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(54) **Title**: UNLEADED GASOLINE FORMULATIONS FOR PISTON ENGINES

(57) **Abstract**: Disclosed herein are fuel formulations comprising C_4-C_{12} aliphatic hydrocarbons and cumidine. In embodiments, the formulations further include a limited amount of aromatic hydrocarbons. In other embodiments, the aliphatic hydrocarbons are alkylates, and in still other embodiment the alkylates are alkanes. These fuel formulations provide unique and advantageous physical properties suitable for piston engines.

UNLEADED GASOLINE FORMULATIONS FOR PISTON ENGINES

BACKGROUND OF THE INVENTION

Field of the Invention

The present invention relates to lead-free piston engine fuels comprising hydrocarbon components and cumidine blended together to produce unique piston-engine motor fuel formulations with a high motor octane number that offers excellent engine and operational performance for aviation purposes. These unique fuels have very low freeze points, low environmental toxicity, and a high degree of compatibility with materials used in aircraft fuel systems.

Description of the Prior Art

Aviation fuels are a product of blending many possible hydrocarbon components to very specific formulations to create a combustible fuel that is tailored for an aviation specific use. For example, turbine engines used on most commercial jets worldwide utilize jet fuels specifically designed for their combustion characteristics using hydrocarbons with longer-chain molecules with carbons typically ranging between C_8 to C_{16}. These fuels typically have a high flash point which makes them safe for handling in a wide range of commercial uses. Piston engines used in general aviation require fuels made from lighter hydrocarbons (typically ranging from C_4 to C_{10} carbon molecules) similar to gasolines used in automobiles, but with much higher octane requirements and somewhat lower vapor pressure requirements.

For many decades the combustion characteristics of avgas used by piston engine aircraft has required tetraethyl-lead as a key component to the fuel to achieve the highest levels of motor octane number – thereby helping to reduce the likelihood of engine knocking. In recent years, the combination of public health hazards and environmental regulations has triggered an effort across the global aviation industry to remove all lead compounds from avgas.

The alternatives for blending and producing a lead-free aviation gasoline which meets the performance requirements for all varieties of piston engine aircraft are complex even for those schooled in the art of aviation gasolines. Aviation fuels used in piston engine aircraft must meet all minimum performance criteria as defined by various fuel specifications managed by ASTM International and overseen by a cross-industry forum of experts. The fuel must also meet minimum fuel operating requirements as defined by Federal Aviation Administration (FAA) and other federal, state and local regulators. Specifically the avgas must meet the minimum motor octane number, the appropriate range for vapor pressure and all related matters impacting combustion, engine knock suppression, volatility, composition, fluidity, anti-corrosion, oxidation stability, environmental toxicology and material compatibility.

To enhance the motor octane rating of avgas for piston aircraft fuels have included high concentrations of aromatic hydrocarbons (particularly methylbenzene, dimethylbenzene or 1,3,5-trimethylbenzene), or have been blended with various aromatic amines (particularly aniline or meta-toluidine), oxygenates (e.g. MTBE, ETBE and Ethanol) and/or certain metals (particularly tetraethyl lead). This invention focuses on the use of base compounds using specific C_4 to C_{10} aliphatic hydrocarbons, preferably blended in the absence of aromatic hydrocarbons (e.g. toluene, xylene trimethylbenzenes), but with the addition of specific aromatic amines to achieve lead-free fuels that meet all the ASTM specifications for aviation gasoline, including freeze point, while achieving high motor octane numbers. The fuel is shown to be safe, low in toxicity and compatible with materials used in aircraft fuel systems and the related supply chain.

US Patent No. 5,470,358 describes a wide variety of aromatic amines (a total of 36 described in research) used in various concentrations to increase the motor octane number of unleaded aviation gasoline. The base compound however is an unleaded aviation fuel blend with a minimum 90-93 MON which contains up to 20% toluene to which are added aromatic amines in specified concentrations with claims ranging from 4 to 20% of the amine that results in a high octane avgas. This application fails to look at the toxicity impact of the fuels with these wide ranging aromatic amines, or the impact these compounds have on freeze point of the fuel using ASTM D2386, or the impact of the fuels on engine deposits, or the exaggerated impact these fuels have on aircraft material compatibility when combined in the presence of toluene, an aromatic hydrocarbon. These factors taken together make this invention impractical and commercially undesirable for aviation use.

US Patent Application No. 12/093,250 describes various lead-free aviation fuels with a minimum 100 MON based upon a blend combination of base alkylate with aromatic hydrocarbons found in the up to 30% reformate (shown as 35 – 70% toluene, plus xylenes and C_9's), plus any of a broad group of aromatic amines. This application fails to look at the toxicity impact of amines on the fuels, or the impact these wide ranging amine compounds have on freeze point of the fuel using ASTM D2386, or the exaggerated impact these fuels have on aircraft material compatibility when combining amines with aromatic hydrocarbons. These factors make this invention impractical and commercially undesirable for aviation use.

US Patent No. 8,628,594 B1 describes an unleaded fuel blended from a base aviation gasoline with a minimum 96 MON which contains various combinations of xylenes (notably meta-xylene) and 1,3,5-trimethylbenzenes of up to 40% or more, to which is added up to 6% of an aromatic amine (notably m-toluidine). This patent fails to address the fact that a) m-toluidine is a highly toxic compound not often handled in the US fuel supply chain, b) the use of m-toluidine causes the freeze point of the fuel (using ASTM method D2386) to rise above the -58°C required limit specified by ASTM D910 for aircraft fuel used at altitude, c) aromatic amines of any amount used in combination with aromatic hydrocarbons will exaggeratedly promote the destructive behavior on material used in aircraft fuel systems (e.g. gaskets, hoses, o-rings, etc), and d) the results of fuel tests in this research failed to utilize appropriate ASTM test methods to assure a minimum MON of 102 as reported by FAA requirements for any unleaded “drop-in” fuel to replace 100LL avgas. Furthermore, this invention uses non-standard terminology and methods like “FSEEMON” which is arbitrary and outside of acceptable ASTM and FAA industry norms for comparison of unleaded fuel test results. These factors make this invention impractical and commercially undesirable for aviation use.

