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(71) Applicant: **LANXESS Deutschland GmbH**  
**50569 Köln (DE)**

(72) Inventor: **The designation of the inventor has not  
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(54) **UNLEADED AVIATION FUEL**

(57) The present invention relates to an aviation gasoline composition, its production and its use in a reciprocating spark ignition aircraft engine.

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## Description

**[0001]** The present invention relates to a unleaded aviation gasoline composition, its production and its use in a reciprocating spark ignition aircraft engines.

**[0002]** The majority of aviation gas today is unleaded, especially within Europe, but there are still blends for reciprocating spark ignition aircraft engines mainly in America which use leaded fuels in order to increase the octane number. Due to the huge environmental impact of lead there is a strong need for substitution and replacement within non-leaded additives.

**[0003]** As published in Industrial and Engineering Chemistry, 1955, Vol 47, No.10 pages 2141-2146 "by J. E. Brown et al several amine-containing additives had been tested in anti-knocking analysis, including N-methyl-p-toluidine and N-methyl-m-toluidine.

**[0004]** Several other US-patents disclose the use of at least one aromatic amine, such as US 5,470,358 B, US 6,258,134 B, US 6,767,372 B and U.S. 7,897,034 B2 as well as in US-A 8.628.594.

**[0005]** Some of the most effective anti-knocking agents have a negative impact on the freezing point which is defined in ASTM D 2386-06 and therefore not useful as an aviation fuel.

**[0006]** As best understood, none of the references discloses compositions free of lead and having both a sufficiently low freezing point and a high octane number (effective for unleaded aviation gasoline) and, moreover, which compositions also ensure large scale commercial availability for reasonable prices.

**[0007]** It was therefore an object of the present invention to provide a highly effective high octane unleaded aviation gasoline composition which also fulfills the criteria of a freezing point lower than -58 °C.

**[0008]** Surprisingly, it has been found that a high octane unleaded aviation gasoline composition, comprising certain amounts of at least one unleaded gasoline base fuel, one or more alkylated benzenes; a composition of one or more of iso-pentane, n-butane, and iso-butane, in combination with aromatic amine(s), said aromatic amine(s) comprising N-methyl-p-toluidine and either or both of N-methyl-m-toluidine and m-Toluidine which are present in the ratio of between about four to one (4:1) and twelve to one (12:1) fulfill the above objectives of a high octane number and a low freezing point.

**[0009]** Furthermore, it was also surprisingly found that the combination of N-methyl-p-toluidine with either or both of N-methyl-m-toluidine and m-Toluidine in a ratio between about four to one (4:1) and twelve to one (12:1) has the particular advantage that commercial supplies are optimized. Illustrative of such optimizations is the nitration of toluene resulting in nitro-toluenes, a key ingredient for various industrial intermediates. During the production of toluidines from nitro-toluenes, the isomeric products are produced which themselves can be used in the synthesis of N-methyl-m-toluidine and N-methyl-p-toluidine. The use of N-methyl-p-toluidine and N-methyl-

m-toluidine or m-toluidine in the ratio of between about four to one (4:1) and twelve to one (12:1), by weight, thereby ensures the utilization of these compounds at a rate proportional to the production of their precursor molecules that result from the commercial manufacture of nitro-toluenes.

**[0010]** Thus, in accordance with the present invention, there is an aviation gasoline composition, comprising:

(a) about forty-five percent (45%) to about sixty-five percent (65%) by weight of at least one unleaded gasoline base fuel having a motor octane number of between ninety-seven (97) and ninety-nine point nine (99.9);

(b) about ten percent (10%) to about thirty-five percent (35%), preferably about fifteen percent (15%) to about thirty percent (30%) by weight by weight of one or more alkylated benzenes;

(c) about six percent (6%) to about twelve percent (12%) by weight, collectively, of a selected composition of one or more of iso-pentane, n-butane, and iso-butane; and

(d) about four percent (4%) to about fifteen percent (15%) by weight aromatic amine(s), said aromatic amine(s) comprising N-methyl-p-toluidine in combination with either or both of N-methyl-m-toluidine and m-Toluidine and are present in the ratio of between about four to one (4:1) and twelve to one (12:1).

