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(71) Applicant: **Repsol, S.A.**
28045 Madrid (ES)

(72) Inventors:
- **DELGADO DIESTRE, Jesús**
  28935 Móstoles - Madrid (ES)
- **LÓPEZ REYES, Manuel**
  28935 Móstoles - Madrid (ES)
- **LUQUE GARRIGA, Francisco Javier**
  08917 Badalona (ES)

(74) Representative: **ABG Intellectual Property Law, S.L.**
Avenida de Burgos, 16D
Edificio Euromor
28036 Madrid (ES)

(54) **GASOLINE COMPOSITION COMPRISING INDOLINE**

(57) The present invention relates to a gasoline fuel composition comprising indoline and a gasoline base fuel which comprises 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons; to a process for preparing such composition; and to the use of indoline to improve the anti-knock properties of said gasoline.

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Description

FIELD OF THE INVENTION

[0001] The present invention relates to the area of petrochemical industry. More specifically, the present invention relates to the use of indoline to improve the antiknock quality of a gasoline; and to a gasoline fuel composition comprising indoline.

BACKGROUND

[0002] Gasoline with better anti-knock properties enables higher compression ratios in spark ignition (SI) engines, which improves engine efficiency, contributing to a reduction in greenhouse gas (GHG) emissions from transport.

[0003] Most standard vehicles in advanced markets use a knock detector device that allows the control of engine parameters to the quality of the gasoline in order to avoid knocking; depending on the gasoline Octane Index and the operation regime, this control leads to a loss of efficiency (higher consumption) or limitation on performance. Optimization of the operation regimes of most high performance vehicles involves the use of gasoline with Octane Index higher than that of standard gasoline.

[0004] The anti-knock quality of gasoline is described by the Octane Index (OI), which is defined by the following equation:

$$O.I. = (1 - K) \cdot RON - K \cdot MON$$

where RON (Research Octane Number) and MON (Motor Octane Number) are determined experimentally in a CFR engine, by well established standards (ASTM D2699 and ASTM D2700, respectively). K is a constant that depends on the engine, specifically on the pressure and temperature history of the unburned mixture in the cylinder. SI engines have become more efficient through the years, so that for a given temperature of the unburned mixture in the cylinder, the pressure has increased. Consequently, the value of K has declined.

[0005] As shown in Figure 1, the value of K has changed significantly over time (G. Kalghatgi, SAE Technical Paper 2005-01-0239; G. Kalghatgi et al., SAE Technical Paper 2005-01-0244; R. Stradling et al., SAE Technical Paper 2015-01-0767; Concawe Report No. 7/19). Experimental studies have confirmed that the value of K for engines manufactured after the 1990's has been gradually declining, such that modern engines have been demonstrated to have negative K values. Therefore, the engine response to fuel octane quality is moving away from MON. Negative K values mean that, for a fuel with a fixed RON, lowering the MON value would result overall in a better anti-knock quality (R. Stradling et al., Transportation Research Procedia 2016, 14, 3159-3168). Downsized and boosted spark-ignition engines require K values lower than -0.5 and a recent revision of intake temperature, backpressures, exhaust gas recirculation (EGR) rates and operation conditions disclosed K values of-1.24 for modern engines (P. Miles, Technical Report. U.S. Department of Energy, 2018, DOE/GO-102018-5041). Even lower values are expected as the engine load increases.

[0006] Close attention to the requirements of new automotive engines must be paid in order to develop new octane boosters. The progressive trend of K to more negative values indicates that an ideal octane booster should increase RON while maintaining or decreasing MON.

[0007] The most technologically and economically advantageous way for producing gasolines with high octane is the use of anti-knock additives. The first anti-knock additives or octane boosters used on a large scale were tetraalkyl lead compounds, which, due to their toxicity and impact on vehicle catalyst, are now prohibited. Additionally, these compounds are very effective as MON boosters, which is not desired in modern automotive engines.

[0008] Oxygenates can enhance the octane of gasolines, the most known being methyl *tert*-butyl ether (MTBE) and ethyl tert-butyl ether (ETBE). Both compounds increase both RON and MON. Another drawback is the necessity of using high amounts, which limits the use of cheaper light components in gasoline. Their partial solubility in water has limited the use of ethers in several regions, due to the risk of contamination of groundwater reservoirs. The use of low aliphatic alcohols is allowed in automotive gasoline, such as methanol, ethanol, isopropanol, tert-butyl alcohol or isobutanol. Their capacity for octane boosting is lower than that of ethers and side effects are more remarkable, since they increase significantly the vapor pressure of gasolines and present very high solubility in water. The list of oxygenates that have been evaluated as octane improvers also includes ketones, esters, furans and carbonates but their use has not been successful due to their cost, harm effects or impact on health and environment. The use of high efficiency octane enhancers that can be used in lower concentrations has been the focus of several studies. Metallic anti-knock agents alternative to lead compounds, such as MMT (methylcyclopentadienyl manganese tricarbonyl) are very efficient but they tend to lead ash deposits after their combustion and their use is forbidden in most automotive gasoline specifications. Additionally, compounds as MMT were developed several years ago and the aim was to be efficient for both RON and

MON boosting. However, MON increase is not further desired in new automotive spark-ignition engines.

[0009] The use of some aromatic amines, and in particular of anilines, to increase the octane number of a base gasoline has been extensively reported, because of their very high efficiency as octane boosters. Aromatic amines are generally more efficient in increasing the octane number than oxygenated additives. However, they usually have a higher price and are sometimes highly toxic (e.g. aniline and o-toluidine). Traditional anilines are designed to increase MON (aviation fuels) or both RON and MON (automotive fuels). Therefore, further developments are needed which allow increasing the RON value with a low or even null increase of MON, as required by modern spark ignition engines to obtain a better anti-knock quality.

[0010] Document US 2881061 refers to the use of hydrogenated quinolines and indoles as anti-knock agents. This document from 1959, deals with fuels for internal combustion engines with antiknock performance requirements very different from today needs. Furthermore, base fuels in that document are those typical from that period, with components from alkylation, isomerization, catalytic cracking, reforming, etc., with a RON between 60 and 80 (unleaded). No oxygenates were present in said fuel compositions, which are quite far from nowadays commercial fuels with significant quantity of oxygenates.

[0011] Cullis et al. (Twenty-first Symposium (International) on Combustion/The Combustion Institute 1986, 1223-1230) studied the ability of amines to mitigate the promoting action of the sulphur compounds on the combustion behavior, in terms of changes both in the chain-propagation steps involved and in the stability of the intermediate radicals. The effect of indoline on the RON value of a mixture of heptane/isooctane was determined. However, this mixture of alkanes does not contain neither olefins nor oxygenates and aromatics and so its performance does not follow that of a standard gasoline. Document WO 2017/050777 relates to a gasoline fuel composition comprising 2-20% v/v of Fischer-Tropsch derived naphtha. This document refers to a method to increase the RON of a gasoline containing less than 40% of aromatics, without increasing the total aromatic content, by using aromatic octane boosters. Aromatic amines and phenols are disclosed as preferred octane boosters. Dihydroindole is mentioned within a list of possible aromatic amine octane boosters, though only N-methyl aniline (NMA) is tested in this document.

[0012] Document WO 2016/135036 cites indoline within a list of possible aromatic amine anti-knock additives. However, this document refers to lubricating compositions and does not disclose gasoline fuel compositions according to the present invention.

[0013] The performance of an antiknock agent is highly dependent on the composition of the gasoline (J. J. McKetta Jr., Encyclopedia of Chemical Processing and Design, vol. 2, 1977, page 3, entry "Additives, Engine Fuel"). Therefore, conclusions from old gasoline compositions lacking oxygenated compounds (US 2881061) or from alkane mixtures lacking aromatic and oxygenated components (Cullis et al.) cannot be extrapolated to current standard gasoline compositions. Additionally, aromatic amines have been typically disclosed to increase both RON and MON.

[0014] Therefore, there is still a need for new octane boosters capable of increasing RON without increasing or with a very low increase of MON, so that they can improve the anti-knock quality of gasoline compositions in modern engines.

BRIEF DESCRIPTION OF THE INVENTION

[0015] The invention is based on the finding that indoline is an excellent anti-knock agent, especially suitable for modern engines.

[0016] First, the inventors have found that indoline (2,3-dihydroindole, CAS No.: 496-15-1) increases the Research Octane Number (RON) in gasolines comprising oxygenated compounds, with a very low or even negative increase of the Motor Octane Number (MON). As explained above, this effect results in a higher increase of the octane index and, therefore, in a higher quality anti-knock agent.

[0017] Surprisingly this effect is not observed in gasolines lacking oxygenated compounds, such as those in US 2881061 or Cullis et al. (see example 2).

[0018] The use of other known anti-knock agents, such as NMA in WO 2017/050777, in a gasoline composition according to the present invention increases both RON and MON, thus leading to a lower increase of the Octane Index and so lower anti-knock quality (see example 3).

[0019] Additionally, the inventors have surprisingly found that addition of low amounts of indoline increases the lubricity of the gasoline. A higher lubricity of the fuel is desired in order to reduce friction and wear issues and to reduce fuel consumption. Additionally, this increased lubricity is not observed for other known aromatic amine antiknock agents (see example 4).

[0020] Finally, indoline has shown low toxic activity (Warning word coding) and so it is not necessary to add it to the gasoline at the refinery. Advantageously, it can be added directly to the gasoline at the gas station with standard preventive measurements, in contrast to other known aromatic amine anti-knock agents that would need very specific preventive measurements (Danger word coding). One example is 1,2,3,4-tetrahydroquinoline, which induces carcinogens (category 1B) according to several notifications to European Chemicals Agency (ECHA). Other example is N-methylaniline (NMA) with acute toxicity (oral H301, dermic H311 and by inhalation H331), according to harmonized classification in ECHA.

[0021] The invention thus provides an antiknock agent with excellent antiknock performance and reduced toxicity.

[0022] Thus, in a first aspect, the invention is directed to a gasoline fuel composition comprising:

(i) indoline, and
(ii) a gasoline base fuel comprising:

- 30-90 vol% of saturated hydrocarbons,
- 0-30 vol% of olefinic hydrocarbons,
- 10-60 vol% of aromatic hydrocarbons,
- 5-50 vol% of oxygenated hydrocarbons.

[0023] In a second aspect, the present invention is directed to the use of indoline for improving the antiknock properties of a gasoline composition comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

[0024] In a third aspect, the present invention is directed to a process for preparing a gasoline fuel composition comprising adding indoline to a gasoline base fuel comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

[0025] In a further aspect, the present invention is directed to a method for improving the antiknock properties of a gasoline comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons, wherein the method comprises adding indoline to the gasoline.