US Patent No. 9,035,114 B1 describes an unleaded fuel with minimum 99.6 MON based upon the use of aniline in combination with 20% to 35% toluene plus some combinations of branched alkyl acetate compounds. This patent fails to address the fact that 1) aniline is a highly toxic compound not handled in the US fuel supply chain, b) the use of aniline causes the freeze point of the fuel (using ASTM method D2386) to rise well above the -58°C required limit by ASTM D910 for aircraft fuel used at altitude, and c) aromatic amines of any amount used in combination with aromatic hydrocarbons will exaggeratedly promote the destructive behavior on material used in aircraft fuel systems (e.g. gaskets, hoses, o-rings, etc). These factors make this invention impractical and commercially undesirable for aviation use.

Many other attempts have been made at devising a lead-free high-octane aviation gasoline starting from a hydrocarbon-based aviation fuel, some by combining lower boiling alkylates and aromatics up to 80% to increase the octane, as well as 5 – 15% of additional C_4-C_5 compounds to reduce the vapor pressure to aviation gasoline standards. See, for example, US Patent Nos. 8,741,126; 7,416,568; 8,324,437; 8,049,048; and 8,686,202.

SUMMARY OF THE INVENTION

In accordance with the present invention there are provided novel fuel formulations of certain aliphatic hydrocarbons blended with cumidine. In another aspect, the present invention provides for an improved fuel comprising isobutane, isopentane, isooctane, cumidine (4-isopropylaniline), and optionally other aliphatic compounds, and optionally other aromatics. These formulations provide an unexpectedly high octane, unleaded fuel suitable for off-road motor fuel and aviation gasoline and a wide variety of related products.

In one aspect, the fuels of the present invention are substantially free of benzene-based aromatic hydrocarbons having 6 or more carbon atoms. Despite years of industry testing using aromatic amines for fuels, the industry has not seen the fact that substantially excluding benzene-based aromatic hydrocarbons and selectively including only cumidine as a fuel component provides a unique and practical solution to the search for a viable, high-octane, lead-free aviation gasoline.

It is an object of the present invention to provide improved fuels having numerous advantageous properties, and which are useful as aviation fuel for many types of aircraft engines including high-performance engines and also legacy aircraft.

Another object of the invention is to provide formulations of the present invention having suitable boiling point characteristics, thereby favorably impacting fuel stability, cold starting features, etc.

A further object of the present invention is to provide fuel formulations having surprisingly high motor octane numbers (MON) and research octane numbers (RON).

Another object of the present invention is to provide an improved fuel that contains a minimal amount of lead compounds to achieve its optimal detonation suppression characteristics. For example, certain formulations of the present invention do not include the use of any tetraethyl lead, or any ethylene dibromide to scavenge for lead in the aircraft fuel system.

In still another aspect, the present invention provides for an improved fuel that meets or exceeds most or all of the requirements of ASTM D910, ASTM D7719, D7592 and/or ASTM D7547.

Additional embodiments of the invention, as well as features and advantages thereof, will be apparent from the descriptions herein.

DESCRIPTION OF THE PREFERRED EMBODIMENT

For the purposes of promoting an understanding of the principles of the invention, reference will now be made to certain embodiments and specific language will be used to describe the same. It will nevertheless be understood that no limitation of the scope of the invention is thereby intended, such alterations and further modifications, and such further applications of the principles of the invention as described herein, being contemplated as would normally occur to one skilled in the art to which the invention relates.

Motor fuels are used in a variety of systems. In the broadest sense, a motor fuel is one which is used in piston or turbine engines. The present invention is directed to fuels for piston engines useful in off-road ground vehicles and/or aircraft. Typically, ground vehicles can use relatively lower octane fuels, while aircraft require higher octane fuels. A basic determinant as to the choice of fuels is the octane rating of the fuel compared to the compression of the engine. For example, higher compression engines generally require higher octane fuels. This invention provides fuels suitable generally for piston engines. Certain embodiments are particularly applicable for use in aircraft engines.

The present invention provides unleaded, piston engine fuels preferably comprising a mixture of select aliphatic hydrocarbons blended with cumidine. The aliphatic hydrocarbons may include alkanes, alkenes, alkynes, cycloalkanes and alkadienes. In preferred embodiments, the aliphatic hydrocarbons comprise lower boiling C_4 to C_{10} alkanes, alkenes and cycloalkanes, but largely excluding arenes found in gasoline. The cumidine isomer used in the fuels is preferably 4-isopropylaniline. The resulting fuel formulations are characterized by an array of desirable properties making them suitable for piston engines.

In certain aspects, the fuels comprise an alkylate product consisting of a variety of hydrocarbons. In refining, the alkylation process transforms low molecular-weight alkenes and iso-paraffin molecules into a product referred to as an “alkylate”, which includes a mixture of high-octane, isoparaffins. This “alkylate” product may contain many hydrocarbon compounds typically in the C4 to C12 range.

“Aviation alkylate” is a premium gasoline blending stock having exceptional anti-knock properties and a final boiling point appropriate for aviation use. The octane number of an aviation alkylate depends mainly upon the kind of alkenes used and upon refinery operating conditions. For example, isooctane typically results from combining isobutylene with isobutane and has an octane rating of 100 by definition. There are other products in the alkylate, so the octane rating will vary accordingly.

As used herein, the term “alkylate” refers to the alkylate product available from a refinery, and also generally to any mixture including C4 to C12 non-aromatic hydrocarbons. These alkylates are useful in the formulations to address the problem of cold starts. Whether from the alkylate product of the refineries, or in more purified form, the inclusion of high volatility / low boiling point components contributes to achieving a desired Reid Vapor Pressure (RVP) range, while also allowing the engines to start in cold temperature situations (cold weather or high altitude).

In one aspect, the alkylate component comprises alkanes. In particular, it has been found that the C4-C10 alkanes, and more preferably branched alkanes, provide especially desirable properties for the inventive fuel formulations. Isobutane, isopentane and/ isooctane are particularly preferred in order to achieve a balance of desirable fuel properties. In one embodiment, the formulations comprise about 7 wt% to about 13 wt% C4-C5 branched chain alkanes by weight.

The formulations also include up to 20% cumidine, more preferably up to about 15 wt% cumidine. Cumidine refers to three isomeric liquid bases ($C_3H_7C_6H_4NH_2$) derived from cumene. It has been discovered that cumidine has unique properties for an aromatic amine related to high octane aviation gasoline. In the present invention, the isomer 4-isopropylaniline is preferably used.

