EP 99304058**

(56) References cited:
WO-A-95/33022 GB-A- 357 179
US-A- 1 624 692 US-A- 1 824 977
US-A- 1 969 249 US-A- 2 232 871
US-A- 2 272 134 US-A- 3 164 449
US-A- 5 723 338

(43) Date of publication of application:
24.04.2002 Bulletin 2002/17

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

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid. (Art. 99(1) European Patent Convention).

EP 1 198 542 B1

DescriptionFIELD OF THE INVENTION

[0001] This invention relates to gasoline compositions, and more-particularly to gasoline compositions having dyes incorporated therein, their preparation and use.

BACKGROUND OF THE INVENTION

[0002] It is known to impart colour to oil products, e.g. hydrocarbon fuels such as gasoline or kerosine (paraffin oil) - see for example The Petroleum Handbook, 5th Ed., 1966, Page 111 (Shell International Petroleum Company) and Kirk-Othmer, Encyclopedia of Chemical Technology, 3rd Ed., 1980, Vol. 11, Page 669 (Wiley). Two formerly well known commercial kerosines containing dyes were "ALADDIN PINK" paraffin and "ESSO BLUE" paraffin (trade marks).

[0003] Commercially available base gasolines are generally not colourless, but at least slightly yellow, in hue. This background colour affects the appearance of gasoline to which dyes are added (e.g. addition of red or pink dyes tends to produce orange to brown gasoline and addition of blue dyes tends to produce green gasoline), unless sufficiently high concentrations of dye are added to mask the background colour. In these latter instances, the colours are deep and distinctive, but the products are far from bright and sparkling.

SUMMARY OF THE INVENTION

[0004] It has now been found possible to provide a gasoline having significant environmental benefits when used as fuel in spark-ignition engines, having a translucent blue hue. This translucent blue hue can provide a sparkling visual effect to an observer akin to that of spray from a waterfall in a mountain stream against a clear blue sunlit sky. Such a visual effect can serve to highlight the purity of such a gasoline product, and have the surprising environmental benefit of making a potential purchaser more likely to choose to purchase such gasoline than conventional gasoline by subjectively highlighting the purity of the gasoline.

[0005] According to the present invention therefore there is provided a gasoline composition which comprises a major amount of a substantially colourless gasoline having a Research Octane No. of at least 95, a Motor Octane No. of at least 85, density at 15°C in the range 720 to 775 kg/m³, sulphur content not greater than 50 mg/kg (ppmw), oxygenate content 0 to 15% v/v contributing to oxygen content not greater than 2.7% w/w, olefins content 0 to 18% v/v, aromatics content 15 to 35% v/v giving overall benzene content not greater than 1.0% v/v, the balance of the gasoline being saturated hydrocarbon, the gasoline composition having a translucent blue hue by incorporation of an effective concentration of blue dye therein.

DETAILED DESCRIPTION OF THE INVENTION

[0006] Gasolines typically contain mixtures of hydrocarbons boiling in the range from about 30°C to about 230°C, the optimal ranges and distillation curves varying according to climate and season of the year. The hydrocarbons in a gasoline as defined above may conveniently be derived in known manner from straight-run gasoline, synthetically-produced aromatic hydrocarbon mixtures, thermally or catalytically cracked hydrocarbons hydrocracked petroleum fractions or catalytically reformed hydrocarbon and mixtures of these. Oxygenates include alcohols (such as methanol, ethanol, isopropanol, tert.butanol and isobutanol) and ethers, and are preferably ethers containing 5 or more carbon atoms per molecule, e.g. methyl tert.butyl ether (MTBE). The ethers containing 5 or more carbon atoms per molecule may be used in amounts up to 15% v/v, but if methanol is used, it can only be in an amount up to 3% v/v, and stabilisers will be required. Stabilisers may also be needed for ethanol, which may be used up to 5% v/v. Isopropanol may be used up to 10% v/v, tert-butanol up to 7% v/v and isobutanol up to 10% v/v.

[0007] Gasolines as defined above have been found to be substantially colourless, an alternative description being nearly completely water-white.

