(54) Title: OCTANE ENHANCING ADDITIVE FOR GASOLINE

(57) Abstract:
An octane increasing additive for gasoline, which includes N-methylaniline or N-ethylaniline, with aniline and ethanol. There is not less than 5% and not more than 70% by volume of at least one of N-methylaniline or N-ethylaniline. There is not less than 10% and not more than 50% by volume of aniline. There is not less than 5% and not more than 60% by volume of ethanol.
ABSTRACT OF THE DISCLOSURE

An octane increasing additive for gasoline, which includes N-methylaniline or N-ethylaniline, with aniline and ethanol. There is not less than 5% and not more than 70% by volume of at least one of N-methylaniline or N-ethylaniline. There is not less than 10% and not more than 50% by volume of aniline. There is not less than 5% and not more than 60% by volume of ethanol.
TITLE OF THE INVENTION:
Octane enhancing additive for gasoline

FIELD OF THE INVENTION
The present invention relates to an octane enhancing additive for gasoline.

BACKGROUND OF THE INVENTION
Gasoline fraction obtained from crude oil distillation typically has an octane number of around 80. In addition to refinery upgrading processes, octane enhancing additives have been used to improve the octane number. The octane number must be increased from 80 to 87 for regular grade gasoline and to 91 for premium gasoline.

One commonly used octane enhancing additive for gasoline was tetraethyl lead. Tetraethyl lead was banned after it was discovered to contribute to human health problems. Another commonly used octane enhancing additive for gasoline was methyl t-butyl ether (MTBE). MTBE was also discovered to create environmental problems. Large quantities of MTBE have been released into the environment from leaking underground storage tanks. Where such leakage occurred, the MTBE contaminated the water table, because of its high mobility and water solubility.

There are numerous chemical additives, which are capable of increasing the octane number of gasoline. It is difficult, however, to find additives which are capable of achieving very high octane increases with very small quantity additions to gasoline. It is also difficult to find additives with acceptable physical characteristics, which will have relatively low potential environmental and toxicological impact.
SUMMARY OF THE INVENTION

What is required is an octane increasing additive for gasoline which is capable of achieving very high octane increases with relatively small quantity additions to gasoline and relatively low potential environmental and toxicological impact.

According to the present invention there is provided an octane increasing additive for gasoline, which includes N-methylaniline and/or N-ethylaniline, with aniline and ethanol. There is not less than 5% and not more than 70% by volume of at least one of N-methylaniline or N-ethylaniline. There is not less than 10% and not more than 50% by volume of aniline. There is not less than 5% and not more than 60% by volume of ethanol.

The normal additional of the octane increasing additive into the gasoline is in the 1% to 10% range.

In applications in which vapour pressure is of concern, iso-octane can be added to increase the vapour pressure for the additive.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The preferred octane increasing additive for gasoline will now be described. During product development, the additive was identified as H.O.P.E which stands for “High Octane Power Enhancer”. In the description which follows and the supporting charts and graphs, the additive is identified as H.O.P.E.

H.O.P.E. development

H.O.P.E. is a newly designed gasoline additive that enhances research (RON), motor (MON) octane numbers and,
consequently, the anti-knock index.

Testing Methods

H.O.P.E. was tested at the laboratories of the Alberta Research Council using standard methods. Among them ASTM methods 2699 and 2700 that were used for RON and MON respectively. H.O.P.E. could be added to gasoline at ranges of 1-10% (v/v).

Performance

H.O.P.E. performance is very good as shown in the following graph. The enhancement of octane number with H.O.P.E. is much larger than with other additives tested or MTBE as shown on the graph. This addition rate could be adjusted based on the formulation of H.O.P.E. and also based on the octane number of the gasoline. Testing dosage in increments of 1% of H.O.P.E. allows increase of RON from 77.8 to 81.4 resulting in a boosting effect of 3.6 points compared to 1.1 of MTBE.
Dosage: 1%, 2%, 3% and 5%

1% of H.O.P.E. increases gasoline RON by up to 3.6 points
2% of H.O.P.E. increases gasoline RON by up to 7.5 points
3% of H.O.P.E. increases gasoline RON by up to 10.8 points
5% of H.O.P.E. increases gasoline RON by up to 15.6 points,

Based on these results, the following information is compiled,

- At 1% dosage, one (1) ton of H.O.P.E. treats 100 tons of base gasoline resulting in 101 tons of treated gasoline with RON increase of 3.6 points.