The following Table 1 highlights a number of aromatic amines which might appear to be desirable as octane enhancing components to aviation gasoline (compared to baseline avgas). However, none of these amines are desirable for aviation gasoline, except cumidine. Only two components (4-isopropylaniline and N-ethylphenylamine) have freeze points that are low enough to be desirable for aviation gasoline when flying in high altitude. Also five of the amines have water solubility problems making them unacceptable for consideration as aviation gasoline due to concern for attracting water which can result in inflight freezing. Thirteen of the compounds are fluoro- or chloro- compounds that are not acceptable candidates for any commercial fuel use. Two compounds have final boiling points that exceed guidelines for all aviation gasolines. The only viable aromatic amine component that meets the critical technical criteria for aviation gasoline is 4-isopropylaniline (cumidine).

Table 1

Aromatic Amines	CAS	Freeze Point	Octane @ 6%*	Octane @ 9%*	Other	Boiling Point
phenylamine	62-53-3	-6°C	5.70	8.70		184°C
N-methylphenylamine	100-61-8	-57°C	2.10	2.60		196°C
2-methylphenylamine	95-53-4	-16°C	1.70	2.10		200°C
N-ethylphenylamine	108-69-5	-63.5°C	-2.50	-	Insoluable > 6%	205°C
3,5-dimethylphenylamine	108-69-0	9°C	5.70	8.70		220°C
3,4-dimethylphenylamine	95-64-7	50°C	5.60	-	Solid @RT	226°C
3-methylphenylamine	108-44-1	-31°C	5.40	7.40		203°C
3-ethylphenylamine	587-02-0	-8°C	3.80	6.60		212°C
4-methylphenylamine	106-49-0	45°C	6.10	-	solid@RT	200°C
4-ethylphenylamine	589-16-2	-5°C	3.80	6.30		217°C
4-isopropylaniline (Cumidine)	99-88-7	-63°C	4.40	7.20		227°C
4-t-butylphenylamine	769-92-6	15°C	4.20	6.60		235°C
2-fluorophenylamine	348-54-9	-29°C	4.20	7.30		182°C
3-fluorophenylamine	372-19-0	-2°C	4.20	6.70		186°C
4-fluorophenylamine	371-40-4	-2°C	4.20	7.50		187°C
2-chlorophenylamine	95-51-2	-3°C	4.50	5.60		209°C

3-chlorophenylamine	108-42-9	-10°C	3.60	-	Insoluable >6%	230°C
2-fluoro-4-metylphenylamine	452-80-2	3°C	4.00	5.10		206°C
2-fluoro-5-metylphenylamine	452-84-6		3.60	5.10		202°C
3-fluoro-2-metylphenylamine	443-86-7	7°C	1.30	2.70		188°C
4-fluoro-2-metylphenylamine	452-71-1	14°C	1.60	2.10		207°C
5-fluoro-2-metylphenylamine	367-29-3	37°C	1.60	2.10		235°C
2,3,4,5-tetrafluorophenylamine	5580-80-3	28°C	1.70	2.50	solid@RT	213°C
N-methyl-4-fluorophenylamine	459-59-6		2.50	2.60		181°
2-fluoro-4-methyl-phenylamine	452-80-2	3°C	4.00	5.10		222°C

Formulations

The fuel formulations of the present invention generally comprise about 80 to about 99 wt% C_4-C_{12} aliphatic hydrocarbons, about 1 to about 20 wt% cumidine, and less than about 5 wt% C_6-C_{12} aromatic hydrocarbons, and the formulations are substantially free of lead-containing constituents. In preferred embodiments, the formulations are substantially free of C_6-C_{12} aromatic hydrocarbons. In a further aspect, the fuel formulations consist essentially of about 80 to about 99 wt% C_4-C_{12} aliphatic hydrocarbons and about 1 to about 20 wt% cumidine. More particularly, the formulations preferably consist essentially of about 85 to about 95 wt% C_4-C_{12} aliphatic hydrocarbons and about 5 to about 15 wt% cumidine. The fuel formulations have a MON of at least about 100 and an RVP of 38 to 49 kPa at 37.8°C.

In another aspect, the piston engine fuel formulations of the present invention comprise about 80 to about 99 wt% C_4-C_{10} alkylates, about 1 to about 20 wt% cumidine, and less than about 5 wt% C_6-C_{12} aromatic hydrocarbons. More preferably, the fuel formulations comprise about 80 to about 99 wt% C_4-C_{10} alkanes, about 1 to about 20 wt% cumidine, and less than about 5 wt% C_6-C_{12} aromatic hydrocarbons.

In certain combinations, the fuel formulations comprise about 80 to about 99 wt%, more preferably about 85 to about 95 wt%, isobutane, isopentane and/or isooctane and about 1 to about 20 wt%, more preferably about 5 to about 15 wt%, cumidine. The cumidine preferably is 4-isopropylaniline. These formulations also are preferably substantially free of C_6-C_{12} aromatic hydrocarbons. In a further aspect, the fuel formulations consisting essentially of about 85 to about 95 wt% isobutane, isopentane and/or isooctane and about 5 to about 15 wt% 4-isopropylaniline. Said formulations also preferably comprise a MON of at least about 100 and an RVP of 38 to 49 kPa at 37.8°C.

Various specific fuel formulations have also been identified. One such formulation includes, and more preferably consists essentially of, about 2 wt% isobutane, about 10 wt% isopentane, about 73 wt% isooctane, and about 15 wt% 4-isopropylaniline, and has a MON of about 103.5. In yet another embodiment, the formulations comprise a blend of 30% low-boiling alkylate, 45% isooctane, 10% isopentane, 2% isobutane and 12.5% cumidine by weight have a MON of 102.5. These embodiments preferably are substantially free of aromatic hydrocarbons.

In another aspect of the invention, there is provided an unleaded, piston engine fuel formulation comprising a blend of isooctane, 4-isopropylaniline, isobutane, isopentane and at least one other component selected from the group consisting of alkylates or alkanes and having a MON of at least 94 and an RVP of 38 to 49 kPa at 37.8°C. In a related aspect, this formulation consists essentially of isooctane, 4-isopropylaniline, isobutane, isopentane and up to 5% by weight of at least one additive selected from the group consisting of octane boosters, antioxidants, co-solvents, toluene, xylene, electrical conductivity additives, corrosion inhibitors, metal deactivators, dyes, and any combinations and mixtures thereof. Specifically, the latter embodiments may comprise alkylates or alkanes, or a combination of alkylates and alkanes but excluding C7-C9 aromatic hydrocarbons.