**[0011]** In a preferred embodiment in this gasoline composition said N-methyl-p-toluidine in combination with either or both of said N-methyl-m-toluidine and m-Toluidine are present at the ratio of about four to one (4:1) up to nine to one (9:1), by weight.

**[0012]** Aviation gasoline base fuel is generally described as a gasoline possessing specific properties suitable for fueling aircraft powered by reciprocating ignition engines, e.g. as defined in ASTM D 910-13a.

**[0013]** In a preferred embodiment of the invention compounds (a) include various unleaded aviation gasoline base fuels refined hydrocarbons derived from crude petroleum, a natural gasoline or blends thereof. As generally known to the skilled artisan, aviation gasoline base fuels are normally manufactured by distilling petroleum crude to obtain a distillate with a desired boiling range. Petroleum refining, distillates obtained directly from crude are called straight-run distillates. The hydrocarbon content of a straight-run distillate and, therefore, its octane number, is determined by the composition of the crude. Crudes containing a relatively high proportion of aromatic hydrocarbons yield straight-run gasoline distillates with higher octane numbers than paraffinic crudes. The manufacturing is preferably performed so as to achieve a base fuel having an octane number between 97 and 99.9 by processes known by persons skilled in art.

**[0014]** As is also known, an important ingredient in aviation gasoline base fuels which are inherently present or its amount can be increased by alkylation processes if higher antiknock ratings are required.

**[0015]** The alkylation process can be performed by processing isobutylene with isobutane to result in the predominant isomer being 2,2,4-trimethylpentane (isooctane), which, by definition, has an octane number of 100.

**[0016]** The isobutylene used in this process is usually not pure as the feed typically comes from the catalytic cracking process and may contain propylene, other isomers of butene, and isomers of pentene as well as isoparaffins with carbon numbers from 7 to 12, or even higher, depending on feed composition and reaction conditions.

**[0017]** The higher carbon number isoparaffins are less desirable for aviation gasoline base fuels because of their lower octane numbers and higher boiling points. So, refineries producing aviation gasoline base fuels may distill the alkylate into two cuts, namely, a light alkylate or rerun alkylate, containing isoparaffins with nine carbons or fewer for aviation gasoline base fuels blending, and a heavy alkylate.

**[0018]** Today, aviation gasoline base fuel is a highly refined product specifically manufactured to meet the demanding performance requirements of aircraft engines. Its specifications make it difficult to meet all the requirements with a single refinery stream, even one such as light alkylate produced specially for aviation gasoline base fuels. So aviation gasoline base fuel, like motor gasoline and most other refinery products, is usually produced by blending two or more components to achieve the desired properties.

**[0019]** It is also preferred that said unleaded gasoline base fuel (a) has a motor octane number (MON) of at about ninety-eight (98).

**[0020]** In a preferred embodiment of the invention the alkylated benzenes (b) are mono- di- or trialkylated benzenes. Dialkylated benzenes are preferably selected from the group of xylenes, such as mixtures of two or three of the isomers o-xylene, m-xylene and p-xylene, preferably m-xylene alone. Monoalkylated benzenes are preferably selected from the group of ethyl benzene toluene or mixtures thereof. Preferred examples of trialkylated benzenes are 1,3,5-trimethylbenzene.

**[0021]** For the sake of clarity the alkylated benzenes (b) differ from compound (d) as they do not contain heteroatoms.

**[0022]** In a preferred embodiment of the invention certain di-alkylated and/or tri-alkylated benzenes, such as m-xylene, or 1,3,5-trimethylbenzene are used.

**[0023]** As compound (c), mixtures containing isopentane are preferred.

**[0024]** As compound (d), N-methyl-p-toluidine with N-methyl-m-toluidine as well as N-methyl-p-toluidine with m-toluidine is preferred. In another preferred embodiment of the invention d) also comprises N,N-dimethylated-p-toluidine.

**[0025]** In another preferred embodiment of aviation gasoline composition said aromatic amine(s) comprise between about six percent (6%) and about fifteen percent (15%) by weight of said high octane unleaded gasoline.

**[0026]** Another preferred embodiment is that said aromatic amine(s) (d) comprise products from the nitration of toluene, hydrogenation of the resulting products, which thereby forms m-toluidine and p-toluidine which themselves may be further alkylated to produce N-methyl-p-toluidine and N-methyl-m-toluidine. This also may comprise N,N-dimethylated-p-toluidine. If d) comprises N, N-dimethylated-p-toluidine, than the amount preferably does not exceed 5 wt. % of compound d) and in another preferred embodiment is higher than 0, 01 wt. %.

