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(54) **AVIATION GASOLINE CONTAINING BRANCHED AROMATICS WITH A MANGANESE OCTANE ENHANCER**

FLUGBENZIN MIT VERZWEIGTEN AROMATEN MIT EINEM MANGANOKTANVERSTÄRKER  
CARBURANT D'AVIATION CONTENANT DES COMPOSÉS AROMATIQUES RAMIFIÉS  
COMPRENANT UN REHAUSSEUR D'OCTANE DE MANGANÈSE

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**EP 3 330 344 B1**

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**Description**

**[0001]** The present invention is directed to aviation gasoline formulations that incorporate branched aromatic compounds therein to improve the Motor Octane Number (MON) of the aviation gasoline.

Background

**[0002]** Due to the demanding nature of operating a piston driven aircraft and high regard for safety, the aviation gasoline industry places strong emphasis on fuel attributes. For example, meeting the Motor Octane Number (MON) minimum requirements and causing minimal engine deposits upon combustion of the fuel are essential attributes of an aviation gasoline. Historically, the MON requirement was met using a combination of strategies. A base fuel of aviation alkylate is typically mixed with an organolead octane enhancing additive and sometimes additional amounts of an aromatic component to improve the octane of the fuel. With the industry moving away from organolead-based additives the urgency to find alternative octane enhancers is great.

**[0003]** Replacing organolead antiknock additives with organomanganese compounds presents a viable and promising solution. In one example, an organometallic manganese compound, specifically methylcyclopentadienyl manganese tricarbonyl (MMT), is employed as an octane booster. With these fuels that contain significant quantities of MMT, it is then desirable to employ a manganese scavenger to reduce combustion chamber and engine component deposit formation caused during the combustion of that fuel. Accordingly, it is desirable to use only as much organomanganese octane enhancer as necessary to reach a target MON.

**[0004]** Aromatic aviation gasoline additives well-known to the industry include toluene, p-xylene, and mesitylene. These aromatic compounds can increase the MON of an aviation gasoline to a desired number, but only in relatively high amounts. Furthermore, excessively high blend volumes of these components can damage seals and other elastomeric components in the fuel system. Another potential drawback to using high blend volumes of aromatics is their propensity to form smoke upon combustion. The use of aromatic components in conjunction with an organomanganese antiknock such as MMT typically results in insensitivity to the organomanganese antiknock. Past research has shown that aromatic components do not respond, that is no octane enhancement is observed, to low treat rates of organomanganese compounds such as MMT. Only the non-aromatic portion of the fuel treated responds to MMT with an increase in octane. Consequently, higher MMT treat rates are required for fuels containing high percentages of aromatic compounds to achieve octane enhancement. EP0609089 discloses organometallic manganese complexes as octane enhancers in aviation gasoline composed of aviation alkylate and toluene.

**[0005]** The discovery set forth herein describes the use of branched aromatic compounds to synergistically cooperate with MMT to increase the MON of an aviation gasoline. This branched aromatic-MMT synergy not only enhances the MON to a significantly greater degree than traditional aromatics; it will allow for the reduction of the amount of organomanganese compound under certain circumstances.

Summary

**[0006]** Accordingly, it is an object of the present invention to provide a branched aromatic in an aviation gasoline to improve the MON of the fuel. Synergies between the branched aromatic and organomanganese antiknock compound significantly enhance the MON over what is typically observed with non-branched aromatics. Furthermore, under certain conditions employment of branched aromatics may in fact lower the organomanganese antiknock treat rate.

**[0007]** In one example according to claim 1, an aviation gasoline formulation comprises at least 20 volume percent of aviation alkylate composition and one to 50 volume percent of aromatic composition. The formulation also includes a manganese-containing compound. The aromatic composition includes a branched aromatic composition that is an aromatic functional group covalently bonded to a branched alkyl group. The aromatic functional group may be selected from the group consisting of benzene, naphthalene and anthracene. The aromatic functional group may be a heteroaromatic group that contains an atom selected from the group consisting of oxygen, nitrogen and sulfur. The aromatic functional group may be a 5 or 6 membered aromatic ring. The branched alkyl group may contain 3 to 15 atoms and may be formed entirely of carbon atoms. The branched alkyl group may include one or more heteroatoms selected from the group consisting of oxygen, nitrogen, sulfur, silicon, phosphorus, boron, fluorine, chlorine, bromine, and iodine. The branched aromatic composition comprises one to 25 volume percent of the aviation gasoline formulation. The branched aromatic composition may comprise a mixture of different branched aromatic compositions. The branched aromatic composition may be tert-butylbenzene. The amount of manganese-containing compound which is an organomanganese, is present in the amount of 1 mg Mn/L to 500 mg Mn/L. It may have a MON of the aviation gasoline of at least 99.6. The aromatic composition may be present in the amount of 30 volume percent of the gasoline formulation or less and the MON of the aviation gasoline is at least 99.6.