In another aspect, the fuel formulations of the present invention contain the following ranges of components:

(Iso)butane: 0 – 2 wt%

Isopentane: 5 – 15 wt%

Isooctane/Alkylate:	60 – 75 wt%
Cumidine:	5 – 15 wt%
Other Aromatics:	0 – 5 wt%

In yet another aspect, the fuel formulations of the present invention contain the following ranges of components:

(Iso)butane:	0 – 2 wt%
Isopentane:	5 – 15 wt%
Isooctane/Alkylate:	60 – 75 wt%
Cumidine:	5 – 15 wt%
Other Aromatics:	0 – 5 wt%

Plus up to 250 ppm of ferrocene additives

These formulations are hereafter referred to as formula UL102AA, and its properties are compared with relevant ASTM standards for certain piston engine fuels.

In further embodiments, the fuel formulation comprises, or consists essentially of, about 2 wt% isobutane, about 10 wt% isopentane, about 73 wt% isooctane, and about 15 wt% 4-isopropylaniline, and having a MON of about 103.5. In other embodiments,the fuel formulation comprises, or consists essentially of, about 2 wt% isobutane, about 10 wt% isopentane, about 76 wt% isooctane, and about 12 wt% 4-isopropylaniline, and having a MON of about 102.

One basic goal of the inventive fuels lies in balancing the synergistic effects of a number of components and compounds to achieve, as closely as possible, the performance properties of the historic ASTM D910 fuel and/or other ASTM standards which may be applicable.

ASTM specification D910 is entitled "Standard Specification for Aviation Gasolines" and describes several characteristics that an aviation gasoline may meet, and is hereby incorporated by reference in its entirety. ASTM D910 also makes reference to documents, for example but not limited to other ASTM specifications, and these references are also hereby incorporated by reference.

The ASTM D910 specification describes many requirements, including the following. The distillation curve has specified vol% levels of the evaporation test

(10%, 40%, 50%, 90% and final boiling point) with minimum and/or maximum fuel temperature requirements such as 75°C, 105°C, 135°C, and 170°C. The distillation curve has a minimum recovery volume of 97%, a residue volume maximum of 1.5%, and a maximum loss of 1.5%. The fuel composition has a freezing point below -58°C and a net heat of combustion of at least 43.5 MJ/kg. The fuel composition has an appropriate density, a sulfur content less than 0.05%, and an oxidation stability of about 6 mg/100mL. The fuel composition exhibits corrosion of a copper strip for 2 hours at 100°C less than the value indicated in ASTM D910. The fuel composition exhibits a water reaction of less than +/- 2 volume changes in mL/100mL, and an electrical conductivity of less than 450 pS/m. The fuel composition exhibits a Reid Vapor Pressure (RVP) between 38 to 49 kPa at 38°C. The Motor Octane Number is a minimum of 99.6. The maximum content of tetraethyl lead (TEL) is 0.53 mL/L.

The following Table 2 compares UL102AA to ASTM D910 (Grade 100LL) as to all the fuel performance properties and related to temperature ASTM D6227 (Grade UL87).

UL102AA has a minimum MON that is 2.9 octane numbers higher than that specified for 100LL, as required to achieve or exceed equivalent knock resistance compared to a leaded fuel.

UL102AA has a net heat of combustion minimum of 43.5 MJ/kg, which is equivalent to the specified limit for 100LL. The fuel has a density of **700-720** kg/m^3, also equivalent to 100LL, which together results in no impact on aircraft weight or range.

The distillation curve for UL102AA varies from the curve for 100LL only at the final boiling point. While the maximum final boiling point allowable for UL102AA is currently higher than ASTM D910, it should be noted that other widely used and certified aviation gasoline specifications such as GOST 1012-72 and ASTM D6227 also support higher final boiling points than historically permitted by ASTM D910, as does the production specification ASTM D7719.

UL102AA is an unleaded fuel that allows for up to 0.013 gPb/L in case of accidental contamination between the refinery and the FBO, whereas 100LL is a leaded fuel that can contain up to 0.56 gPb/L. High-Octane UL102AA, being an unleaded fuel, will have zero lead precipitate.

UL102AA contains less than 20% (m/m) aromatics largely from a unique nitrogen-based aromatic amine; in fact the preferred formulation contains less than 15% cumidine. This is well within the norm of industry standards for aviation gasolines.

The freezing point for UL102AA, using the standard method ASTM D2386, is -58 °C maximum, which is identical to ASTM D910.

The electrical conductivity for UL102AA is 450 pS/m maximum, which is identical to ASTM D910.

Table 2

ASTM Test Method	ASTM Requirements	ASTM D910	High-Octane Unleaded 102AA
	Grade	100LL, Avgas	102AA
COMBUSTION			
D4809	Net Heat of Combustion, MJ/kg	43.5, min	43.5, min
	Octane Rating		
D2700	Knock value, lean mixture		
	Motor Octane Number	99.6, min	102.5, min
COMPOSITION			
D2622	Sulfur, mass %	0.05, max	0.005, max
D5059	Tetraethyl lead, mL		
	g Pb/L	0.56, max	0.013, max
VOLATILITY			
D5191	Vapor pressure, 38°C, kPa	38-49	38-49
D1298	Density at 15°C, kg/m^3	Report	Report
D86	Distillation		
	Initial Boiling Point, °C	Report	Report
	Fuel Evaporated		
	10, volume % at °C	75, max	75, max
	40, volume % at °C	75, min	75, min
	50, volume % at °C	105, max	105, max
	90, volume % at °C	135, max	135, max
	Final boiling point, °C	170, mix	225, max
	Sum of 10% + 50% evaporated temperatures, °C	135, min	135, max
	Recovery, volume %	97, min	97, min
	Residue, volume %	1.5, max	1.5, max
	Loss, volume %	1.5, max	1.5, max
FLUIDITY			
D2386	Freezing Point, °C	-58, max	-58, max
CORROSION			
D130	Corrosion, copper strip, 2 h @100°C	No. 1, max	No. 1, max
CONTAMINANTS			
D873	Oxidation, stability (5 h aging)		
	Potential gum, mg/100 mL	6, max	6, max
D1094	Water reaction		

	Volume change, mL	$\pm$2, max	+2, max
OTHER			
D2624	Electrical conductivity, 19.9°C, pS/m	450, max	450, max

The present invention has been developed to provide an unleaded aviation grade fuel for engine / aircraft types capable of operating as a drop-in replacement for ASTM D910 Grade 100LL leaded aviation gasoline (Avgas). The unleaded fuels of this invention meet the performance characteristics of the ASTM D910 standard, except for lead content and final boiling point. However, this property as outlined in D910 is not a critical operating factor, as other unleaded aviation gasolines have already been approved with such higher final boiling point limits. The fuel additionally offers benefits of 100% elimination of the use of tetraethyl lead while meeting the anti-knock characteristics of the high-performance piston engine aircraft. See Table 2.