FIGURES

[0026]

Figure 1 is a graph showing the evolution of K value over time.

Figures 2A and B represent the increase of RON (Fig. 2A) and MON (Fig. 2B) values at different indoline concentrations in a composition lacking oxygenated components (Nafta SR, straight run production), a 90:10 iso-octane/n-heptane mixture, a gasoline according to the present invention with RON>95 (Efitec 95), and a gasoline according to the present invention with RON>98 (Efitec 98).

Figures 3A and B represent the increase of RON (Fig. 3A) and MON (Fig. 3B) values at different indoline and NMA concentrations in a gasoline according to the present invention with RON>95 (Effitec 95), and a gasoline according to the present invention with RON>98 (Efitec 98). Figures 3C represents the increase of the Octane Index at different K values for a gasoline according to the present invention with RON>98 comprising indoline or NMA.

Figure 4 shows photographs of polyethylene elastomers (HDPE-G45060UV and LLDPE-RESISTEX1810F) before and after soaking them in pure indoline or NMA at 40°C for 5 days.

Figure 5 shows the effect of the addition of detergent (Dorf Ketal SR8208) to a gasoline composition comprising indoline.

DETAILED DESCRIPTION OF THE INVENTION

[0027] Unless defined otherwise, all technical and scientific terms used herein have the same meaning as commonly understood to one of ordinary skill in the art to which this disclosure belongs. As used herein, the singular forms "a" "an" and "the" include plural reference unless the context clearly dictates otherwise.

[0028] The Octane Number can be determined either according to the "Research" method (RON) or to the "Motor" method (MON). In the present document, the octane number refers to the Research Octane Number (RON), unless the opposite is clearly stated.

[0029] The most common type of octane rating is the Research Octane Number (RON) and gasolines are usually classified based on it. RON is determined by running the fuel in a test engine with a variable compression ratio under controlled conditions, and comparing the results with those for standard mixtures of iso-octane, n-heptane and octane improver. RON can be measured in accordance with ASTM D2699. Motor Octane Number (MON) complements the antiknock performance evaluation and can be measured in accordance with ASTM 2700. The combination of RON and MON defines the Octane Index and the relative impact of each one depends on the type of engine. Higher RON values result in better antiknock performance in all type of engines, especially in current engines where MON has less influence or even negative effect.

[0030] The terms "octane booster", "anti-knock agent" or "anti-knock additive" are used herein interchangeably to refer to compounds or mixture of compounds that raise the octane number of a fuel composition.

[0031] The term "Octane Index" as used herein is defined by the following equation:

$$O.I. = (1 - K) \cdot RON - K \cdot MON$$

wherein RON and MON can be determined by well established standards (ASTM D2699 and ASTM D2700, respectively), and K is a constant that depends on the engine, as it has been detailed previously.

[0032] The term "sensitivity" as used herein refers to the octane sensitivity of the fuel and is defined as the difference between the RON and the MON of said fuel.

$$S = RON - MON$$

[0033] All the embodiments and definitions disclosed in the context of one aspect of the invention are also applicable to the other aspects of the invention.

[0034] In a first aspect, the invention is directed to a gasoline fuel composition comprising:

(i) indoline, and
(ii) a gasoline base fuel comprising:

- 30-90 vol% of saturated hydrocarbons,
- 0-30 vol% of olefinic hydrocarbons,
- 10-60 vol% of aromatic hydrocarbons,
- 5-50 vol% of oxygenated hydrocarbons.

[0035] In an embodiment, the indoline is present in the gasoline fuel composition in an amount of from 0.3% to 5.0% by volume relative to the volume of the gasoline fuel composition; preferably from 0.4% to 3.0% by volume; more preferably from 0.4% to 2.0% by volume; even more preferably from 0.4% to 1.2% by volume.

[0036] In a more preferred embodiment, the indoline is present in the gasoline fuel composition in an amount of from 0.5% to 2.0% by volume relative to the volume of the gasoline fuel composition, preferably from 0.5% to 1.5% by volume, more preferably from 0.5% to 1.2% by volume or even more preferably from 0.5% to 1.0% by volume.

[0037] The amount of gasoline base fuel in the gasoline composition is typically at least 95% by volume based on the volume of the gasoline fuel composition, or at least 97% by volume, and preferably at least 98% or 99% by volume. In an embodiment, the amount of gasoline base fuel in the gasoline composition is from 97% to 99.5% by volume based on the volume of the gasoline fuel composition, preferably from 98% to 99.5% by volume.

[0038] The gasoline base fuel may be any gasoline suitable for use in an internal combustion engine of the spark-ignition type known in the art, such as automotive engines.

[0039] Gasoline base fuels typically comprise a mixture of hydrocarbons in the gasoline boiling range. Suitable hydrocarbons in the gasoline boiling range are mixtures of hydrocarbons having a boiling range of from about 25°C to about 232°C and comprise mixtures of saturated hydrocarbons, olefinic hydrocarbons, aromatic hydrocarbons and oxygenated hydrocarbons as defined herein.

[0040] In an embodiment, the content of saturated hydrocarbons in the gasoline base fuel is in the range of from 40% to 90% by volume based on the volume of the gasoline base fuel; preferably from 40% to 80% by volume; even more preferably from 40% to 65% by volume. Content of saturated hydrocarbons can be determined according to UNE EN ISO 22854.

[0041] In an embodiment, the content of olefinic hydrocarbons in the gasoline base fuel is in the range of from 2% to 30% by volume based on the volume of the gasoline base fuel; preferably from 5% to 25% by volume; more preferably from 5% to 20% by volume. Content of olefinic hydrocarbons can be determined according to UNE EN ISO 22854.

[0042] In an embodiment, the content of aromatic hydrocarbons in the gasoline base fuel is in the range of from 10% to 45% by volume based on the volume of the gasoline base fuel; preferably from 15% to 35% by volume. Content of aromatic hydrocarbons can be determined according to UNE EN ISO 22854.

[0043] Typically, the benzene content of the gasoline base fuel is at most 5% by volume; preferably at most 2% by volume; more preferably at most 1% by volume. In an embodiment, the content of benzene in the gasoline base fuel is in the range of from 0.1% to 1% by volume based on the volume of the gasoline base fuel. Content of benzene can be determined according to UNE EN ISO 22854.

[0044] In an embodiment, the content of oxygenated hydrocarbons in the gasoline base fuel is from 5% to 40% by volume relative to the gasoline base fuel; preferably from 5% to 30% by volume; even more preferably from 5% to 25% by volume. Suitable oxygenated hydrocarbons include alcohols, ethers, esters, ketones, aldehydes, carboxylic acids and their derivatives. Preferably, the oxygenated hydrocarbons are selected from alcohols (preferably alcohols having from 1 to 4 carbon atoms) and ethers (preferably ethers having 5 or 6 carbon atoms) such as, for example, methanol, ethanol, isopropyl alcohol, isobutyl alcohol, tert-butyl alcohol, methyl tert-butyl ether, di-ispropropyl ether, ethyl *tert*-butyl ether, *tert*-amyl methyl ether, and mixtures thereof. Content of oxygenated hydrocarbons can be determined according to UNE EN ISO 22854.

[0045] Preferably, the gasoline base fuel comprises 40% to 90% by volume of saturated hydrocarbons, from 2% to 30% by volume of olefinic hydrocarbons, from 10% to 45% by volume of aromatic hydrocarbons, and from 5% to 40% by volume of oxygenated hydrocarbons, based on the volume of the gasoline base fuel. More preferably, the gasoline base fuel comprises 40% to 80% by volume of saturated hydrocarbons, from 5% to 25% by volume of olefinic hydrocarbons, from 15% to 35% by volume of aromatic hydrocarbons and from 5% to 30% by volume of oxygenated hydrocarbons.

[0046] Typically, the maximum oxygen content of the gasoline base fuel is up to 10% by weight based on the weight of the gasoline base fuel; preferably up to 5% by weight or up to 4% by weight. Oxygen content can be determined according to UNE EN ISO 22854.

[0047] The gasoline base fuel, and the gasoline fuel composition, preferably have a low or ultra-low sulphur content, for example at most 0.01% by weight of sulphur based in the weight of the gasoline base fuel or the gasoline fuel composition, respectively; preferably at most 0.005% by weight; more preferably at most 0.001% by weight. Sulphur content can be determined according to ASTM D4294.

[0048] The gasoline base fuel, and the gasoline fuel composition, preferably have a low lead content, such as at most 5 mg/l, more preferably being unleaded gasoline base fuel, i.e. having no lead compounds added thereto. Lead content can be determined according to UNE EN 237.

[0049] The gasoline base fuel can be derived from straight run gasoline, polymer gasoline, natural gasoline dimer and trimerized olefins, synthetically produced aromatic hydrocarbon mixtures, or from catalytically cracked or thermally cracked petroleum stocks, and mixtures of these.

[0050] In an embodiment, the gasoline base fuel (and the gasoline fuel composition without indoline) has a Research Octane Number (RON) of 90 or more, preferably 95 or more, more preferably 98 or more. In an embodiment, it has a RON of 105 or less, preferably 100 or less. RON is determined according to method ASTM D2699. In an embodiment, the gasoline base fuel has a RON of from 90 to 105, preferably from 95 to 105, more preferably from 98 to 105 or from 95 to 100.

[0051] In an embodiment, the gasoline base fuel (and the gasoline fuel composition without indoline) has a Motor Octane Number (MON) of 80 or more, preferably 85 or more, more preferably 86 or more. MON is determined according to method ASTM D2700. In an embodiment, the gasoline base fuel has a MON of from 80 to 90, preferably from 85 to 90, more preferably from 86 to 90.

[0052] In a particular embodiment, the gasoline base fuel (and the gasoline fuel composition without indoline) has a RON of 95 or more, preferably 98 or more, and a MON of 85 or more, preferably 87 or more.

[0053] In an embodiment, the gasoline fuel composition of the invention (comprising indoline) has a RON of 96 or more, preferably 97 or more, more preferably 99 or more. In an embodiment, the gasoline fuel composition has a RON of from 96 to 110, preferably from 97 to 110, more preferably from 98 to 110. In a further embodiment, the gasoline fuel composition has a RON of from 96 to 105, preferably from 97 to 105, more preferably from 98 to 105 or from 99 to 105.

[0054] In an embodiment, the gasoline fuel composition of the invention (comprising indoline) has a sensitivity (RON-MON) higher than 9, preferably 10 or higher, more preferably 11 or higher. In an embodiment, the gasoline fuel composition of the invention has a sensitivity (RON-MON) from 10 to 16, preferably from 11 to 15.