**[0008]** In another example according to claim 12, a method is described for reducing the amount of manganese-

containing engine deposits formed in the combustion of an aviation gasoline formulation. The method includes the following steps. A first aviation gasoline formulation is provided that comprises at least about 20 volume percent of aviation alkylate composition, a first amount of manganese-containing compound, and about one to 50 volume percent of unbranched aromatic compound. Next, prior to mixing the first aviation gasoline formulation, a second aviation gasoline formulation is prepared by substituting a branched aromatic composition for at least about 25 volume percent of the unbranched aromatic compound, and at the same time incorporating only a second amount of manganese-containing compound that is less than the first amount of manganese-containing compound wherein the branched aromatic composition comprises 1 to 25 volume percent of the aviation gasoline formulation and the manganese-containing compound is an organo manganese and incorporated in the aviation gasoline in an amount from 1 mg Mn/L to 500 mg Mn/L. The combustion of the second aviation gasoline formulation results in the formation of less manganese-containing engine deposits than the combustion of the first aviation gasoline formulation.

#### Detailed Description

**[0009]** The high octane requirements for aviation gasoline, currently a Motor Octane Number (MON) of at least 99.6 (based on ASTM D-2700), mean there is a challenge to obtain sufficient detonation resistance when formulating aviation gasoline. Organometallic antiknock additives, with or without a substantial aromatic fraction of the aviation gasoline formulation, present a viable pathway to achieve the at least 99.6 MON target. Specifically, as one example, the use of effective amounts of organomanganese are acceptable to reach octane requirements. However, there is a motivation to concurrently increase the MON to even greater levels while minimizing the amount of organomanganese additive in order to reduce potential fouling and deposits. It has been discovered that the use of branched aromatic compounds can increase fuel octane both alone and in a mixture with an organometallic additive. Particular synergistic benefits are realized when branched aromatic compounds are used in conjunction with organomanganese antiknocks.

**[0010]** A branched aromatic is defined as a compound that contains both an aromatic functional group covalently bonded to a branched alkyl group. An aromatic functional group is typically benzene (single ring) but may be naphthalene (two rings), anthracene (three rings) or other polyaromatic groups. A single benzene ring is one example but multiple aromatic groups are within the scope of this description. Heteroaromatic groups containing oxygen, nitrogen, or sulfur are also included in the scope of this description. The number of atoms in the aromatic ring includes, but is not limited to, 5 or 6 membered aromatic rings. Higher numbered rings in polyaromatic systems may also be the aromatic functional group that is described herein.

**[0011]** An unbranched aromatic is by definition a simple aromatic ring or rings with no groups bonded to it/them or other groups bonded to it/them than a branched alkyl group. Commercial examples of such unbranched aromatics, in addition to the simple aromatic groups noted above, include toluene, p-xylene and mesitylene.

**[0012]** The branched alkyl group that is part of the branched aromatic described herein contains a minimum of three atoms, preferably carbon, up to 15 atoms. Common examples of branched alkyl groups are iso-propyl, iso-butyl, sec-butyl, tert-butyl, iso-pentyl, neo-pentyl, tert-pentyl, and so forth. Iso-propyl is a preferred example of such a branched alkyl group. Tert-butyl is also a preferred example of such branched alkyl group. On longer carbon chains, multiple branches off the backbone are acceptable. In the above mentioned examples of branched alkyl groups, all carbon atoms were  $sp^3$  hybridized. Incorporation of carbon atoms exhibiting  $sp$  or  $sp^2$  hybridization may also be used. Additionally, incorporation of heteroatoms, either as part of the alkyl chain backbone or anywhere else in the branched alkyl groups is included herein. Such heteroatoms include, but are not limited to, oxygen, nitrogen, sulfur, silicon, phosphorous, boron, fluorine, chlorine, bromine, and iodine. A branched aromatic compound must have at least one of the above defined branched alkyl groups. However, branched aromatic compounds containing 2-6 additional branched alkyl groups are within the scope of this invention. Furthermore a compound containing a branched alkyl group, for example iso-propyl, as well as a non-branched alkyl group, for example a methyl group, bonded to the aromatic ring still falls under the scope of this invention. An example of this compound would be 4-tert-butyl toluene.