ASTM specification D7719 describes a fuel specification for high octane aviation fuel, and is hereby incorporated by reference in its entirety. ASTM D7719 also makes reference to documents, for example but not limited to other ASTM specifications, and these references are hereby incorporated by reference in their entirety.

ASTM specification D7592 describes a fuel specification for unleaded aviation fuel. ASTM D7592 is hereby incorporated by reference in its entirety. ASTM D7592 also makes reference to documents, for example but not limited to other ASTM specifications and these references are hereby incorporated by reference in their entirety.

ASTM specification D7547 describes a fuel specification for unleaded aviation fuel. ASTM D7547 is hereby incorporated by reference in its entirety. ASTM D7547 also makes reference to documents, for example but not limited to other ASTM specifications and these references are hereby incorporated by reference in their entirety.

MON and Anti-Knock

Motor fuel must meet the power demands for the selected engines. The motor octane number, or MON, is a standard measure of the performance of a fuel. A gasoline-fueled reciprocating engine requires fuel of sufficient octane rating to prevent uncontrolled combustion known as engine knocking ("knock" or "ping"). The higher the MON, the more compression the fuel can withstand before detonating. In broad terms, fuels with a higher motor octane rating are most useful in high-compression engines that generally have higher performance. The MON is a measure of how the fuel behaves when under load (stress). ASTM test method 2700 describes MON testing using a test engine with a preheated fuel mixture, 900 rpm engine speed, and variable ignition timing to stress the fuel's knock resistance. The MON of an aviation gasoline fuel can be used as a guide to the amount of knock-limiting power that may be obtained in a full-scale engine under take-off, climb and cruise conditions.

A particular aspect of the present invention is to provide formulations which are useful as piston engine fuels, and are particularly suited for use as aviation gasoline. Aviation gas, or avgas, has a number of special requirements as compared to ground vehicle gasoline. Aviation gasoline is an aviation fuel used in spark-ignited (reciprocating) piston engines to propel aircraft. Avgas is distinguished from mogas (motor gasoline), which is the everyday gasoline used in motor vehicles and some light aircraft. It has been determined that 4-isopropylaniline has a uniquely positive impact on motor octane number – and thereby engine knock resistance.

Various MON ratings are considered to be base requirements for aircraft use, depending on the type of engine and other factors. The present invention provides aviation fuels which have a MON of at least 100, preferably 102 or greater. A second consideration can be the research octane number (RON), which is determined similarly to MON but under lower engine load or reduced stress (i.e., lower RPM, lower temperature, fixed ignition). The fuels of the present invention meet MON and RON requirements.

RVP

The vapor pressure of a fuel is another important factor for avgas. Aircraft engines operate in wide ranges of temperatures and atmospheric pressures (e.g., altitudes), and the fuels must start and provide sufficient combustion characteristics throughout those ranges. Lower vapor pressure levels are desirable in avoiding vapor lock during summer heat and/or high altitude flying, and higher levels of vaporization are desirable for winter starting and operation. Fuel cannot be pumped when there is vapor in the fuel line (summer) and winter starting ("cold start') will be more difficult when liquid gasoline in the combustion chambers has not vaporized. Vapor pressure is critically important for aviation gasolines, affecting starting, warm-up, and tendency to vapor lock with high operating temperatures or high altitudes.

The ability of an aviation gas to satisfy the foregoing requirements may be assessed based on the Reid Vapor Pressure (RVP). The Reid Vapor Pressure is the absolute vapor pressure exerted by a liquid at 37.8 °C (100 °F) as determined by the test method ASTM-D5191. The RVP differs from the true vapor pressure due at least in part to the presence of water vapor and air in the confined space. A typical requirement for avgas is that it has an RVP of 38-49 kilopascals (kPa) at 37.8°C, as determined in accordance with applicable ASTM standards. The formulations of the present invention meet RVP requirements for aviation gas.

Combustion Performance

The fuels of the present invention have suitable combustion performance. The present invention provides fuels having a net heat of combustion by mass of 43.5 MJ/kg, which is equivalent to 100LL. The density of the fuel is equivalent to 100LL; therefore, the weight and range of the aircraft will be identical to that of 100LL.

Cold Start

Preliminary testing of the fuels of this invention conducted in an engine test cell indicated that the fuel achieved cold start at -20°C, and the preliminary engine performance results were "positive".

Fluidity

Fluidity is a critical operating parameter for flight safety. Avgas must not freeze at cold temperatures typical of high altitude operations. All industry standards for avgas call for fuel to remain in a liquid state down to -58°C according to the ASTM freeze point test method D2386. Many aromatic amines have freeze points much higher than -58°C (e.g. aniline freezes is -6°C) which tends to add complexity for these compounds to be useful components for blending into avgas formulations. Cumidine has a freeze point of -63°C making it a unique and ideal blending component for avgas (e.g., m-toluidine is -33°C and aniline is -6°C). This allows the blended fuels of the present invention to adhere to rigorous ASTM fuel requirements with a freeze point at -58°C.

The fluidity of fuel is consistent with 100LL, with a freezing point maximum of -58°C. None of the components of the inventive fuels (including cumidine) have a freeze point above -60°C, which allows the fuel to meet the rigorous requirement necessary to ensure flow in a liquid state during high-altitude / low temperature operations.

Volatility

Volatility of the fuels of this invention is another critical operating parameter for reliability and flight safety. The fuels meet the traditional aviation gasoline standard of 38 – 49 kPa, particularly with the presence of isopentane and not more than 2% isobutane. Tests reveal that fuels with isobutane concentrations higher than 3% will exceed the maximum vapor pressure limit and experience loss >1.5%. Fuels that are too volatile can experience vapor lock causing problems in normal operations, or causing the engine not to start on the ground, or not restarting in an emergency situation at altitude.