[0055] In a particular embodiment, the gasoline fuel composition of the invention has a RON of 97 or more, preferably 99 or more, and a sensitivity (RON-MON) of 10 or higher, preferably 11 or higher. In an embodiment, the gasoline fuel composition of the invention has a RON of 97 or more, preferably 99 or more, and a sensitivity (RON-MON) from 10 to 16, preferably from 11 to 15.

[0056] The gasoline fuel composition can further comprise conventional fuel additives such as antioxidants, corrosion inhibitors, detergents or dispersants, dehazers, demulsifiers, metal deactivators, valve-seat recession protectant compounds, solvents, carrier fluids, diluents, friction modifiers, dyes and markers.

[0057] Preferably, the total amount of such conventional fuel additives in the gasoline fuel composition is up to 2% by weight based on the weight of the gasoline fuel composition, more preferably up to 1% by weight. In an embodiment, the amount of such conventional fuel additives in the gasoline fuel composition is in the range of from 0.001% to 1.5% by weight based on the weight of the gasoline fuel composition; preferably from 0.01% to 1.0% by weight. In a particular embodiment, the amount of conventional additives is in the range of from 0.01% to 0.5% by weight based on the weight of the gasoline fuel composition.

[0058] In a particular embodiment, the gasoline fuel composition comprises a multifunctional package comprising one or more of said conventional additives.

[0059] Suitable antioxidants are known in the art and include phenolic and phenylenediamine compounds, such as 2,4-di-*tert*butylphenol, 3,5-di-*tert*butyl-4-hydroxy-phenylpropionic acid, BHT, BHB or N,N'-di-*sec*-butyl-*p*-phenylenediamine, hydrazine-based antioxidants or thiourea-based antioxidants.

[0060] The inventors have observed that the use of thiourea-based antioxidants and hydrazine-based antioxidants provides highly stable gasoline fuel compositions. Therefore, in a particular embodiment, the gasoline fuel composition of the invention comprises a thiourea-based antioxidant, a hydrazine-based antioxidant or a mixture thereof, preferably a hydrazine-based antioxidant. In an embodiment, the gasoline fuel composition comprises an antioxidant in an amount from 2 to 100 mg, preferably from 3 to 30 mg and more preferably from 4 to 10 mg, per Kg of the gasoline fuel composition.

[0061] Examples of thiourea-based antioxidants include, but are not limited to, compounds represented by the formula $R^1R^2NC(=S)NR^3R^4$, wherein R^1, R^2, R^3 and R^4 are independently selected from hydrogen C_{1-4} alkyl optionally substituted by (C_{1-4} alkyl)amino, di(C_{1-4} alkyl)amino or C_{1-4} alkoxy; C_{3-4} cycloalkyl; and C_{6-10} aryl; or R^1 and R^3 may form together a C_{2-4} alkylene; or R^1 and R^2 or R^3 and R^4 may form a C_{3-5} alkylene optionally interrupted with an oxygen or nitrogen atom. Examples of thiourea-based antioxidants include thiourea, 1,3-ethylenethiourea, trimethylthiourea, tributylthiourea, 1,3-diethylthiourea, 1,3-dibutylthiourea, 1,3-bis(dimethylaminopropyl)-2-thiourea, N-phenylthiourea, 1-methoxypropyl-3-butyl-2-thiourea, 1-dimethylaminopropyl-3-butyl-2-thiourea, 1-methoxypropyl-3-cyclohexyl-2-thiourea, 1-dimethylaminopropyl-3-phenyl-2-thiourea, 1-methoxypropyl-3,3-dibutyl-2-thiourea, 1-dimethylaminopropyl-3,3-diisopropyl-2-thiourea, 1-diethylaminopropyl-3-methyl-3-cyclohexyl-2-thiourea, 1-methoxypropyl-3-phenyl-3-cyclohexyl-2-thiourea, 1-methoxypropyl-3-oxydiethylene-2-thiourea, 1-n-butyl-3-oxydiethylene-2-thiourea, 1-diethylaminopropyl-3-oxydiethylene-2-thiourea. Preferably, the thiourea-based antioxidant is 1,3-ethylenethiourea.

[0062] Examples of hydrazine-based antioxidants include, but are not limited to, hydrazine, hydrazine hydrate, 1,1-dimethylhydrazine, 1,2-diphenylhydrazine, acetohydrazide, benzohydrazide, cyclohexanecarbohydrazide, adipic acid dihydrazide, sebacic acid dihydrazide, dodecanedioic acid dihydrazide, isophthalic acid dihydrazide, propioic acid hydrazide, salicylic acid hydrazide, 3-hydroxy-2-naphthoic acid hydrazide, benzophenone hydrazone, aminopolyacrylamide, N,N'-bis[3-(3,5-di-*tert*butyl-4-hydroxyphenyl)propionyl]hydrazine, isopropylhydrazyne sulfate, tert-butylhydrazine sulfate, decamethylene dicarboxylic acid-bis(N'-salicyloyl hydrazide), isophthalic acid bis(2-phenoxypropionyl hydrazide), N-formyl-N'-salicyloyl hydrazine, N,N'-bis[beta(3,5-di-*tert*-butyl-4-hydroxyphenyl)propan-acyl]hydrazine, N,N'-bis(3,5-di-*tert*-butyl-4-hydroxyphenylpropionyl)hydrazine, and N-salicyloyl-N'-aldehydehydrazine. Preferably, the hydrazine-based antioxidant is hydrazine or a hydrate thereof.

[0063] Suitable corrosion inhibitors are known in the art. They consist typically of a polar head to enable adhesion to the metal surfaces to be protected, and a hydrocarbon tail to ensure fuel solubility. Examples of corrosion inhibitors include carboxylic acids, anhydrides, amines and amine salts of carboxylic acids. In an embodiment, the gasoline fuel composition can comprise a corrosion inhibitor in an amount of up to 200 mg, preferably up to 100 mg, more preferably up to 50 mg, per Kg of the gasoline fuel composition.

[0064] Suitable deposit control additives or dispersants, often referred to as fuel detergents, are known in the art. They typically consist of a polar head, the polarity of which is derived from oxygen or nitrogen molecules, and a hydrocarbon tail, which enables the additive to be fuel soluble. Examples of detergents or dispersants include amides, amines, polybutene succinimides, polyisobutylene amines, polyether amines, polyolefin amines and Mannich amines. Preferably, the detergent is a nitrogen-containing or oxygen-containing detergent having a hydrophobic hydrocarbon radical with a number average molecular weight in the range of from 300 to 5000 Da. More preferably, it is obtained by Mannich reaction of a polyisobutylene phenol with an aldehyde (such as formaldehyde) and mono- or polyamines (such as ethylenediamine, tetraethylenepentamine or triethylenetetramine), preferably wherein the polyisobutylene group has a number average molecular weight from 300 to 5000 Da as determined by DOSY (Difussion Ordered SpectroscopY)

[0065] Preferably, the gasoline fuel composition comprises a detergent or dispersant, for example in an amount of up to 5000 mg, preferably up to 1000 mg, more preferably up to 500 mg, per Kg of the gasoline fuel composition. For example, in an amount from 25 to 500 mg/Kg, preferably from 25 to 100 mg/Kg.

[0066] Demulsifiers, dehazers and water emulsion preventatives are known in the art. Key functions are both coalescing water droplets in larger ones and flocculating small droplets together; these compounds are called droppers and treaters, respectively. Usually these additives are mixed to get both functions. They are typically mixtures of alkoxylate compounds including phenolic resins, esters, polyamines, sulphonates or alcohols which have been reacted with ethylene or propylene oxide. Examples of these compounds include glycol oxyalkylate blends, alkoxylated phenol formaldehyde polymers, phenol/formaldehyde or C_{1-18} alkylphenol/formaldehyde resin oxyalkylates modified by oxyalkylation with C_{1-18} epoxides and diepoxides, and C_{1-4} epoxide copolymers cross-linked with diepoxides, diacids, diesters, diols, diacrylates, dimethacrylates or diisocyanates, and blends thereof. Dehazers are frequently used in fuels to prevent haze from residual water and flocculation efficiency of these compounds is very important. On the other hand, demulsifiers are very useful to assure emulsion break when additized fuels contact any water within distributions systems, and coalescence is very important in this case. In an embodiment, the gasoline fuel composition can comprise a dehazer with proper demulsifying properties, preferably a polyol alkoxylate, such as an ethylene oxide (EO) and/or propylene oxide (PO) based polyol; more preferably an EO/PO based polyol. In a preferred embodiment, the gasoline fuel composition comprises a polyol alkoxylate with a monomer weight ratio of propylene oxide to ethylene oxide from 70:30 to 80:20, with minimum 25% of primary hydroxyl, preferably minimum 50%, and with a multimodal molecular weight higher than 4000 Da, preferably higher than 6000 Da, more preferably between 6.000 and 25.000 Da as determined by DOSY (Difussion Ordered SpectroscopY). In an embodiment, the demulsifier is present in the gasoline composition in an amount of up to 50 mg, preferably up to 10 mg, more preferably up to 5 mg, per Kg of the gasoline fuel composition.

[0067] Suitable solvents, carriers and diluents are well known in the art and include synthetic and mineral oils and solvents.

[0068] Examples of suitable mineral carrier oils include fractions obtained in crude oil processing, such as brightstock or base oils having viscosities, for example, from the SN 500 - 2000 class; and also aromatic hydrocarbons, paraffinic hydrocarbons and alkoxyalkanols. Also useful as a mineral carrier oil is a fraction which is obtained in the refining of mineral oil and is known as "hydrocrack oil" (vacuum distillate cut having a boiling range of from about 360 to 500 °C, obtainable from natural mineral oil which has been catalytically hydrogenated under high pressure and isomerized and also deparaffinized). Examples of suitable synthetic carrier oils are polyolefins (poly-alphaolefins or poly (internal olefins)), (poly)esters, (poly)alkoxylates, polyethers, polyglycols, aliphatic polyether amines, alkylphenol-started polyethers, alkylphenol-started polyether amines and carboxylic esters of long-chain alkanols.

[0069] Any solvent and optionally co-solvent suitable for use in fuels may be used in the gasoline fuel composition of the invention. Examples of suitable solvents for use in fuels include: non-polar hydrocarbon solvents such as kerosene, heavy aromatic solvent, toluene, xylene, paraffins, petroleum, white spirits, and the like. Examples of suitable co-solvents include: polar solvents such as esters and, in particular, alcohols (e.g. t-butanol, i-butanol, hexanol, 2-ethylhexanol, 2-propyl heptanol, decanol, isotridecanol, butyl glycols) and alcohol mixtures.