**[0013]** The aviation fuel composition as described herein typically contains aviation alkylate components. Those components may comprise at least 20 to 80 volume percent of the fuel. Aromatic hydrocarbons are incorporated into the fuel to improve the octane rating of the fuel. These aromatic hydrocarbons are incorporated according to one example of the present invention at a rate of 1 to 30 volume percent of the fuel composition. In another example, the aromatic hydrocarbons are incorporated at a rate of 10 to 20 volume percent of the fuel composition.

**[0014]** Aviation gasoline must meet certain physical property and performance characteristics that set it apart from motor gasoline. Aviation gasoline must possess strong detonation resistance; the ASTM D-910 spec for leaded aviation gasoline quantifies this property as a Motor Octane Number of at least 99.6. A premium motor gasoline (93 Octane by R+M/2 Method) typically has a Motor Octane Number of 88, which those skilled in the art will recognize as a significant difference. Aviation gasoline furthermore requires strict adherence to minimum freeze point and specific volatility values to ensure safe in flight operation under a variety of possible conditions.

**[0015]** To meet such stringent requirements aviation gasoline is formulated differently from motor gasoline. Motor

gasoline typically comprises a number of refinery streams such as reformat, isomerate, naphtha, catalytically cracked naphtha, and alkylate, with each of these streams containing dozens, up to hundreds, of unique hydrocarbons. Due to the high demand of motor gasoline its composition can differ dramatically from region to region and refinery to refinery. Inherent technological differences between refineries, the identity of the crude oil feedstock, and refinery economics all contribute to the inherent variability of motor gasoline blends. The susceptibility of motor gasoline to MMT varies widely based on the blend volumes of refinery gasoline feedstock. Although broad generalizations can be made, for example aromatics are not susceptible to MMT, it is difficult to identify specific molecules in motor gasoline that are synergistic with organomanganese antiknocks. Furthermore, due to the need to manage costs while meeting high demand, it is practically impossible to blend a large volume of any particular molecule into motor gasoline. Therefore, the aromatics portion of motor gasoline comprises a blend of numerous aromatic molecules.

**[0016]** Since aviation gasoline must meet such stringent physical property and performance requirements, its composition is tightly controlled. Typical leaded aviation gasoline contains at least 75 vol% aviation alkylate (C5-C8 paraffins), 0-15 vol% toluene, 0-10% iso-pentane, and butane as required to meet the vapor pressure. Acknowledging aviation gasoline only contains predominantly one aromatic compound (whereas motor gasoline contains a blend of aromatic compounds), it is logical to attempt to optimize the aromatic component of aviation gasoline. Comparing Example 1 to Example 13 demonstrates the fundamental difference between aviation gasoline and motor gasoline. Example 1, representative of aviation gasoline containing only toluene as the aromatic component, exceeds the minimum MON threshold of 99.6. Example 13, representative of motor gasoline by containing a mixture of aromatic hydrocarbons, fails to meet the minimum MON threshold of 99.6. The uniquely well controlled composition of aviation gasoline allows for experimentation with novel blend components to enhance physical and performance properties such as Motor Octane Number.

**[0017]** The development of unleaded aviation gasoline poses unique challenges to the aviation fuel industry, primarily because lead provides the significant increase in octane required by aviation engines. Organomanganese antiknock additives present a viable solution to address the challenges of meeting the same minimum octane requirement as leaded aviation gasoline. However, fundamental differences exist between organoleads antiknock compounds and organomanganese antiknock compounds in aviation gasoline. Since tetraethyl lead has a different response curve compared to MMT, one cannot assume simply replacing TEL with MMT will result in the same detonation resistance. The response to individual components to MMT differs from TEL. For example toluene is susceptible to octane enhancement from TEL but shows no susceptibility to MMT. Antagonism of the antiknock compound also differs - certain amines can inhibit the antiknock effectiveness of TEL but in the presence of MMT these amines will act synergistically.

**[0018]** All of the aviation gasoline referenced in this description is substantially lead-free. For the purposes of this application, an aviation gasoline composition is described in ASTM 4814 as substantially "lead-free" or "unleaded" if it contains 13 mg of lead or less per liter (or about 50 mg Pb/gal or less) of lead in the fuel. Alternatively, the terms "lead-free" or "unleaded" mean about 7 mg of lead or less per liter of fuel. Still further alternatively, it means an essentially undetectable amount of lead in the fuel composition. In other words, there can be trace amounts of lead in a fuel; however, the fuel is essentially free of any detectable amount of lead. It is to be understood that the fuels are unleaded in the sense that a lead-containing antiknock agent is not deliberately added to the gasoline. Trace amounts of lead due to contamination of equipment or like circumstances are permissible and are not to be deemed excluded from the fuels described herein.