Insolubility

Avgas must also be highly insoluble in water. Water dissolved in aviation fuels can cause serious problems, particularly at altitude. As the temperature lowers, the dissolved water becomes free water. This then poses a problem if ice crystals form, clogging filters and other small orifices, which can result in engine failure. The present fuels are insoluble in water.

Material Compatibility

Avgas must function in the engine and fuel system without reacting unfavorably to the materials in these systems. Fuels typically result in seal swell, a favorable trait for reducing leaks. However, aromatic amines can have destructive tendencies. This invention discovered the unique requirement to reduce or eliminate the use of aromatic hydrocarbons with aromatic amines – thereby eliminating the tendency to promote destructive behaviors to such materials.

Previous tests using base alkylates with aromatics in combination with aromatic amines caused an exaggerated and destructive reaction to material compatibility results impacting fuel system components and had generally high toxicity creating environmental challenges in the fuel supply chain.

Many others have tried unsuccessfully to produce fuels with aromatic amines. However, components such as aniline and m-toluidine tend to be highly corrosive and/or destructive to fuel systems due in some part to their molecular size and polarity. They overly exaggerate seal swell and reduce tensile strength in buna / vinyl rubber and neoprene fuel systems when mixed with toluene.

Oxidation Stability

The fuels of this invention meet the strict oxidation stability requirements of the aviation fuel specification with a very low potential for insoluble gums (maximum 2 mg/100ml, using ASTM method D873) but without the risk of lead precipitate, as it is an unleaded fuel.

Corrosion

The corrosion testing done shows that the fuels of this invention meet the strict D910 standard for accelerated soak testing of a copper strip. Corrosion inhibitors that conform to the latest issue of D910, D7592 or D7547 may be added to the fuel in amounts not exceeding the maximum allowable concentrations listed.

Pre-Combustion and Post Combustion Properties

It is not uncommon in aviation that fuel can be inadvertently spilled in close proximity to persons when maintaining or refueling the aircraft. The fuel is a flammable hydrocarbon-based liquid, with the addition of cumidine as an octane enhancer. It evaporates quickly. As with all fuels containing aromatic amines, as the fuel evaporates, the amine evaporates more slowly. Care should be taken to avoid contacting this concentrated amine with skin. In consideration of the environmental toxicology of the fuel, cumidine was chosen for the fuel, rather than aniline, m-toluidine or other aromatic amines, due in part to its overall lower toxicity.

The fuels, according to test results, has slightly less smoke than 100LL (using ASTM D1322 - smoke point test), albeit with less-toxic emissions due to the absence of lead and its scavengers (e.g. diethylene bromide).

The base fuel has pre- and post-combustion occupational exposure limits similar to those of automotive gasoline, which typically range from 25ppm – 300ppm [TWA: 8 hours OSHA]. The TWA for cumidine is estimated to be 2 ppm. Cumidine is not classified as a mutagen or carcinogen. It is 88% biodegradable within 10 days, has an LD_{50} (rat, oral) of 757 mg/kg, is readily eliminated from water, and is not expected to bioaccumulate. See *4-Isopropylaniline*; MSDS No. 818472 [Online]; EMD Millipore: Billerica, MA, August 22, 2013, http://www.emdmillipore.com.

Toxicity

Aromatic amines tend to be highly toxic (e.g. aniline is defined by Merck Index as “poisonous” and by OSHA as an irritant). The fuel compositions of the present invention contain cumidine, which is a low toxicity aromatic. Below in Table 3 is a brief recap of the overall toxicity of many candidate fuel components.

Table 3

Component	LD_{50} (rat, oral)	OSHA Hazards
Mesitylene	5,000 mg/kg	Irritant
ETBE	5,000 mg/kg	Irritant
Toluene	5,000 mg/kg	Irritant, Teratogen, Reproductive hazard
Benzene	2,990 mg/kg	Carcinogen, Mutagen, Irritant

Cumidine	757 mg/kg	Irritant. Causes respiratory tract irritation. Causes eye and skin irritation. Can form methemoglobin, may cause cyanosis. May cause central nervous system depression.
m-Toluidine	450 mg/kg	Toxic. Causes cyanosis. Harmful or fatal if inhaled, swallowed, or absorbed through skin. May be irritating to skin, eyes and mucous membranes. Target organs: Bladder; kidneys; blood; liver.
Aniline	250 mg/kg	Carcinogen, toxic if swallowed, toxic in contact with skin, causes skin irritation, causes serious eye damage, fatal if inhaled, suspected of causing genetic defects.
Dibromoethane	55 mg/kg	Carcinogen, toxic by inhalation, toxic by skin absorption.
TEL	14 mg/kg	Carcinogen, toxic by inhalation, highly toxic by ingestion, highly toxic by skin absorption, teratogen.

Source: MSDS data from Sigma-Aldrich, et al.

Table 3 highlights the relative acute toxicity based on public data using LD_{50} as an internationally accepted baseline. In addition, chronic effects from long term exposure and other effects like carcinogenicity, mutagenicity, and teratogenicity have to be considered for the objective evaluation of the fuel.

Another key factor is the relative concentration of potentially toxic components in a particular fuel formulation, e.g., certain aromatic amines may require 60 to 250 times the concentration level in a high-octane unleaded aviation fuel vs.

TEL found in 100LL. See Albuzat, T., *Understanding the Merits of 1,3,5-Trimethylbenzene*. CRC Aviation Meetings, April 28, 2014, p. 6.

In summary, the present invention provides fuel formulations which are capable of meeting all of these strict requirements. They meet the MON standards, have suitable RVP, have low freeze points, acceptable material compatibility and are not soluble in water. The fuels of this invention further demonstrated the following results compared to 100LL. Cold Start: Both fuels started below -20°C. Exhaust Gas Temp (EGT): the fuel ran on average 16-32°C hotter than 100LL. Cylinder Head Temp (CHT): the fuel ran on average 8-15°C hotter than 100LL. Fuel consumption: ran equivalently for both fuels. *This test experienced occasional misfires on 100LL, which reduced the EGT and CHT of 100LL, which explains the minor discrepancies.*

In a preferred embodiment, the formulations of the present invention meet the specifications set forth in ASTM D7719 for a high aromatic, unleaded hydrocarbon based aviation fuel.