[0070] In an embodiment, the gasoline fuel composition can comprise a solvent, carrier or diluent in an amount of up to 8000 mg, preferably up to 5000 mg, more preferably up to 3000 mg, per Kg of the gasoline fuel composition. For example, in an amount from 50 to 5000 mg/Kg.

[0071] Suitable valve-seat recession protectant compounds are known in the art and include, for example, sodium or potassium salts of polymeric organic acids. In an embodiment, the gasoline fuel composition can comprise a valve-seat recession protectant in an amount of up to 200 mg, preferably up to 100 mg, more preferably up to 50 mg, per Kg of the gasoline fuel composition. For example, in an amount from 1 to 100 mg/Kg. Suitable friction modifiers of gasoline are known in the art and include, for example, linoleic acid and its derivatives. In an embodiment, the gasoline fuel composition can comprise a friction modifier in an amount of up to 1000 mg, preferably up to 500 mg, more preferably up to 200 mg, per Kg of the gasoline fuel composition. For example, in an amount from 10 to 1000 mg/Kg.

[0072] One or more conventional fuel additives, or a multifunctional package comprising them, can be added to the gasoline base fuel or to a gasoline fuel composition comprising the gasoline base fuel and indoline.

[0073] In an embodiment, the gasoline fuel composition is free of metallic octane boosters, i.e. having no metallic octane boosters added thereto. In a further embodiment, the gasoline fuel composition of the invention has a very low content of metallic compounds or is free of metallic compounds, that is, the total content of metallic compounds is less than 0.0005% by weight based on the gasoline fuel composition.

[0074] It is preferred that the gasoline fuel composition does not include other aromatic amine antiknock agents apart from indoline. Preferably, indoline is the only antiknock agent added to the gasoline fuel composition.

[0075] Preferably, the gasoline fuel composition is free of Fischer-Tropsch derived naphtha. That is, the gasoline fuel composition is free of naphtha that is a product of a Fischer-Tropsch synthesis process or is derived from a product of a Fischer-Tropsch synthesis process (e.g. by fractionation and/or by hydrotreatment, polymerization, alkylation, distillation, cracking-decarboxylation, isomerization or hydroreforming of Fischer-Tropsch synthesis products). A Fischer-Tropsch derived naphtha may also be referred as a Gas to Liquid (GTL) naphtha. The term "naphtha" is well-known by those skilled in the art. It typically means a mixture of hydrocarbons generally having between 5 and 12 carbon atoms and having a boiling point in the range of 30 to 200°C. It is preferred that the gasoline fuel composition of the invention is free of Fischer-Tropsch derived naphtha as defined in WO 2017/050777, which is herein incorporated by reference.

[0076] The gasoline fuel composition of the invention is suitable for use in an internal combustion engine of the spark-ignition type known in the art. The specific boosting of indoline, which increases RON without MON increase, is particularly beneficial in modern engines, where MON effect is negative on knocking behavior. Therefore, the gasoline fuel composition is preferably used in engines manufactured since 1995. These engines have tighter emission and efficiency specifications, using different strategies like downsizing and boosting, where Octane Index equation presents better anti-knocking accuracy with negative values of K. Modern engines include those which comply at least with Euro 2 emissions standards, with implementation date (new approvals) since 1 January 1996 (Directives 70/220/CEE and 94/12/CE).

[0077] In a second aspect, the invention is directed to the use of indoline as an anti-knock agent in a gasoline composition. That is, the invention is also directed to the use of indoline for improving the antiknock properties of a gasoline fuel composition comprising gasoline base fuel having 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

[0078] The gasoline fuel composition can further comprise conventional fuel additives such as antioxidants, corrosion inhibitors, detergents or dispersants, dehazers, demulsifiers, metal deactivators, valve-seat recession protectant compounds, solvents, carrier fluids, diluents, friction modifiers, dyes and markers.

[0079] Suitable and preferred embodiments for the gasoline fuel composition, gasoline base fuel, conventional fuel additives and indoline are as defined herein in relation to the first aspect of the invention.

[0080] Preferably, the amount of indoline in the final gasoline fuel composition (i.e. after addition of this anti-knock agent) is from 0.4% to 2.0% by volume relative to the total volume of the gasoline fuel composition, more preferably from 0.5% to 1.5% by volume or even 0.5% to 1.2% by volume.

[0081] In an embodiment, improving the antiknock properties of a gasoline means increasing the Octane Index compared to the same gasoline composition without indoline.

[0082] In another embodiment, improving the antiknock properties of a gasoline means increasing the RON, preferably increasing the RON without increasing or with a very low increase of the MON, such as a MON increase of less than 1.0, compared to the same gasoline composition without indoline.

[0083] Preferably, before addition of indoline, the gasoline composition has a RON of 95 or more, preferably 98 or more, and a MON of 85 or more, preferably 87 or more.

[0084] After addition of indoline, the gasoline fuel composition preferably has a RON of 97 or more, preferably 99 or more.

[0085] The increase of RON in the gasoline composition may be, for instance, 1 unit or greater, 1.5 units or greater, preferably 2 units or greater or even 3 units or greater, compared to the RON of the gasoline composition without indoline. The increase in RON of the gasoline fuel composition may be at most 10 units, or at most 5 units, compared to the same gasoline composition without indoline. In an embodiment, the increase in RON is from 1 to 5 units, preferably from 1.5 units to 5 units.

[0086] The increase of MON in the gasoline composition may be, for instance, 2 units or less, preferably 1.5 units or less, more preferably 1.0 units or less, or even 0.5 units or less, compared to the MON of the gasoline composition without indoline. In an embodiment, the increase of MON is 0.2 or less, or even 0 or less. In an embodiment, the increase in MON is from -2 units to 2 units, preferably from -1.0 to 1.0 units and more preferably from -1.0 to 0.5 units or even from -1.0 to 0.2 units or from -1.0 to 0 units, compared to the same gasoline composition without indoline.

[0087] In a particular embodiment, indoline increases the RON of the gasoline fuel composition without increasing the MON or increasing it by 1.5 units or less, preferably by 1.0 units or less or even 0.2 units or less, compared to the same gasoline composition without indoline. In a further embodiment, indoline increases the RON of the gasoline fuel composition by 1 units or more, preferably 1.5 units or more, while increasing the MON by 1 units or less, preferably by 0.5 units or less or even 0.2 units or less, compared to the same gasoline composition without indoline.

[0088] In an embodiment, the gasoline fuel composition (after addition of indoline) has a sensitivity (RON-MON) of 10 or higher, preferably 11 or higher. In an embodiment, the gasoline fuel composition of the invention has a sensitivity (RON-MON) from 10 to 16, preferably from 11 to 15.

[0089] In a particular embodiment, the gasoline fuel composition indoline has a RON of 97 or more, preferably 99 or more, and a sensitivity (RON-MON) of 10 or higher, preferably 11 or higher.

[0090] In a third aspect, the present invention is directed to a process for preparing a gasoline fuel composition according to the present invention, comprising adding indoline to a gasoline base fuel comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

[0091] In a fourth aspect, the invention is directed to a method for improving the anti-knock properties of a gasoline composition comprising gasoline base fuel having 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons, said method comprising adding indoline to the gasoline composition.

[0092] In an embodiment, improving the antiknock properties of a gasoline means increasing the Octane Index compared to the same gasoline composition without indoline.

[0093] In another embodiment, improving the antiknock properties of a gasoline means increasing the RON, preferably increasing the RON without increasing or with a very low increase of the MON, such as a MON increase of less than 1.0, compared to the same gasoline composition without indoline.

[0094] The gasoline fuel composition can further comprise conventional fuel additives such as antioxidants, corrosion inhibitors, detergents or dispersants, dehazers, demulsifiers, metal deactivators, valve-seat recession protectant compounds, solvents, carrier fluids, diluents, friction modifiers, dyes and markers.

[0095] Suitable and preferred embodiments for the gasoline fuel composition, gasoline base fuel, conventional fuel additives, indoline, improving the anti-knock properties, RON and MON in relation to the third and fourth aspects are as defined herein in relation to the first and second aspects of the invention.

[0096] The step of adding the fuel additive to the gasoline can be performed in any stage of the fuel supply process, from the refinery to the retail gasoline station (filling station), including intermediate storage terminals and transport devices.

[0097] In contrast to other known aromatic amine anti-knock agents, indoline has been found by the inventors to present a low toxicity. Consequently, it can be advantageously added to the gasoline composition at the retail gasoline station even without the need of additional safety considerations.

[0098] The indoline can be added to the gasoline fuel composition comprising one or more conventional fuel additives. Alternatively, the indoline can be added to the gasoline base fuel, optionally one or more conventional fuel additives may then be added to the resulting composition. In another embodiment, the indoline may be blended with one or more conventional additives to provide a blend that is later added to a gasoline base fuel or to a gasoline fuel composition.

[0099] Therefore, in a particular embodiment, the process and the method of the invention comprise:

(a) preparing a gasoline fuel composition comprising gasoline base fuel having 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons, and
(b) adding indoline to said composition.

[0100] The gasoline fuel composition in step (a) can comprise one or more conventional fuel additives as described herein.

[0101] In an embodiment, the method of the invention further comprises adding one or more conventional fuel additives as described herein to the composition obtained after the addition of indoline.

EXAMPLES

[0102] The invention is illustrated by means of the following examples which in no case limit the scope of the invention.

Example 1: Preparation of a gasoline composition comprising indoline

[0103] The gasoline base fuel used in the test was an EN-228 automotive gasoline, Premium type E5 (less than 2.7% oxygen content) and RON higher than 98 (Efitec 98). This gasoline includes 900 ml/m^3 of Repsol multifunctional additive package CTR-BP-6-2827 that includes several components, such as: detergent or dispersant, marker, dyer, demulsifier and anticorrosion additive.

[0104] Indoline (99% minimum purity) was added to the above gasoline at 0.7% v/v in closed flasks in order to prevent the loss of volatile compounds.

[0105] The composition and physical properties of the gasoline composition comprising indoline are shown in Table 1. Data were measured using the test method indicated in the Table.