**[0019]** The amounts of organomanganese that are incorporated in the aviation gasoline is from 1 mg Mn/L to 500 mg Mn/L, or alternatively 20 to 250 mg Mn/L, or still further alternatively 25 to 225 mg Mn/L. The amount of manganese may vary depending on the target octane increase in the aviation gasoline formulation. These organomanganese additives are typically, but not limited to, cyclopentadienyl manganese tricarbonyl compounds.

**[0020]** Cyclopentadienyl manganese tricarbonyl compounds which can be used in the practice of the fuels herein include cyclopentadienyl manganese tricarbonyl, methylcyclopentadienyl manganese tricarbonyl, dimethylcyclopentadienyl manganese tricarbonyl, trimethylcyclopentadienyl manganese tricarbonyl, tetramethylcyclopentadienyl manganese tricarbonyl, pentamethylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, diethylcyclopentadienyl manganese tricarbonyl, propylcyclopentadienyl manganese tricarbonyl, isopropylcyclopentadienyl manganese tricarbonyl, tertbutylcyclopentadienyl manganese tricarbonyl, octylcyclopentadienyl manganese tricarbonyl, dodecylcyclopentadienyl manganese tricarbonyl, ethylmethylcyclopentadienyl manganese tricarbonyl, indenyl manganese tricarbonyl, and the like, including mixtures of two or more such compounds. Preferred are the cyclopentadienyl manganese tricarbonyls which are liquid at room temperature such as methylcyclopentadienyl manganese tricarbonyl, ethylcyclopentadienyl manganese tricarbonyl, liquid mixtures of cyclopentadienyl manganese tricarbonyl and methylcyclopentadienyl manganese tricarbonyl, mixtures of methylcyclopentadienyl manganese tricarbonyl and ethylcyclopentadienyl manganese tricarbonyl, etc. The aviation fuels of this invention will contain an amount of one or more of the foregoing cyclopentadienyl manganese tricarbonyl compounds sufficient to provide the requisite octane number and/or valve seat wear performance characteristics.

**[0021]** The following examples demonstrated the benefits in the use of the branched aromatics described herein both alone and in combination with organometallic additives, in these examples, MMT.

## EP 3 330 344 B1

### Example 1

[0022] An aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent toluene, 50 volume percent isooctane, and 5 volume percent isopentane. To this gasoline blend, 225 mg Mn/L, as MMT was added. The Motor Octane Number rating of this fuel ranged from 101.0 - 101.5.

### Example 2

[0023] An aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent aromatic listed in Table 1, 50 volume percent isooctane, and 5 volume percent isopentane. To this gasoline blend, 225 mg Mn/L, as MMT was added. The Motor Octane Number ratings of the blends are listed in Table 1. It becomes readily apparent aviation gasoline formulations containing mono-, di-, and tri-substituted aromatics meet the minimum ASTM D910 MON rating of at least 99.6.

Table 1

Blend	Aromatic Component	Motor Octane Number
1	Toluene	101.0
2	Mesitylene	101.3
3	Mixed Xylenes	100.8
4	Para-Xylene	101.0
5	Ethyl Benzene	101.6

### Example 3

[0024] An aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent cumene, 50 volume percent isooctane, and 5 volume percent isopentane. To this gasoline blend, 225 mg Mn/L, as MMT was added. The Motor Octane Number rating of this fuel was measured to be 102.5. The configuration of the substituents attached to the aromatic plays an intrinsic role in enhancing the octane number of the fuel. Mesitylene, which contains three carbon atom substituents as methyl groups, gave a Motor Octane Rating of 101.3. Cumene, which also contains three carbon atom substituents except as an isopropyl group, gave a higher Motor Octane Number.

### Example 4

[0025] An aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent tert-butylbenzene, 50 volume percent isooctane, and 5 volume percent isopentane. To this gasoline blend, 225 mg Mn/L, as MMT was added. The Motor Octane Number rating of this fuel was measured to be 104.0.

### Example 5

[0026] Aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent of either toluene or tert-butylbenzene, 50 volume percent isooctane, and 5 volume percent isopentane. The Motor Octane Numbers were measured before and after the addition of 225 mg Mn/L, as MMT and are summarized in Table 2. The base fuel blend containing tert-butylbenzene had a higher octane rating than the base fuel containing toluene as the aromatic component. Upon addition of MMT, the fuel containing tert-butylbenzene saw a greater increase in Motor Octane Number despite the untreated fuel having a higher Motor Octane Number than the toluene based fuel. To those skilled in the art, this is an unexpected result. It is commonly understood that the higher the octane rating of the fuel the less responsive (MON or RON gain) it is to organomanganese antiknock additives. Based on the table below it is apparent there is an unexpected synergy between tert-butylbenzene and MMT that significantly enhances the octane rating of the fuel even at high base octane numbers.