These fuels may optionally include other components or additives, particularly to modify or enhance characteristics such as octane rating, vapor pressure, viscosity, anti-icing, anti-static, oxidation stability, anti-corrosion, boiling point, engine cold start, exhaust smoke and engine deposits.

Oxidation Inhibitors

Oxidation inhibitors may be added to the fuel separately, or in combination, in total concentration not to exceed 12 mg of inhibitor (not including weight of solvent) per liter of fuel, such as:

(1) 2,6-ditertiary butyl-4-methylphenol.

(2) 2,4-dimethyl-6-tertiary butylphenol.

(3) 2,6-ditertiary butylphenol.

(4) 75 % minimum 2,6-ditertiary butylphenol plus 25 % maximum mixed tertiary and tritertiary butylphenols.

(5) 75 % minimum di- and tri-isopropyl phenols plus 25 % maximum di- and tri-tertiary butylphenols.

(6) 72 % minimum 2,4-dimethyl-6-tertiary butylphenol plus 28 % maximum

monomethyl and dimethyl tertiary butylphenols.

(7) N,N'-di-isopropyl-para-phenylenediamine.

(8) N,N'-di-secondary-butyl-para-phenylenediamine.

Icing Inhibitors

Fuel system icing inhibitors may also be used, e.g.:

(1) Isopropyl Alcohol (IPA, propan-2-ol), in accordance with the requirements of Specification D4171 (Type II). Fuel system icing inhibitors may also be used in concentrations recommended by the aircraft manufacturer when required by the aircraft owner/operator.

(2) Di-Ethylene Glycol Monomethyl Ether (Di-EGME), conforming to the requirements of Specification D4171 (Type III). May be used in concentrations of 0.10 to 0.15 volume % when required by the aircraft owner/operator.

Octane Boosters

A variety of fuel additives have been known and used in the art to increase octane ratings, and thereby reduce knocking. Typical "octane booster" gasoline additives include methyl *tert*-butyl ether (MTBE) and ethyl *tert*-butyl ether (ETBE), both of which are known as oxygenates which are compounds that contain oxygen as part of their chemical structure. Oxygenates help gasoline burn more completely, reducing tailpipe emissions.

Some embodiments of the present invention may utilize non-leaded combustion enhancing additives individually or in combination with up to 6% by weight, such as esters, ethers, carbonates, C5-C7 cycloalkanes, or the use of triptane and other known octane boosters.

The inventive fuels may "comprise" the described formulations, in which other components may be included. However, in a preferred embodiment, the inventive fuels "consist of" the described formulations, in which no other components are present. In addition, the inventive fuels may "consist essentially of" the formulations, in which case other fuel excipients may be included. As used herein, the term "fuel excipients" refers to materials which afford improved performance when used with fuels, but which do not directly participate in the combustion reactions. Fuel excipients thus may include, for example, antioxidants, etc.

Blends

The formulations are also useful for combining with other fuel components to form blends that are useful as motor fuels, including as aviation gasoline. As used herein, the term “fuel components” refers to materials which are themselves combustible and have varying motor octane ratings and are included primarily to provide improved combustion characteristics of the blend. In preferred embodiments, such fuel components are present in the blend at less than 5 wt%, and more preferably less than 1 wt%.

Blending of the formulations described herein can be performed in any suitable order. The examples and exemplary language provided herein are intended to better illuminate the invention and do not pose a limitation on the scope of the invention unless otherwise claimed. No language in the specification should be construed as indicating any non-claimed element as essential to the practice of the invention.

Lead

Most grades of avgas have historically contained tetraethyl lead (TEL), a toxic substance used to prevent engine knocking (detonation). This invention produces an unleaded grade of avgas with fuel properties that meet minimum power rating (motor octane number), appropriate combustion anti-knocking (detonation suppression), volatility (vapor pressure), and related criteria. The inventive fuels allow a range of piston engine aircraft, including those with high-compression engines, to perform effectively to manufacturer requirements. It is necessary that avgas provide sufficient power under varying conditions, including take-off and climb as well as at cruise.

Tetraethyl lead, abbreviated TEL, is an organolead compound with the formula $(CH_3CH_2)_4Pb$. It has been mixed with gasoline since the 1920’s as an inexpensive octane booster which allowed engine compression to be raised substantially, which in turn increased vehicle performance and fuel economy. Over the years, certain of these leaded fuel grades have been referred to as low lead, or “LL”. One advantage of TEL is the very low concentration needed. Other anti-knock agents must be used in greater amounts than TEL, often reducing the energy content of the gasoline. However, TEL has been in the process of being phased out since the mid-1970s because of its neurotoxicity and its damaging effect on catalytic converters. Most grades of avgas have historically contained TEL.

This invention advantageously produces an unleaded grade of avgas which allows a range of piston engines, including high-compression engines, to perform effectively. Therefore, in a preferred embodiment the inventive formulations and blends are unleaded, i.e., free of TEL. This is made possible, at least in part, by the presence of the cumidine, which provides sufficiently high MON performance and anti-knocking characteristics under stress to offset the absence of TEL in the aviation gasoline. It is an object of the present invention to provide avgas formulations that do not require deleterious octane boosters, and which meet or exceed requirements for aviation gasoline.

The fuel formulations may also include a limited amount of aromatic hydrocarbons, e.g., toluene, xylene, trimethylbenzenes, etc. These compounds are frequently found in minor amounts in product streams useful for the present formulations. Moreover, in preparing fuels it is not economical to use analytical grade or reagent grade chemicals, or even technical grade chemicals, as the presence of other fuel-compatible components is not a concern, provided the resulting fuel formulation meets ASTM and other applicable standards. Thus, the present invention contemplates the presence of such other fuel-compatible components in limited amounts, e.g., less than 5 wt%, preferably less than 2 wt%, and more preferably less than 1 wt%.