[0008] Gasoline compositions as defined above may variously include one or more additives such as anti-oxidants, corrosion inhibitors, ashless detergents, dehazers and synthetic or mineral oil carrier fluids. Examples of suitable such additives are described generally in US Patent No. 5,855,629.

[0009] Additive components can be added separately to the gasoline or can be blended with one or more diluents, forming an additive concentrate, and together added to the gasoline. The blue dye can be added to the gasoline independently of other additives, or as a component of such an additive concentrate.

[0010] The blue dye must be soluble in the gasoline. Very effective blue dyes have been found to have a maximum light absorbance peak in the range 630 to 660 nm, preferably 645 to 655 nm. Light absorbance peaks may conveniently be measured using a Lambda 25 Perkin-Elmer UV-VIS (trade mark) spectrometer. Suitable blue dyes may include, for

example, DyeGuard Blue 79R ex John Hogg Technical Solutions, Automate Blue 8G ex Morton, and Unisol Liquid Blue A ex UCM.

[0011] Preferred gasoline compositions are compositions wherein the blue dye is a dyestuff having a maximum light absorbance peak in the range 630 to 660 nm at a concentration to give a blue colour corresponding in intensity to that achieved by incorporation of DyeGuard Blue 79R at a concentration in the range 3 to 30 ppmv, (parts per million volume/volume) more preferably 5 to 25 ppmv, and very conveniently 5 to 15 ppmv. DyeGuard Blue 79R itself has been found to give very effective results. The appropriate concentration of a chosen dyestuff depends on the intensity of blue colour desired and the nature of the active matter and its concentration in the chosen dyestuff.

[0012] DyeGuard Blue 79R is sold with a specified active matter content of 48% w/w. Automate Blue 8G is stated to have an active matter content of about 40%w/w. Unisol Liquid Blue A is stated to have active matter content of 50% w/w.

[0013] Preferably the light absorbance maxima for gasoline compositions of the invention within the range 630 to 660 nm, more preferably 645 to 655 nm, are in the range 0.1 to 0.5 absorption units, more preferably 0.11 to 0.48 absorption units, and very conveniently 0.12 to 0.47 absorption units as measured using a Lambda 25 Perkin-Elmer UV-VIS Spectrometer.

[0014] In preferred gasoline compositions of the invention the translucent blue hue provides a sparkling visual effect to an observer akin to that of spray from a waterfall in a mountain stream against a clear blue sunlit sky. This is very attractive to a potential purchaser and serves to emphasise in the mind the environmental benefits of the gasoline compositions of the invention, which have the potential to reduce emissions of harmful pollutants such as nitrogen oxides and benzene compared with conventional unleaded 95 Research octane gasoline such as that commercially available in The Netherlands in 1998.

[0015] In order to influence motorists to use environmentally advantageous gasoline in vehicles powered by spark-ignition engines, a gasoline composition of the invention as defined above may be dispersed from a forecourt dispenser associated with a visual display of liquid having a colour corresponding to that of said gasoline composition.

[0016] The visual display may comprise a transparent pipe or chamber in the delivery system of the forecourt dispenser, so that a customer can see the gasoline composition as it passes through the delivery system whilst dispensing the gasoline composition, or it may comprise an enclosed tank containing a sample of the gasoline composition or another liquid (e.g. water, for fire-safety reasons) having substantially the same visual effect as the gasoline composition.

[0017] The invention will be further understood from the following illustrative examples thereof, in which a substantially colourless gasoline having characteristics within the above ranges was employed in comparison with a conventional high-quality unleaded gasoline according to EN 228:93 as sold in April 1999 by Shell Nederland B.V. These gasolines had the properties as shown in Table 1 following.

Table 1

Property	Units	Substantially Colourless Gasoline (SCG)	Conventional Gasoline (EN 228:93) (CG)
Research octane number, RON (EN 25164:1993)		96,1	96
Motor octane number, MON (EN 25163:1993)		86,9	85.1
Density (at 15°C) (EN ISO 12185)	kg/m ³	741	736
Sulfur content (EN ISO 14596:1998)	MG/KG	33	85
Hydrocarbon type content - olefins - aromatics (ASTM D 1319:1995)	% (v/v)	3.54 34.05	11.72 36.61
Benzene content (EN 12177:1998)	% (v/v)	0.66	1.41
Oxygen content (EN 1601:1997)	% (w/w)	0.88	0

EP 1 198 542 B1

Table 1 (continued)

Property	Units	Substantially Colourless Gasoline (SCG)	Conventional Gasoline (EN 228: 93) (CG)
Oxygenate content: MTBE (EN 1601: 1997)	% (v/v)	4.79	0

[0018] The conventional gasoline, although of high quality, had a noticeable yellow colour.