Table 2

Blend	Aromatic Component	[Mn] mg Mn/L	Motor Octane Number	MON Gain
1	Toluene	0	95.7	N/a

**EP 3 330 344 B1**

(continued)

Blend	Aromatic Component	[Mn] mg Mn/L	Motor Octane Number	MON Gain
2	Toluene	225	101.3	5.6
3	Tert-Butylbenzene	0	97.3	N/a
4	Tert-Butylbenzene	225	104.0	6.7

Example 6

**[0027]** An aviation gasoline was formulated with 25 volume percent alkylate, 20 volume percent styrene, 50 volume percent isooctane, and 5 volume percent isopentane. To this gasoline blend, 225 mg Mn/L, as MMT was added. The Motor Octane Number rating of this fuel was measured to be 100.6. This demonstrates adding unsaturated substituents to the aromatic ring will yield fuels with acceptable Motor Octane Numbers.

Example 7

**[0028]** Tert-butylbenzene and toluene were treated with MMT ranging from 0 - 225 mg Mn/L. The response data is show in Table 3. It is readily apparent toluene shows no response to increasing concentrations of MMT. Tert-butylbenzene, on the other hand, does show an increase in MON as MMT treat rate increases. An additional unexpected result is apparent from the data below. Toluene, by itself has a higher MON than tert-butylbenzene. One would expect fuels containing toluene to have a higher MON than fuels containing tert-butylbenzene. As shown in the previous examples, the opposite trend is observed.

Table 3

Blend	[Mn] mg Mn/L	MON of Toluene	MON of tert-butylbenzene
1	0	108	102.2
2	125	109	102.8
3	225	108	103.4

Example 8

**[0029]** An aviation gasoline was formulated with 80 volume percent alkylate, 15 volume percent toluene, and 5 volume percent isopentane. To this gasoline blend, 125 mg Mn/L, as MMT was added. The Motor Octane Number of this fuel was 98.0. Replacing 15 volume percent toluene with 15 volume percent tert-butylbenzene raises the Motor Octane Number to 100.3.

Example 9

**[0030]** Aviation gasoline was formulated with 25 volume percent alkylate, 50 volume percent isooctane, 20 volume percent tert-butylbenzene, and 5 volume percent isopentane. To this base formulation, manganese, as MMT was added at treat rates ranging from 25 mg Mn/L to 225 mg Mn/L. The Motor Octane Number of the resultant formulations was measured by the ASTM D2700 method. Based on the results below in Table 4, it is readily apparent incorporating 20 volume percent tert-butylbenzene allows for a significant reduction in MMT treat rate. Reduction in Mn treat rate via the addition of tert-butylbenzene will reduce manganese oxide engine deposits.

**[0031]** Importantly, this example demonstrates that a conventional aviation gasoline formulation can be modified with substituting branched aromatic compositions for some or all of conventional unbranched aromatics and then using less manganese-containing compounds (e.g., MMT) as an octane enhancer. For instance, a first aviation gasoline formulation may contain at least 20 volume percent of aviation alkylate (in the example above, 25 volume percent). This first aviation gasoline formulation would also include a first amount of manganese-containing compound to reach a desired MON. Finally, as demonstrated in other examples, the first aviation gasoline might include one to 50 volume percent of unbranched aromatic composition. This Example 9 demonstrates that the unbranched aromatic can be substituted in whole or in part, or alternatively at least 25 volume percent, with a branched aromatic composition. This formulation would then require less manganese-containing compound to meet desired MON requirements. As a result, less manganese-containing engine deposits (such as for instance manganese oxide) would result during combustion of the second aviation

EP 3 330 344 B1

gasoline formulation.

Table 4

Blend	[Mn] mg Mn/L	MON of Formulation
1	25	99.2
2	75	101.7
3	125	102.0
4	225	103.3

Example 10

**[0032]** Four aviation gasoline blends were formulated with 50 volume percent isooctane, 5 volume percent isopentane, 5-20 volume percent tert-butylbenzene, and 25-40 volume percent alkylate. The Mn treat rate, as MMT, was held constant at 175 mg Mn/L. The Motor Octane Number of the resultant formulations was measured by the ASTM D2700 method. Based on the results below in Table 5, at 175 mg Mn/L, the aromatics component of the aviation gasoline formulation can be reduced to 5 volume percent while still meeting the ASTM D-910 specification for detonation. Incorporation of tert-butylbenzene allows for lowered aromatics content. This is advantageous from the standpoint of increasing energy content of the fuel, reducing smoke emissions, and improving elastomer compatibility.