Fuel components typically are not chemically pure, but instead may contain of other, non-deleterious fuel components. The term “non-deleterious fuel components” refers to components which are present in a formulation other than as an intended component. Thus, selected additives such as mentioned above are not encompassed by this term. Instead, it refers more particularly to the fact that materials used in commercial embodiments of piston engine fuels may include constituents, e.g., hydrocarbons, which are present as contaminants to the components of primary interest. For example, an alkylate stream from a refinery may be primarily composed of desired isobutane, isopentane and/or isooctane, but may contain limited amounts of other hydrocarbons such as aromatic hydrocarbons. As used herein, the term “substantially free of” refers to the fact that the amount of such non-deleterious fuel components is less than about 5 wt%, preferably less than 2 wt% and more preferably less than 0.5 wt%, of the weight of the overall fuel formulation.

In another aspect, it has been determined that the presence of C6-12 aromatic hydrocarbons (e.g., toluene, xylenes or mesitylene) with the cumidine can result in material compatibility results that exaggerate seal swell and demonstrate signs of material erosion. It is therefore advantageous in certain embodiments of the present invention that the fuel formulations are substantially free of C6-12 aromatic hydrocarbons.

All component percentages expressed herein refer to percentages by weight of the formulation, unless indicated otherwise. Given the similarity of the densities of the components of the present invention, it will be appreciated that the use of volume or weight percents of the components in the ranges indicated provide comparable results.

The uses of the terms "a" and "an" and "the" and similar references in the context of describing the invention (especially in the context of the following claims) are to be construed to cover both the singular and the plural, unless otherwise indicated herein or clearly contradicted by context. Recitation of ranges of values herein are merely intended to serve as a shorthand method of referring individually to each separate value falling within the range, unless otherwise indicated herein, and each separate value is incorporated into the specification as if it were individually recited herein.

While the invention has been illustrated and described in the foregoing description, the same is to be considered as illustrative and not restrictive in character, it being understood that only certain preferred embodiments have been described and that all changes and modifications that come within the spirit of the invention are desired to be protected. In addition, all references cited herein are indicative of the level of skill in the art and are hereby incorporated by reference in their entirety.

Claims

1. A piston engine fuel formulation comprising:

about 80 to about 99 wt% C_4-C_{12} aliphatic hydrocarbons;

about 1 to about 20 wt% cumidine; and

less than about 5 wt% C_6-C_{12} aromatic hydrocarbons,

said fuel formulation being substantially free of lead-containing constituents.

2. The fuel formulation of claim 1 being substantially free of C_6-C_{12} aromatic hydrocarbons.

3. The fuel formulation of claim 1 consisting essentially of:

about 80 to about 99 wt% C_4-C_{12} aliphatic hydrocarbons; and

about 1 to about 20 wt% cumidine.

4. The fuel formulation of claim 1 consisting essentially of:

about 85 to about 95 wt% C_4-C_{12} aliphatic hydrocarbons; and

about 5 to about 15 wt% cumidine.

5. The fuel formulation of claim 1 comprising a MON of at least about 100 and an RVP of 38 to 49 kPa at 37.8°C.

6. The piston engine fuel formulation of claim 1 comprising:

about 80 to about 99 wt% C_4-C_{10} alkylates;

about 1 to about 20 wt% cumidine; and

less than about 5 wt% C_6-C_{12} aromatic hydrocarbons.

7. The piston engine fuel formulation of claim 1 comprising:

about 80 to about 99 wt% C_4-C_{10} alkanes;

about 1 to about 20 wt% cumidine; and

less than about 5 wt% C_6-C_{12} aromatic hydrocarbons.

8. The fuel formulation of claim 7 comprising:

about 80 to about 99 wt% isobutane, isopentane and/or isooctane and about 1 to about 20 wt% cumidine.

9. The fuel formulation of claim 8 in which said cumidine is 4-isopropylaniline.

10. The fuel formulation of claim 9 comprising about 85 to about 95 wt% of isobutane, isopentane and/or isooctane and about 5 to about 15 wt% 4-isopropylaniline.

11. The fuel formulation of claim 10 being substantially free of C_6-C_{12} aromatic hydrocarbons.

12. The fuel formulation of claim 10 consisting essentially of about 85 to about 95 wt% isobutane, isopentane and/or isooctane and about 5 to about 15 wt% 4-isopropylaniline.

13. The fuel formulation of claim 12 comprising a MON of at least about 100 and an RVP of 38 to 49 kPa at 37.8°C.

14. The fuel formulation of claim 13 comprising about 2 wt% isobutane, about 10 wt% isopentane, about 73 wt% isooctane, and about 15 wt% 4-isopropylaniline, and having a MON of about 103.5.

15. The fuel formulation of claim 14 consisting essentially of about 2 wt% isobutane, about 10 wt% isopentane, about 73 wt% isooctane, and about 15 wt% 4-isopropylaniline, and having a MON of about 103.5.

16. The fuel formulation of claim 13 comprising about 2 wt% isobutane, about 10 wt% isopentane, about 76 wt% isooctane, and about 12 wt% 4-isopropylaniline, and having a MON of about 102.

17. The fuel formulation of claim 14 consisting essentially of about 2 wt% isobutane, about 10 wt% isopentane, about 76 wt% isooctane, and about 12 wt% 4-isopropylaniline, and having a MON of about 102.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/US2015/040256

A. CLASSIFICATION OF SUBJECT MATTER

C10L 1/04(2006.01)i, C10L 10/00(2006.01)i

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C10L 1/04; C10L 1/02; C10L 1/22; C10L 1/06; C10L 1/18; C10L 10/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched
Korean utility models and applications for utility models
Japanese utility models and applications for utility models

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
eKOMPASS(KIPO internal) & Keywords: piston engine fuel, aliphatic hydrocarbons, cumidine, aromatic hydrocarbons, C4-C10 alkylates, C4-C10 alkanes

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 7462207 B2 (CLARK, A. Q.) 09 December 2008 See column 43, lines 38 - 56, column 69, lines 27 - 38 and claims 1, 2.	1-17
Y	US 2413262 A (STIRTON, R. I.) 24 December 1946 See column 3, lines 20 - 40, column 6, lines 1 - 6 and claim 1.	1-17
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A	US 6238446 B1 (HENDERSON, D. H.) 29 May 2001 See abstract and claim 1.	1-17
A	US 2002-0005008 A1 (STUDZINSKI, W. M. et al.) 17 January 2002 See abstract and claim 1.	1-17

☐ Further documents are listed in the continuation of Box C.   ☒ See patent family annex.

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

Date of the actual completion of the international search	Date of mailing of the international search report
18 September 2015 (18.09.2015)	**18 September 2015 (18.09.2015)**

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