[0019] In the examples and comparative examples, DyeGuard Blue 79R ex John Hogg Technical Solutions was used as the blue dye, and light absorbance was measured at 648 nm using a Lambda 25 Perkin-Elmer UV-VIS spectrometer. The blue dye was dispersed homogeneously into samples of the gasolines at various concentrations of active matter, and results obtained are given in Table 2 following.

Table 2

Example	Gasoline	Dye Concentration (ppmv)	Light Absorbance (units)	Appearance	Pass/Fail
Comp. A	SCG	2	0.09	no definite colour - merest hint of blue	Fail
1	SCG	5	0.12	pale iceberg translucent blue	Pass
2	SCG	10	0.20	pale translucent cerulean blue	Pass
3	SCG	15	0.27	translucent cerulean blue	Pass
4	SCG	25	0.47	translucent light ultramarine blue	Pass
Comp. B.	SCG	50	0.80	murky, almost opaque dark blue	Fail
Comp. C.	CG	2	0.06	pale lime green	Fail
Comp. D.	CG	5	0.12	pale algae green	Fail
Comp. E.	CG	10	0.20	pale phthalo green	Fail
Comp. F.	CG	15	0.25	pale turquoise	Fail
Comp. G.	CG	25	0.40	turquoise	Fail
Comp. H.	CG	50	0.8	murky, almost opaque dark turquoise	Fail

[0020] Examples 1 and 2 were particularly preferred, as they conveyed a visual impression akin to that of spray from a waterfall in a mountain stream against a clear blue sunlit sky.

[0021] Engine emissions tests were carried out in order to demonstrate the environmental benefits of the gasoline of the SCG of Table 1 in comparison with a blend of conventional unleaded 95 Research octane gasolines commercially available in The Netherlands in 1998 (market gasoline, MG).

[0022] The properties of the MG (determined as in Table 1) were as follows: RON 96.0, MON 85.5, density 740 kg/m³, sulfur content 95 mg/kg, olefins 11.7% (v/v), aromatics 36.3% (v/v), benzene content 1.78% v/v, oxygen content 0.01% m/m, oxygenate content 0.71% v/v. The MG had a clear yellowish appearance.

[0023] The emissions tests were carried out on two vehicles, and the results were averaged, in order to give a result indicative of the overall effect possible on large-scale switch-over of use from presently conventional, gasoline compositions to those of the present invention.

[0024] The vehicles were (1) Vauxhall/Opel Vectra with C18 XEL Ecotec 4 cylinder spark-ignition engine of cylinder capacity 1799 cc, bore/stroke 86 mm/81.6 mm and rated power output 115 bhp at 5400 rpm, and (2) Ford Fiesta with DHA 2 ETEC 16 valve 4 cylinderspark-ignition engine of cylinder capacity 1250 cc, bore/stroke 71.9 mm/76.5 mm and rated power output 73.8 bhp at 5200 rpm. Both cars were equipped with standard catalytic convectors.

[0025] The vehicles were run on a chassis dynamometer following a standard European emissions driving cycle (Directive 91/441/EEC). The cycle used was ECE 15.04 and EUDC with an 11 second idle.

[0026] Compared with the MG, the SCG gave measured emissions reductions (%w) of 44%w oxides of nitrogen and 30%w benzene.