Table 5

Blend	Vol % Alkylate	Vol% Tert-butylbenzene	MON of Formulation
1	40	5	102.3
2	35	10	102.7
3	30	15	102.8
4	25	20	103.9

Example 11

**[0033]** Branched aromatics other than tert-butylbenzene are effective as well. An aviation gasoline was formulated to contain 22 volume percent alkylate, 50 volume percent isooctane, 17.5 volume percent p-cymene, and 10.5 volume percent isopentane. The Motor Octane Number of this fuel without MMT is 96.3. Upon addition of 125 mg Mn/L as MMT, the Motor Octane Number rises to 102.1.

Example 12

**[0034]** Branched aromatics other than tert-butylbenzene are effective as well. An aviation gasoline was formulated to contain 25 volume percent alkylate, 50 volume percent isooctane, 5 volume percent isopentane, and 20 volume percent aromatic. The Mn treat rate, as MMT, was held constant at 225 mg Mn/L. The Motor Octane Number of the resultant formulations was measured by the ASTM D2700 method and summarized in Table 6.

Table 6

Blend	Aromatic (20 vol%)	MON of Formulation
1	Toluene (Control)	101.5
2	4-tert-butyltoluene	103.4
3	5-tert-butyl-m-xylene	103.4
4	p-cymene	102.1

Example 13

**[0035]** An aviation gasoline was formulated to contain 25 volume percent alkylate, 50 volume percent isooctane, 20

volume percent Aromatic 150 Solvent, and 5 volume percent isopentane. Aromatic 150 Solvent consists of a blend of dozens of alkyl and branched alkyl substituted aromatic compounds. To this base fuel, 225 mg Mn/L as MMT was added. The Motor Octane Number of this fuel was measured at 99.1.

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**Claims**

1. An aviation gasoline formulation comprising:

10 at least 20 volume percent of aviation alkylate composition;  
a manganese-containing compound; and  
one to 50 volume percent of aromatic composition, wherein the aromatic composition includes a branched aromatic composition that is an aromatic functional group covalently bonded to a branched alkyl group, wherein the branched aromatic composition comprises 1 to 25 volume percent of the aviation gasoline formulation and the manganese-containing compound is an organomanganese and incorporated in the aviation gasoline in an amount from 1 mg Mn/L to 500 mg Mn/L.

2. An aviation gasoline formulation as described in claim 1, wherein the aromatic functional group is selected from the group consisting of benzene, naphthalene and anthracene.

3. An aviation gasoline formulation as described in claim 1, wherein the aromatic functional group is a heteroaromatic group that contains an atom selected from the group consisting of oxygen, nitrogen and sulfur.

4. An aviation gasoline formulation as described in claim 1, wherein the aromatic functional group is a 5 or 6 membered aromatic ring.

5. An aviation gasoline formulation as described in claim 1, wherein the branched alkyl group contains 3 to 15 atoms.

6. The aviation gasoline formulation as described in claim 5, wherein the branched alkyl group is formed entirely of carbon atoms.

7. An aviation gasoline formulation as described in claim 5, wherein the branched alkyl group includes one or more heteroatoms selected from the group consisting of oxygen, nitrogen, sulfur, silicon, phosphorous, boron, fluorine, chlorine, bromine and iodine.

8. An aviation gasoline formulation as described in claim 1, wherein the branched aromatic composition comprises a mixture of different branched aromatic compositions.

9. An aviation gasoline formulation as described in claim 1, wherein the branched aromatic composition is tert-butylbenzene.

10. An aviation gasoline formulation as described in claim 1, wherein the amount of manganese-containing compound is present in 500 mg Mn/L or less, and the Motor Octane Number (MON) of the aviation gasoline is at least 99.6.

11. An aviation gasoline formulation as described in claim 1, wherein the aromatic composition is present in the amount of 30 volume percent of the gasoline formulation or less, and the Motor Octane Number (MON) of the aviation gasoline is at least 99.6.