Table 1

Property	Test Method	Units	Gasoline base	Gasoline with 0.7% v/v of indoline
Research Octane Number (RON)	ASTM D 2699-19	-	98.4	99.9
Motor Octane Number (MON)	ASTM D 2700-19	-	88.5	88.3
Density (at 15°C)	ASTM D 4052-18	Kg/m^3	732.7	736.0
Vapor pressure (DVPE)	ASTM D 5191-15	KPa	57.5	55.5
Initial boiling point	ASTM D 86-17	°C	35.6	33.6
% evaporated at 70°C (E70)		% v/v	23.5	25.0
% evaporated at 100°C (E100)		% v/v	57.1	58.4
% evaporated at 150°C (E150)		% v/v	91.6	91.0
Final boiling point		°C	188.1	192.3
Distillation residue		% v/v	1	1.1
VLI (10 VP + 7 E70)		-	733	730

(continued)

Property	Test Method	Units	Gasoline base	Gasoline with 0.7% v/v of indoline
Sulfur content	ASTM D 4294-16e1	mg/Kg	7.3	9.0
Lead content	UNE EN 237:2005	mg/L	<0.0025	<0.0025
Copper strip corrosion (3h at 50°C)	ASTM D 130-18	rating	1a	1a
Oxidation stability	ASTM D 525-12a	min	>1440	>1440
Existent gum content (washed)	ASTM D 381-12 (2017)	mg/ 100mL	<0.5	<0.5
Hydrocarbons:	UNE EN ISO 22854: 2016			
Olefins		% v/v	8.9	9.1
Aromatics		% v/v	20.1	21.5
Saturated		% v/v	55.1	54.6
Oxygen content		% m/m	2.33	2.31
Oxygenates content				
methanol		% v/v	<0.01	<0.01
ethanol		% v/v	0.57	0.56
isopropyl alcohol		% v/v	<0.01	<0.01
tertbutyl alcohol		% v/v	<0.01	0.09
isobutyl alcohol		% v/v	<0.01	<0.01
MTBE		% v/v	0.11	0.11
ETBE		% v/v	13.1	13.1
other oxygenates		%v/v	<0.01	<0.01

[0106] As shown in Table 1, indoline increased the octane number (RON) of the gasoline without increasing the MON and while maintaining the specifications of the EN-228 automotive gasoline.

Example 2: Evaluation of the RON and MON increase by addition of indoline to:

[0107]

(a) a composition lacking oxygenated components (Nafta Straight Run),
(b) a 90:10 iso-octane/n-heptane mixture,
(c) a gasoline according to the present invention with RON>95 (Efitec 95), and
(d) a gasoline according to the present invention with RON>98 (Efitec 98).

[0108] Sample (a) is a naphtha obtained from direct distillation at industrial scale from refinery. Sample (b) was obtained by simple blending isooctane (2,2,4-trimethylpentane anhydrous, purity >99.5) and n-heptane (anhydrous, 99.0%) in closed flasks of samples. Samples (c) and (d) are commercial gasolines from Spanish market, both satisfying EN-228 specification for automotive gasoline with Repsol multifunctional performance packages. Efitec 95 is a regular grade (RON 95) and Efitec 98 is a premium quality one (RON 98). Table 2 details the composition of these samples.

Table 2. Composition (% v/v) of different samples, determined by UNE EN ISO 22854:2016

Composition	Straight run naphtha	90:10 mixture isooctane: n-heptane	Gasoline EN-228 Efitec 95	Gasoline EN-228 Efitec 98
Hydrocarbons:				
Olefins	4.4	< 0.01	14.6	8.9
Aromatics	14.4	< 0.01	26.8	20.1
Saturated	81.2	100.0	47.6	55.1

(continued)

Composition	Straight run naphtha	90:10 mixture isooctane: n-heptane	Gasoline EN-228 Efitec 95	Gasoline EN-228 Efitec 98
Oxygenates content				
methanol	< 0.01	< 0.01	< 0.01	<0.01
ethanol	< 0.01	< 0.01	1.78	0.57
isopropyl alcohol	< 0.01	< 0.01	< 0.01	<0.01
tertbutyl alcohol	< 0.01	< 0.01	< 0.01	<0.01
isobutyl alcohol	< 0.01	< 0.01	< 0.01	<0.01
MTBE	< 0.01	< 0.01	0.09	0.11
ETBE	< 0.01	< 0.01	9.04	13.1
other oxygenates	< 0.01	< 0.01	< 0.01	<0.01

[0109] Indoline (minimum 99% purity) was added to the each composition (a)-(d) at the indicated amount in closed flasks in order to prevent the loss of volatile compounds, and magnetic mechanical stirring was applied at room temperature until total dissolution was observed.

[0110] Research Octane Number (RON) measurements were carried out according to method ASTM D 2699-19. The Motor Octane Number (MON) measurements were carried out according to method ASTM D 2700-19. Table 3 details the octane numbers for each sample.

Table 3. Indoline effect on octane for different samples

Sample	Indoline, % v/v	RON	MON
Naphtha Straigth Run	0.0	64.0	63.3
	0.5	67.0	66.6
	1.0	70.0	69.9
	2.0	75.7	72.5
iso-C8/n-C7 mixture	0.0	90.3	90.3
	0.5	92.6	91.5
	1.0	94.9	92.6
	2.0	99.0	94.0
Efitec 95	0.0	95.6	86.5
	0.5	97.4	86.1
	1.0	98.3	86.9
	2.0	100.2	86.8
Efitec 98	0.0	98.4	88.5
	0.5	99.5	88.0
	0.7	99.9	88.3
	1.0	100.3	88.1
	2.0	102.0	88.2

[0111] The increase of octane by indoline is summarized in Fig. 2A (RON increase) and Fig. 2B (MON increase), which shows that indoline highly boosts both RON and MON in compositions lacking oxygenated compounds (Naphtha

Straight Run and 90:10 mixture of isoC8/nC7). In contrast, in gasoline compositions according to the present invention, indoline increases the RON without increasing (Efitec 98) or with a very low increase (Efitec 95) of the MON. This surprising lack of effect on MON and high boosting on RON for oxygenated samples is very important in current engines, where MON has a negative impact on antiknock properties.

Example 3: Evaluation of the RON, MON and Octane Index increase by addition of indoline and NMA to a gasoline according to the present invention with RON>95 (Efitec 95) and to a gasoline according to the present invention with RON>98 (Efitec 98).

[0112] The samples used in this example were commercial gasolines from Spanish market, both satisfying EN-228 specification for automotive gasoline with Repsol multifunctional performance packages. Efitec 95 is a regular grade (RON 95) and Efitec 98 is a premium quality one (RON 98). Table 2 details the composition of these samples.

[0113] The antiknock compounds evaluated in this example were indoline (minimum 99%) and N-methyl-aniline (NMA, minimum 98%). These compounds were added to the gasoline at the indicated amount in closed flasks in order to prevent the loss of volatile compounds, and magnetic mechanical stirring was applied at room temperature until total dissolution was observed.

[0114] Research Octane Number (RON) measurements were carried out according to method ASTM D 2699-19. The Motor Octane Number (MON) measurements were carried out according to method ASTM D 2700-19. Table 4 details the results of octane testing for the same gasolines with the two octane boosters evaluated.

Table 4. Comparison of indoline and NMA octane boosting capability.

Sample	Octane booster	% v/v octane booster	RON	MON
Efitec 95	Base fuel	0.0	95.6	86.5
	Indoline	0.5	97.4	86.1
		1.0	98.3	86.9
		2.0	100.2	86.8
	NMA	0.5	97.3	88.3
		1.0	98.5	88.8
		2.0	100.5	89.4
Efitec 98	Base fuel	0.0	98.4	88.5
	Indoline	0.5	99.5	88.0
		1.0	100.3	88.1
		2.0	102.0	88.2
	NMA	0.5	99.4	89.6
		1.0	100.8	90.1
		2.0	101.8	90.8

[0115] The results obtained are shown in Fig. 3A (RON) and Fig. 3B (MON), which indicate that a similar RON increase is provided by indoline and NMA. However, NMA also leads to a high increase of MON, whereas indoline does not increase or provides a very low increase of MON. Therefore, indoline has a clear advantage when MON has a negative effect on antiknocking properties, as it is the case in modern engines (for example, since Euro 2 engines in Europe).

[0116] Antiknock requirements of engines are associated to a combination of RON and MON. The Octane Index equation is widely accepted as follows:

$$\text{Octane Index} = \text{RON} - \text{K*sensitivity}$$

[0117] Sensitivity is the difference between RON and MON, thus:

$$\text{Octane Index} = (1\text{-}K)^*\text{RON} + K^*\text{MON}$$

[0118] K values in current engines are negative, which indicates a negative effect of MON in antiknock performance. Therefore this parameter is very relevant in any octane booster research for nowadays gasolines.

[0119] The increase of the Octane Index provided by the addition of indoline and NMA to gasoline composition Efitec 98 was calculated for different K values. As shown in Fig. 3C, the anti-knock effect (Octane Index) provided by indoline in modern engines (i.e. with negative K values) is much higher than that provided by NMA.

Example 4: Effect of the addition of indoline, NMA and NMPA in the lubricity of the gasoline composition.

[0120] The gasoline base fuel used in the test was an EN-228 automotive gasoline, Premium type E5 (less than 2.7% oxygen content) and RON higher than 98. This gasoline includes 900 ml/m^3 of Repsol multifunctional additive package CTR-BP-6-2827 that includes several components, such as: detergent or dispersant, marker, dyer, demulsifier and anticorrosion additive.

[0121] The antiknock compounds evaluated in this example were indoline (minimum 99%), N-methyl-aniline (NMA, minimum 98%) and N-methyl-p-anisidine (NMPA, 95% minimum purity). These compounds were added to the gasoline at the indicated amount in closed flasks in order to prevent the loss of volatile compounds, and magnetic mechanical stirring was applied at room temperature until total dissolution was observed.

[0122] Lubricity of gasoline blends was determined by using a standard modification of HFRR (High Frequency Reciprocating Rig) method described in ISO-12156-1. Ball and disc specimens, load applied (200 g), stroke frequency (50 Hz) and length (1 mm) of friction movement were the same. Tools for gasoline were adapted for a higher sample volume (15 mL instead of 2 mL) and avoided the loss of volatiles (closing cap). The temperature was also lowered to reduce evaporation of sample (25°C instead of 60°C). A PCS Instrument device with cabinet for temperature and humidity control was used. Average Wear Scar Diameter (WSD) of 2 testing runs is shown, in order to reduce the uncertainty of the method.

[0123] Table 5 details the lubricity results, at typical concentrations as anti-knock agents. Indoline reduces the wear scar diameter of friction test, which means a beneficial increase of the lubricity of the gasoline. This effect is considerably lower for other known aromatic amine anti-knock agents, such as NMA and NMPA. Higher lubricity of gasolines has been disclosed to reduce friction and wear issues and to reduce fuel consumption.