**[0027]** In various embodiments, high octane unleaded aviation gasoline blend may have a freezing point at or below minus fifty-eight degrees centigrade (-58°C).

**[0028]** Another embodiment of the present invention is a method for the manufacture of a high octane unleaded aviation fuel composition according to the invention by blending together each of the compounds (a), (b), (c), and (d) to provide a finished high octane unleaded aviation fuel composition.

**[0029]** The compounds (a), (b), (c), and (d) can be added in various orders during the blending. It is preferred that the compounds (a), (b), (c), and (d) are mixed at temperatures below the lowest boiling point of the selected compounds (a), (b), (c) and (d). It is even more preferred to use temperatures above the melting point of m-toluidine.

**[0030]** Another objective of the present invention is the use of an aviation gasoline composition for operating a reciprocating spark ignition aircraft engine.

**[0031]** The scope of the invention includes all indices, parameters and illustrations, if any, mentioned herein, and those mentioned in preferred ranges with one another, i.e. also any combinations of the respective ranges and preferred ranges.

**[0032]** The examples which follow serve to illustrate the invention but have no limiting effect except as otherwise expressly said forth in the claims.

### Examples

**[0033]** Various blends were formulated while using a standard fuel which falls into the ranges and definitions of claim 1.

**[0034]** This standard fuel was used with different compounds d), such as about 11 wt. % of the mixtures of

a) m-toluidine with N-methyl-p-toluidine in a ratio of 1 to 4.

b) N-methyl-p-toluidine and N-methyl-m-toluidine in ratios of 8 to 1 and 9 to 1.

**[0035]** All the unleaded fuel blends comprising compounds (d) showed an increased octane number and freezing points of lower than - 58°C and were therefore

viable alternatives to the standard leaded aviation fuels.

## Claims

### 1. Aviation gasoline composition, comprising:

- (a) about forty-five percent (45%) to about sixty-five percent (65%) by weight of at least one unleaded gasoline base fuel having a motor octane number of between ninety-seven (97) and ninety-nine point nine(99.9);
- (b) about ten percent (10%) to about thirty-five percent (35%), preferably about fifteen percent (15%) to about thirty percent (30%) by weight by weight of one or more alkylated benzenes;
- (c) about six percent (6%) to about twelve percent (12%) by weight, collectively, of a selected composition of one or more of iso-pentane, n-butane, and iso-butane; and
- (d) about four percent (4%) to about fifteen percent (15%) by weight aromatic amine(s), said aromatic amine(s) comprising N-methyl-p-toluidine in combination with N-methyl-m-toluidine or m-Toluidine and are present in the ratio of between about four to one (4:1) and twelve to one (12:1).

- 2. Aviation gasoline as set forth in claim 1, wherein said N-methyl-p-toluidine and said N-methyl-m-toluidine or m-Toluidine are present at the ratio of about four to one (4:1) up to nine to one (9:1), by weight.
- 3. Aviation gasoline (a) as set forth in claim 1, wherein said aromatic amine(s) comprise between about six percent (6%) and about fifteen percent (15%) by weight of said gasoline.
- 4. Aviation gasoline as set forth in claim 1, wherein compound (d) comprise N,N-dimethylated-p-toluidine
- 5. Aviation gasoline as set forth in claim 4, wherein the amount of N,N-dimethylated-p-toluidine does not exceed 5 wt. % of compound d).
- 6. Aviation gasoline as set forth in claim 1, wherein said unleaded gasoline base fuel has a motor octane number of at about ninety-eight (98).
- 7. A method for manufacture of an aviation fuel composition, according to claim 1, wherein compounds (a), (b), reciprocating (c), and (d) are blended together.
- 8. Use of an aviation gasoline composition as set forth in one of the claims 1 to 6 for operating a spark ignition aircraft engine.



## EUROPEAN SEARCH REPORT

Application Number  
EP 16 15 4197

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The present search report has been drawn up for all claims			
Place of search The Hague		Date of completion of the search 25 July 2016	Examiner Galleiske, Anke
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**ANNEX TO THE EUROPEAN SEARCH REPORT  
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This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.  
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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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