12. A method of reducing the amount of manganese-containing engine deposits formed in the combustion of an aviation gasoline formulation, the method comprising the steps of:

providing a first aviation gasoline formulation that comprises at least 20 volume percent of aviation alkylate composition, a first amount of a manganese-containing compound, and one to 50 volume percent of an unbranched aromatic compound;

55 prior to mixing the first aviation gasoline formulation, preparing a second aviation gasoline formulation by substituting a branched aromatic composition for at least 25 volume percent of the unbranched aromatic compound and at the same time incorporating only a second amount of manganese-containing compound that is less than the first amount of manganese-containing compound, wherein the branched aromatic composition comprises



1 to 25 volume percent of the aviation gasoline formulation and the manganese-containing compound is an organomanganese and incorporated in the aviation gasoline in an amount from 1 mg Mn/L to 500 mg Mn/L; wherein the combustion of the second aviation gasoline formulation results in the formation of less manganese-containing engine deposits than the combustion of the first aviation gasoline formulation.

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## Patentansprüche

### 1. Flugbenzinformulierung, umfassend:

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mindestens 20 Volumenprozent Flugalkylatzusammensetzung;  
eine Mangan enthaltende Verbindung; und  
ein bis 50 Volumenprozent aromatische Zusammensetzung, wobei die aromatische Zusammensetzung eine verzweigte aromatische Zusammensetzung beinhaltet, die eine aromatische funktionelle Gruppe ist, die kovalent an eine verzweigte Alkylgruppe gebunden ist, wobei die verzweigte aromatische Zusammensetzung 1 bis 25 Volumenprozent der Flugbenzinformulierung umfasst und die Mangan enthaltende Verbindung ein Organomangan ist und in das Flugbenzin in einer Menge von 1 mg Mn/l bis 500 mg Mn/l aufgenommen ist.

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### 2. Flugbenzinformulierung nach Anspruch 1, wobei die aromatische funktionelle Gruppe aus der Gruppe bestehend aus Benzol, Naphthalin und Anthracen ausgewählt ist.

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### 3. Flugbenzinformulierung nach Anspruch 1, wobei die aromatische funktionelle Gruppe eine heteroaromatische Gruppe ist, die ein Atom enthält, das aus der Gruppe bestehend aus Sauerstoff, Stickstoff und Schwefel ausgewählt ist.

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### 4. Flugbenzinformulierung nach Anspruch 1, wobei die aromatische funktionelle Gruppe ein 5- oder 6-gliedriger aromatischer Ring ist.

### 5. Flugbenzinformulierung nach Anspruch 1, wobei die verzweigte Alkylgruppe 3 zu 15 Atome enthält.

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### 6. Flugbenzinformulierung nach Anspruch 5, wobei die verzweigte Alkylgruppe vollständig aus Kohlenstoffatomen gebildet ist.

### 7. Flugbenzinformulierung nach Anspruch 5, wobei die verzweigte Alkylgruppe ein oder mehrere Heteroatome beinhaltet, die aus der Gruppe bestehend aus Sauerstoff, Stickstoff, Schwefel, Silizium, Phosphor, Bor, Fluor, Chlor, Brom und Iod ausgewählt sind.

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### 8. Flugbenzinformulierung nach Anspruch 1, wobei die verzweigte aromatische Zusammensetzung ein Gemisch aus unterschiedlichen verzweigten aromatischen Zusammensetzungen umfasst.

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### 9. Flugbenzinformulierung nach Anspruch 1, wobei die verzweigte aromatische Zusammensetzung tert-Butylbenzol ist.

### 10. Flugbenzinformulierung nach Anspruch 1, wobei die Menge an Mangan enthaltender Verbindung in 500 mg Mn/l oder weniger vorhanden ist und die Motor-Oktananzahl (MOZ) des Flugbenzins mindestens 99,6 beträgt.

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### 11. Flugbenzinformulierung nach Anspruch 1, wobei die aromatische Zusammensetzung in der Menge von 30 Volumenprozent der Benzinformulierung oder weniger vorhanden ist und die Motor-Oktananzahl (MOZ) des Flugbenzins mindestens 99,6 beträgt.

### 12. Verfahren zum Reduzieren der Menge an Mangan enthaltenden Motorablagerungen, die sich bei der Verbrennung einer Flugbenzinformulierung bilden, wobei das Verfahren die folgenden Schritte umfasst:

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Bereitstellen einer ersten Flugbenzinformulierung, die mindestens 20 Volumenprozent Flugalkylatzusammensetzung, eine erste Menge an einer Mangan enthaltenden Verbindung und ein bis 50 Volumenprozent einer unverzweigten aromatischen Verbindung umfasst;