Table 5. Effect of octane boosters on lubricity in HFRR (25°C)

Octane booster	% v/v octane booster	Average WSD, microns	WSD effect
Base fuel	0.0	473	-
Indoline	0.5	420	-53.0
	0.7	413	-60.0
	1.0	426	-47.0
NMA	0.5	488	14.5
	1.0	447	-26.0
NMPA	0.5	488	15.0

Example 5: **Compatibility of polyethylene (PE) with indoline and NMA.**

[0124] The antiknock compounds evaluated in this example were indoline (minimum 99%), and N-methyl-aniline (NMA, minimum 98%). Polyethylene (PE) compatibility is very important to handle this type of products at low scale level, for example to be used for on line additivation on petrol dispenser at the service station.

[0125] Two different types of PE were chosen, which are representative of the materials that have demonstrated to fit the purpose: high density polyethylene (HDPE Repsol reference Alcudia® 45060UV) and low density one (LLDPE Repsol reference Resistex® 1810F). Samples of 3x26x19 mm (10% tolerance) are used.

[0126] PE probes were soaked in antiknock compounds (25 mL) during 5 days at 40°C, representing the most critical situation when they are used at service station. Change in volume, hardness and visual colour change were controlled.

[0127] As shown in Fig. 4, the PE elastomers showed higher compatibility after soaking in pure indoline at 40°C for 4 days, compared to NMA. This probes that indoline could be stored in PE containers at the gas station for its direct addition to the gasoline composition.

Example 6: Toxicity evaluation of indoline

[0128] Cytotoxicity, genotoxicity and skin sensitization caused by indoline were evaluated. Indoline (minimum 99%) was tested in all the cases.

[0129] *In vitro* cytotoxicity of indoline was measured by the MTT assay in the HepG2 cell line, by the procedure described at guidelines DB-ALM Protocol n° 17 (MTT Assay) and ISO 10993-5:2009 (test for *in vitro* cytotoxicity). The overall mean and inhibition concentration 50% (IC50) percentage of cell mortality was 1.455 mg/mL that is associated to a moderate-low toxicity, with an unspecific systemic toxicity of indoline low to moderate. This reinforces the low oral acute toxicity reported in ECHA (CPL category 4, H302).

[0130] Skin sensitization of indoline was determined by Local Lymph Node Assay (OECD TG 429) in female mice. Groups of animals were allocated and each one was treated, at dorsum of both ears, with negative control (acetone:olive oil 4:1), 50% indoline and positive control (dopped with 0.1% 1-chloro-2,4-dinitrobenzene). Stimulation Index was calculated for each treatment. Negative control, indoline and positive control gave values of 1.0, 2.4 and 5.8, respectively. Indoline can be considered as a negative skin-sensitizing agent as the stimulation index was below 3.0.

[0131] Mutagenety/genotoxicity of indoline was tested by Bacterial Reverse Mutation Test (OECD TG 471; Ames test). The ability of indoline to reverse mutations was assessed. Salmonella typhimurium strains (TA98, TA100, TA102, TA1535 and TA1537) were evaluated. Indoline was found to be non-mutagenic and non-promutagenic at concentrations of 1.58 microliters/plate and does not categorize according to CLP classification.

[0132] These complementary testing endorses the low toxicity of indoline, its high potential to be used safely in fuel service stations with standard preventive measurements and its handling advantage towards other anilines.

Example 7: Effect of the addition of a demulsifier to a gasoline composition comprising indoline

[0133] The gasoline base fuel used in the test was an EN-228 commercial automotive gasoline, type E5 (less than 2.7% oxygen content) and RON higher than 98. This gasoline includes standard additives of commercial gasoline, such as detergent, anticorrosion, marker, etc. Dehazer/demulsifier added to improve the performance of the sample was Nalco EC 7187 A. Additive blending procedure was performed with magnetic stirrer assistance and in closed flasks in order to prevent the loss of volatile compounds.

[0134] Indoline (99% minimum purity) was added to the above gasoline at 0.7% v/v using the above mentioned procedure.

[0135] Water reaction was evaluated following the standard ASTM D7451, including measurement of time for 75% of water separation as an indicator of stability of emulsion. The results obtained are shown in table 6.

[0136] Indoline is compatible with a proper demulsifier/dehazer that is able to accelerate the separation of the water, to reduce unresolved emulsion layer and to improve the rating of the interface.

Table 6. Compatibility with demulsifier/dehazer additive

Water reaction ASTM D7451	Gasoline EN-228 with 0.7% v/v indoline	
	NALCO EC 7187 dosage	
	0 mg/kg	2 mg/kg
Time for 15 mL water separation, seconds	173	27
Unresolved emulsion layer at 5 minutes	< 0.5	0.0
Aqueous layer at 5 minutes	20.0	20.0
Rating of fuel clarity	1	1
Rating of interfase condition	3	2
Rating of separation degree	2	2

Example 8: Effect of the addition of a detergent to a gasoline composition comprising indoline

[0137] The gasoline base fuel used in the test was an EN-228 commercial automotive gasoline, type E5 (less than 2.7% oxygen content) and RON higher than 98. This gasoline includes standard additives of commercial gasoline, such as demulsifier, anticorrosion, marker, etc. Detergent/dispersant added to improve the performance of the sample was Dorf Ketal SR 8208. Additive blending procedure was performed with magnetic stirrer assistance and in closed flasks in order to prevent the loss of volatile compounds.

[0138] Indoline (99% minimum purity) was added to the above gasoline at 0.7% v/v using the above mentioned procedure.

[0139] Detergency was tested at Falex Thermal Fouling Tester with an in-house procedure based on ASTM D3241. Aluminum tubes were used for testing. Tube temperature was 300°C and pressure was 59 bar. Single pass sample was tested at 21% pump rate without stirring of sample at reservoir. Pressure drop in DP specific metallic filter downstream the heated test tube was controlled along the test. Pressure drop higher than 25 mm Hg at the end of the test is associated to low detergency. If pressure drop does not reach 25 mm Hg along the test, the detergency could be summarized by TFD index (Fouling Tendency):

$$TFD = 25 / \text{Pressure drop (mm Hg)}$$

[0140] Table 7 details the results of the testing and figure 5 summarizes the effect of detergent/dispersant on Deposit Forming Tendency (TFD index).

Table 7. Compatibility with detergent/dispersant

Detergency in thermal fouling testing (300°C, 59 bar)	Gasoline EN-228 with 0.7% v/v indoline		
	Dorf Ketal SR8208 dosage		
	0 mg/kg	25 mg/kg	50 mg/kg
Assay time, minutes	Pressure drop, mm Hg		
0	0.0	0.0	0.0
10	0.3	0.1	0.1
20	0.5	0.1	0.1
40	1.2	0.3	0.3
60	2.3	0.4	0.4
80	3.9	0.7	0.5
100	5.6	1.0	0.6
120	7.9	1.2	0.7
140	10.1	1.3	0.9
148	11.0	1.4	0.9
150	11.2	1.5	0.9
160	12.3	1.6	0.9
180	14.4	2.1	1.0
200	16.9	2.5	1.1
210	18.1	2.8	1.2
220	19.2	3.1	1.3
240	21.7	4.0	1.5

[0141] This example demonstrates the compatibility of indoline with an appropriate detergent/dispersant, that is able to avoid the formation of deposits in conditions of high pressure and temperature and the performance could be confidently escalated to engine performance.

Claims

1. Gasoline fuel composition comprising:

(i) indoline, and

(ii) a gasoline base fuel comprising:

- 30-90 vol% of saturated hydrocarbons,
- 0-30 vol% of olefinic hydrocarbons,
- 10-60 vol% of aromatic hydrocarbons,
- 5-50 vol% of oxygenated hydrocarbons.

2. Gasoline fuel composition according to claim 1, comprising from 0.3% to 5% by volume of the fuel additive relative to the total volume of the gasoline fuel composition, preferably from 0.4 to 3.0 vol%, even more preferably from 0.5% to 1.2 vol%.

3. Gasoline fuel composition according to any one of claims 1 or 2, wherein the gasoline base fuel has a RON of 93 or more, preferably 95 or more, more preferably 98 or more, as determined according to ASTM D2699.

4. Gasoline fuel composition according to any one of claims 1 to 3, wherein the gasoline fuel composition has a RON of 96 or more, preferably 97 or more, more preferably 99 or more, as determined according to ASTM D2699.

5. Gasoline fuel composition according to any one of claims 1 to 4, wherein the gasoline fuel composition has a RON of 97 or more, preferably 99 or more and a sensitivity of 10 or more, preferably 11 or more.

6. Gasoline fuel composition according to any one of claims 1 to 5, which is free of Fischer-Tropsch derived naphtha.

7. Gasoline fuel composition according to any one of claims 1 to 6, which further comprises one or more additives selected from the group consisting of anti-oxidants, corrosion inhibitors, detergents or dipersants, dehazers, demulsifiers, metal deactivators, valve-seat recession protectant compounds, dyes, solvents, carrier fluids, friction modifiers, diluents and markers.

8. Gasoline fuel composition according to any one of claims 1 to 7, which further comprises a detergent and/or a demulsifier.

9. Gasoline fuel composition according to any one of claims 1 to 8, comprising:

(i) 0.4-3.0 vol% of indoline;
(ii) at least 97 vol% of a gasoline base fuel comprising:

- 30-90 vol% of saturated hydrocarbons,
- 0-30 vol% of olefinic hydrocarbons,
- 10-60 vol% of aromatic hydrocarbons,
- 5-50 vol% of oxygenated hydrocarbons; and

(iii) up to 2 wt% of one or more additives selected from the group consisting of anti-oxidants, corrosion inhibitors, detergents or dispersants, dehazers, demulsifiers, metal deactivators, valve-seat recession protectant compounds, dyes, solvents, carrier fluids, friction modifiers, diluents and markers.

10. Gasoline fuel composition according to any one of claims 1 to 9, wherein the gasoline base fuel comprises 40-90 vol% of saturated hydrocarbons, 2-30 vol% of olefinic hydrocarbons, 10-45 vol% of aromatic hydrocarbons and 5-40 vol% of oxygenated hydrocarbons, based on the volume of the gasoline base fuel.

11. Process for preparing a gasoline fuel composition as defined in any one of claims 1 to 9, comprising adding indoline to a gasoline base fuel comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

12. Use of indoline for improving the antiknock properties of a gasoline fuel composition comprising 30-90 vol% of saturated hydrocarbons, 0-30 vol% of olefinic hydrocarbons, 10-60 vol% of aromatic hydrocarbons and 5-50 vol% of oxygenated hydrocarbons.

13. Use according to claim 12, wherein the amount of indoline in the gasoline fuel composition is 0.4 to 3.0 vol% based on the total volume of the fuel composition.

14. Use according to any one of claims 12 or 13, wherein the gasoline fuel composition comprising indoline has a RON of 96 or more, preferably 97 or more, more preferably 99 or more, as determined according to ASTM D2699.