Claims

1. A gasoline composition which comprises a major amount of a substantially colourless gasoline having a Research Octane No. of at least 95, a Motor Octane No. of at least 85, density at 15°C in the range 720 to 775 kg/m³, sulphur content not greater than 50 mg/kg (ppmw), oxygenate content 0 to 15% v/v contributing to oxygen content not greater than 2.7% w/w, olefins content 0 to 18% v/v, aromatics content 15 to 35% v/v giving overall benzene content not greater than 1.0% v/v, the balance of the gasoline being saturated hydrocarbon, the gasoline composition having a translucent blue hue by incorporation of an effective concentration of blue dye therein.
2. A gasoline composition according to Claim 1 wherein the blue dye is a dyestuff having a maximum light absorbance peak in the range 630 to 660 nm at a concentration to give a blue colour corresponding in intensity to that achieved by incorporation of DyeGuard Blue 79R at a concentration in the range 3 to 30 ppmv.
3. A gasoline composition according to Claim 2 wherein said range is 5 to 25 ppmv.
4. A gasoline composition according to Claim 3 wherein said range is 5 to 15 ppmv.

Patentansprüche

1. Benzinzusammensetzung, die eine Hauptmenge an einem im wesentlichen farblosen Benzin mit einer Research-Oktananzahl von wenigstens 95, einer Motor-Oktananzahl von wenigstens 85, einer Dichte bei 15°C im Bereich von 720 bis 775 kg/m³, einem nicht über 50 mg/kg (Gewichtsteile pro Million, ppmw) liegenden Schwefelgehalt, einem Oxygenatgehalt von 0 bis 15% Volumen/Volumen, der zu einem Sauerstoffgehalt von nicht über 2,7% Gewicht/Gewicht beiträgt, einem Gehalt an Olefinen von 0 bis 18% Volumen/Volumen, einem Aromatengehalt von 15 bis 35% Volumen/Volumen, der einen Gesamtbenzolgehalt von nicht über 1,0% Volumen/Volumen ergibt, wobei der Rest des Benzins aus gesättigtem Kohlenwasserstoff besteht, umfaßt, wobei die Benzinzusammensetzung einen klaren blauen Farbton durch Einverleiben einer wirksamen Konzentration eines blauen Farbstoffes aufweist.
2. Benzinzusammensetzung nach Anspruch 1, worin der blaue Farbstoff ein Farbstoff mit einem maximalen Lichtabsorptionspeak im Bereich von 630 bis 660 nm bei einer Konzentration ist, die eine blaue Farbe ergibt, die in der Intensität jener entspricht, die durch Einverleiben von DyeGuard Blue 79R mit einer Konzentration im Bereich von 3 bis 30 ppmv (Volumenteile pro Million Volumen) erzielt wird.
3. Benzinzusammensetzung nach Anspruch 2, worin der Bereich 5 bis 25 ppmv beträgt.
4. Benzinzusammensetzung nach Anspruch 3, worin der Bereich 5 bis 15 ppmv beträgt.

Revendications

1. Composition d'essence qui comprend une quantité majeure d'une essence pratiquement incolore ayant un indice d'octane recherche d'au moins 95, un indice d'octane moteur d'au moins 85, une densité à 15°C dans la plage de 720 à 775 kg/m³, une teneur en soufre non supérieure à 50 mg/kg (ppmp), une teneur en oxygénéat de 0 à 15% en volume/volume contribuant à une teneur en oxygène non supérieure à 2,7% en poids/poids, une teneur en oléfines de 0 à 18% en volume/volume, une teneur en aromatiques de 15 à 35% en volume/volume conférant une teneur en benzène totale non supérieure à 1,0% en volume/volume, le restant de l'essence étant constitué d'hydrocarbure saturé, la composition d'essence ayant une teinte bleue translucide par l'incorporation dans celle-ci d'une concentration efficace de colorant bleu.
2. Composition d'essence suivant la revendication 1, dans laquelle le colorant bleu est une matière colorante ayant un pic d'absorption lumineuse maximal dans la plage de 630 à 660 nm à une concentration permettant de conférer une couleur bleue correspondant en intensité à celle obtenue par l'incorporation de bleu DyeGuard Bleu 79R à une concentration dans la plage de 3 à 30 ppmv.
3. Composition d'essence suivant la revendication 2, dans laquelle la plage précitée est de 5 à 25 ppmv.
4. Composition d'essence suivant la revendication 3, dans laquelle la plage précitée est de 5 à 15 ppmv.