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vor dem Mischen der ersten Flugbenzinformulierung Herstellen einer zweiten Flugbenzinformulierung durch Ersetzen einer verzweigten aromatischen Zusammensetzung durch mindestens 25 Volumenprozent der unverzweigten aromatischen Verbindung und gleichzeitig Aufnehmen lediglich einer zweiten Menge an Mangan enthaltender Verbindung, die kleiner als die erste Menge an Mangan enthaltender Verbindung ist, wobei die

## EP 3 330 344 B1

verzweigte aromatische Zusammensetzung 1 zu 25 Volumenprozent der Flugbenzinformulierung umfasst und die Mangan enthaltende Verbindung ein Organomangan ist und in das Flugbenzin in einer Menge von 1 mg Mn/l bis 500 mg Mn/l aufgenommen ist;

wobei die Verbrennung der zweiten Flugbenzinformulierung zur Bildung von weniger Mangan enthaltenden Motorablagerungen führt als die Verbrennung der ersten Flugbenzinformulierung.

### Revendications

- 10 1. Formulierung d'essence d'aviation comprenant :  
au moins 20 pour cent en volume de composition d'alkylate d'aviation :
- un composé contenant du manganèse ; et  
un à 50 pour cent en volume de composition aromatique, dans laquelle la composition aromatique inclut une  
15 composition aromatique ramifiée qui est un groupe fonctionnel aromatique lié par covalence à un groupe alkyle ramifié, dans laquelle la composition aromatique ramifiée constitue 1 à 25 pour cent en volume de la formulation d'essence d'aviation et le composé contenant du manganèse est un organomanganèse et est incorporé dans l'essence d'aviation en une quantité allant de 1 mg de Mn/L à 500 mg de Mn/L.
- 20 2. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle le groupe fonctionnel aromatique est choisi dans le groupe constitué de benzène, naphthalène et anthracène.
3. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle le groupe fonctionnel aromatique est un  
25 groupe hétéroaromatique qui contient un atome choisi dans le groupe constitué d'oxygène, azote et soufre.
4. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle le groupe fonctionnel aromatique est un noyau aromatique à 5 ou 6 chaînons.
5. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle le groupe alkyle ramifié contient 3 à 15  
30 atomes.
6. Formulierung d'essence d'aviation selon la revendication 5, dans laquelle le groupe alkyle ramifié est formé entièrement d'atomes de carbone.
- 35 7. Formulierung d'essence d'aviation selon la revendication 5, dans laquelle le groupe alkyle ramifié inclut un ou plusieurs hétéroatomes choisis dans le groupe constitué d'oxygène, azote, soufre, silicium, phosphore, bore, fluor, chlore, brome et iode.
8. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle la composition aromatique ramifiée comprend un mélange de différentes compositions aromatiques ramifiées.  
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9. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle la composition aromatique ramifiée est du tert-butylbenzène.
- 45 10. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle la quantité de composé contenant du manganèse est présente à 500 mg de Mn/L ou moins, et l'indice d'octane moteur (MON) de l'essence d'aviation est d'au moins 99,6.
11. Formulierung d'essence d'aviation selon la revendication 1, dans laquelle la composition aromatique est présente  
50 dans la quantité de 30 pour cent en volume de la formulation d'essence ou moins, et l'indice d'octane moteur (MON) de l'essence d'aviation est d'au moins 99,6.
12. Procédé de réduction de la quantité de dépôts de moteur contenant du manganèse formés dans la combustion d'une formulation d'essence d'aviation, le procédé comprenant les étapes consistant à :
- 55 fournir une première formulation d'essence d'aviation qui comprend au moins 20 pour cent en volume de composition d'alkylate d'aviation, une première quantité d'un composé contenant du manganèse, et un à 50 pour cent en volume d'un composé aromatique non ramifié ;

### EP 3 330 344 B1

avant mélange de la première formulation d'essence d'aviation, préparer une deuxième formulation d'essence d'aviation en remplaçant par une composition aromatique ramifiée au moins 25 pour cent en volume de la composé aromatique non ramifié et en incorporant en même temps seulement une deuxième quantité de composé contenant du manganèse qui est inférieure à la première quantité de composé contenant du manganèse, dans lequel la composition aromatique ramifiée constitue 1 à 25 pour cent en volume de la formulation d'essence d'aviation et le composé contenant du manganèse est un organomanganèse et est incorporé dans l'essence d'aviation en une quantité allant de 1 mg de Mn/L à 500 mg de Mn/L ; dans lequel la combustion de la deuxième formulation d'essence d'aviation entraîne la formation de moins de dépôts de moteur contenant du manganèse que la combustion de la première formulation d'essence d'aviation.

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**REFERENCES CITED IN THE DESCRIPTION**

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