15. Use according to any one of claims 12 to 14, wherein the indoline increases the RON of the gasoline fuel composition without increasing the MON or increasing it by 1.0 units or less, preferably 0.5 units or less or even 0.2 units or less, compared to the same gasoline composition without indoline, wherein MON is determined according to ASTM D2700.

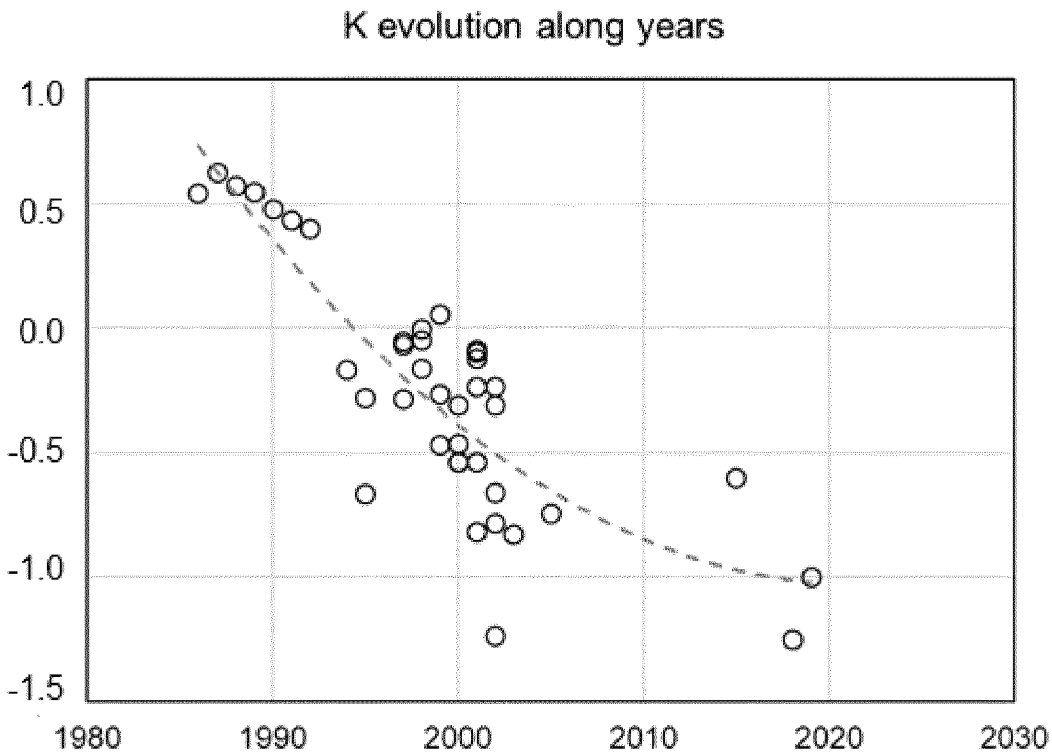

Figure 1

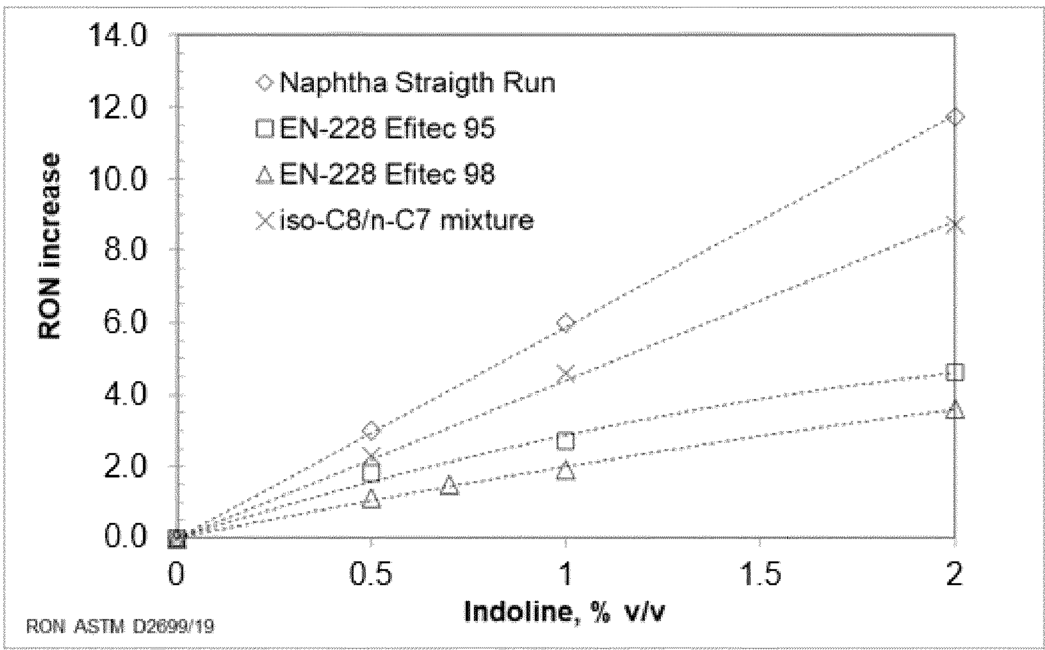

Figure 2A

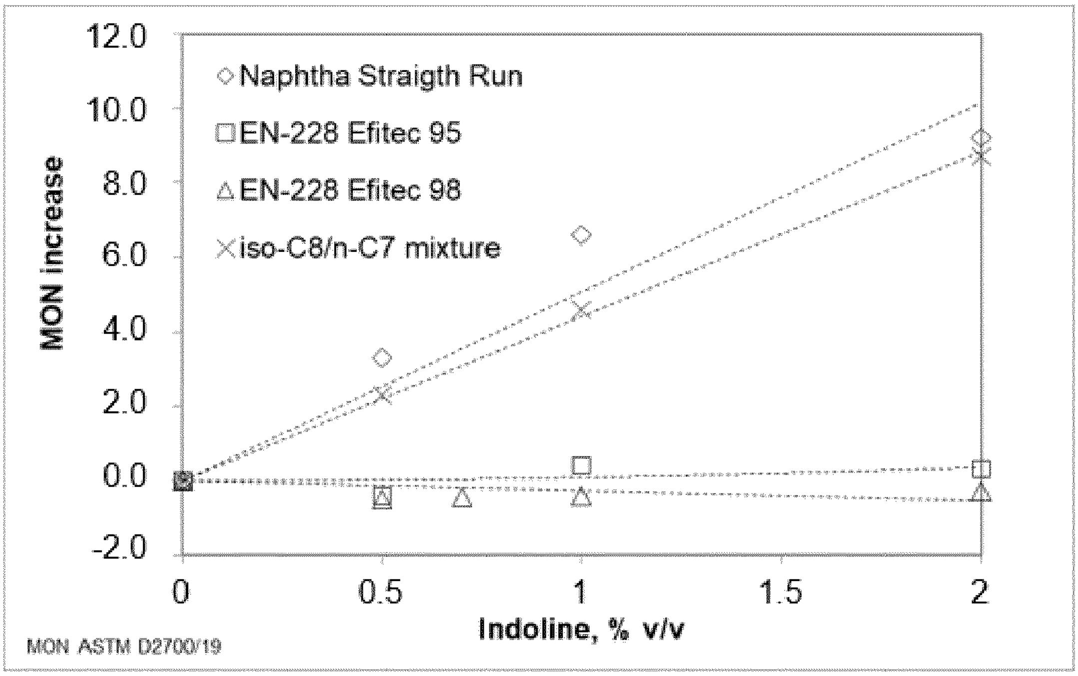

Figure 2B

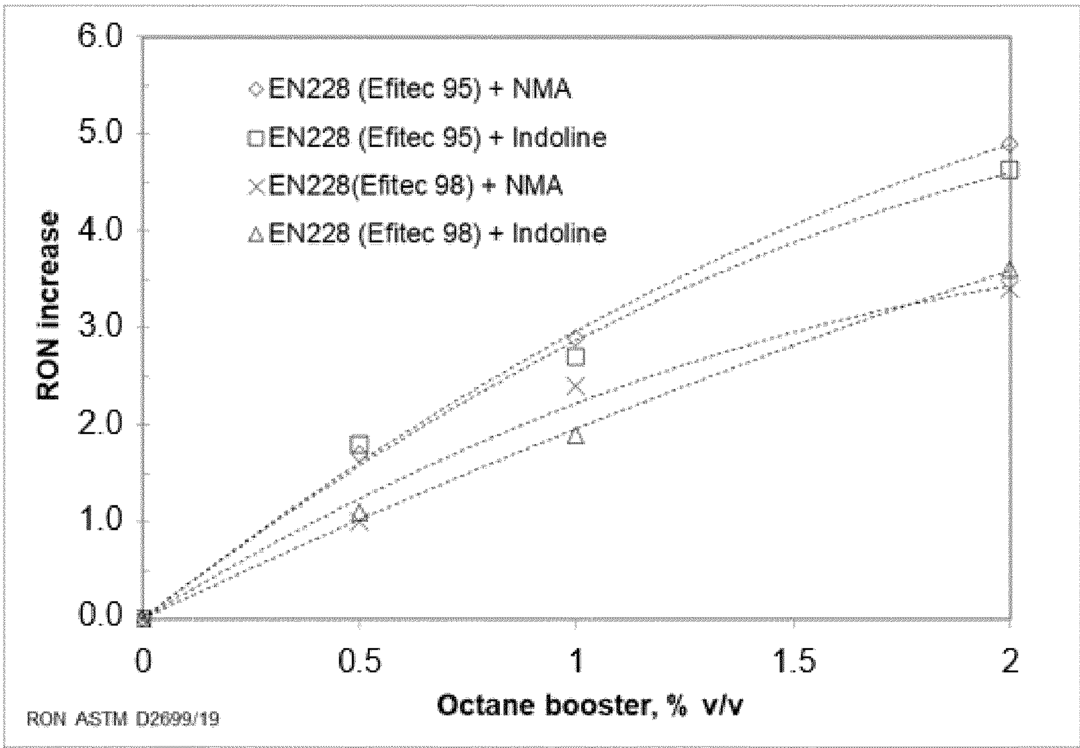

Figure 3A

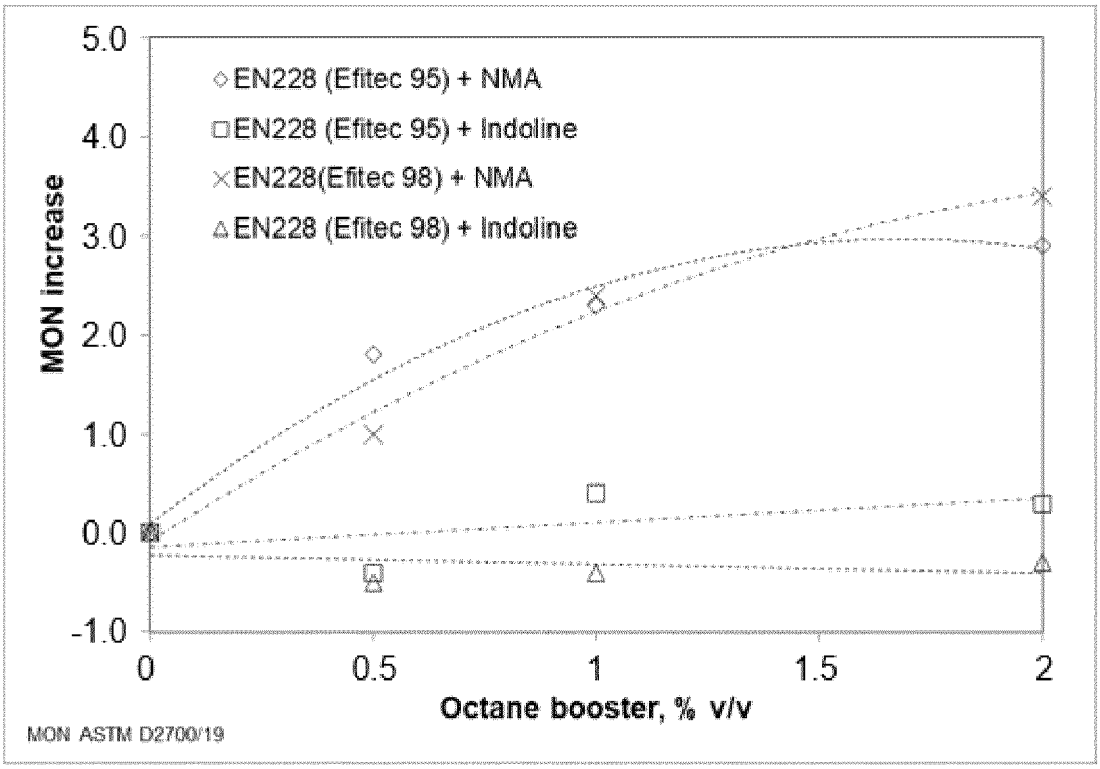

Figure 3B

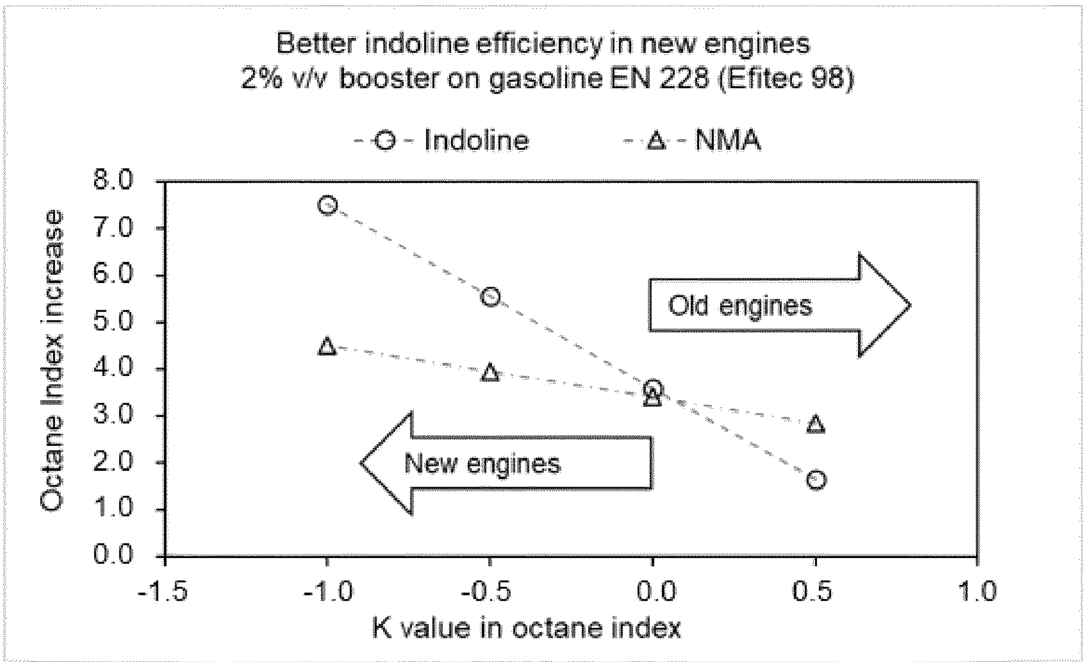

Figure 3C

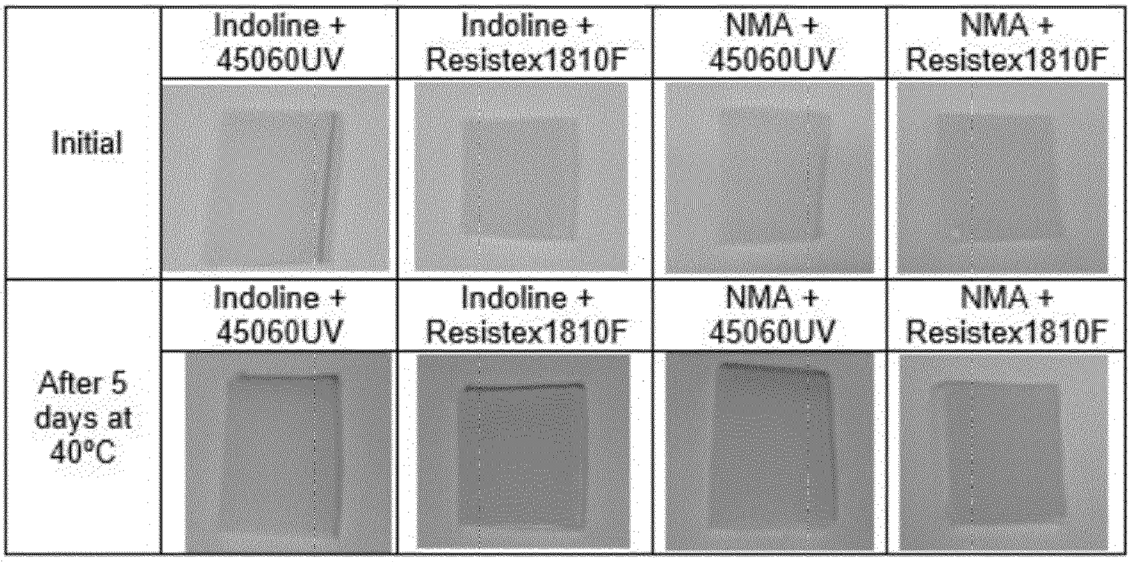

Figure 4

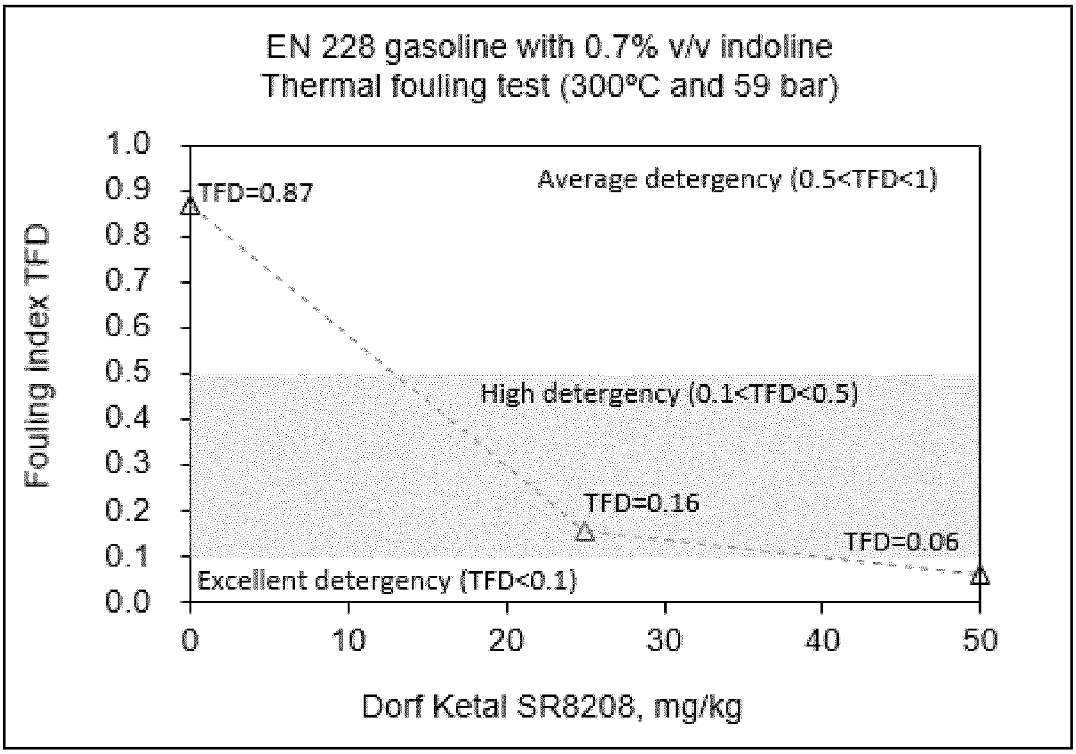

Figure 5

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EUROPEAN SEARCH REPORT

Application Number
EP 20 38 2663

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X,D	WO 2016/135036 A1 (SHELL INT RESEARCH [NL]; SHELL OIL CO [US]) 1 September 2016 (2016-09-01) * page 7, lines 14-17 * * page 21, lines 30-33 * * page 22, lines 1, 19-23 * * page 24, lines 3-5, 21-23 * * page 26, lines 16-22 * * page 27, lines 12-29 * -----	1-15	INV. C10L1/10 C10L1/02 C10L1/06
A	KUNO SCHÄDLICH1 ET AL: "Octane Enhancers", ULLMANN'S ENCYCLOPEDIA OF INDUSTRIAL CHEMISTRY, XX, XX, 1 January 2005 (2005-01-01), pages 1-15, XP007908552, DOI: 10.1002/14356007.A18 037 [retrieved on 2003-01-15] * page 5, column 1, lines 25-28; table 2 * -----	1-15	

TECHNICAL FIELDS SEARCHED (IPC)

C10L

The present search report has been drawn up for all claims

1

Place of search	Date of completion of the search	Examiner
The Hague	25 November 2020	Ruiz Martínez, C

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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25-11-2020

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For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

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