To perform this, simply add 1 ton of H.O.P.E. to 100 tons of base gasoline.

- At 2% dosage, two (2) tons of H.O.P.E. treats 100 tons of base gasoline resulting in 102 tons of treated gasoline with RON increase of 7.5 points.

- At 5% dosage, one (1) ton of H.O.P.E. treats 20 tons of base gasoline resulting in 21 tons of treated gasoline with RON increase of 15.6 points.

Physical Characteristics

H.O.P.E. is a mixture of liquid organic chemicals.

These chemicals have a clear to slightly yellow colour, no
metals and no phosphorus as determined by ASTM methods. The vapor pressure of its major constituents is lower than gasoline. No lead is present in H.O.P.E. and other constituents are with specification.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Content</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Color</td>
<td>Light Yellow</td>
<td>Visual</td>
</tr>
<tr>
<td>Metals</td>
<td>None</td>
<td>Inductively Coupled Plasma (ICP)</td>
</tr>
<tr>
<td>Phosphorus</td>
<td>None</td>
<td>Inductively Coupled Plasma (ICP)</td>
</tr>
<tr>
<td>Lead</td>
<td>None</td>
<td>ASTM D 3237</td>
</tr>
<tr>
<td>Water and Sediment</td>
<td>None</td>
<td>ASTM D 2709</td>
</tr>
<tr>
<td>Sulfur</td>
<td>None</td>
<td>ASTM D 5453</td>
</tr>
<tr>
<td>Nitrogen</td>
<td>0.12% at 1% addition in gasoline 12.37% in H.O.P.E. pure</td>
<td>Calculated</td>
</tr>
<tr>
<td>Oxygen</td>
<td>0.017 at 1% addition in gasoline 1.7% in H.O.P.E. pure</td>
<td>Calculated</td>
</tr>
<tr>
<td>BTEX</td>
<td>None</td>
<td>Gas Chromatography (GC)</td>
</tr>
<tr>
<td>Chlorine</td>
<td>None</td>
<td>Gas Chromatography (GC)</td>
</tr>
<tr>
<td>Corrosion</td>
<td>No Corrosion</td>
<td>ASTM D 130</td>
</tr>
<tr>
<td>Emission</td>
<td>No Impact (No change in VOCs, SO₂, NOx, PM, CO and CO₂)</td>
<td>Dynamometer</td>
</tr>
<tr>
<td>Olefins</td>
<td>None</td>
<td>CGSB-3.0 No.14</td>
</tr>
<tr>
<td>RON</td>
<td>See Text and Graph</td>
<td>ASTM D 2699</td>
</tr>
<tr>
<td>MON</td>
<td>See Text and Graph</td>
<td>ASTM D 2700</td>
</tr>
</tbody>
</table>

Environmental and Toxicological impact

H.O.P.E. environmental parameters (Kow, Koc) are estimated to be similar to gasoline's, as shown in the table below. Its solubility in water is smaller than MTBE's. It's lower vapor pressure than gasoline makes it less susceptible for inhalation. Its flash point is estimated to be 37 C and its TGA flammability classification is 3. It's freezing point is less than -10 C. The major constituents of H.O.P.E. are much less toxic than other additives such as MMT, based on comparison of LD50 values.
### Conclusion

H.O.P.E. is a very efficient in boosting antiknock index for gasoline. It is an attractive and very promising additive since it exhibits low water solubility, low toxicity and low mobility in the environment. Its addition to gasoline did not show any change to the regular emitted chemicals (emissions) from tail pipes. This classifies H.O.P.E. as environmentally friendly additive.

Broad Working Range:
not less than 5% and not more than 70% by volume of at least one of N-methylaniline or N-ethylaniline;

not less than 10% and not more than 50% by volume of aniline; and

not less than 5% and not more than 60% by volume of ethanol.

In this formulation a synergy is obtained through use of

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<table>
<thead>
<tr>
<th>Chemical</th>
<th>BP</th>
<th>VP</th>
<th>Water Solubility</th>
<th>Log Kow</th>
<th>Koc</th>
<th>LD50</th>
</tr>
</thead>
<tbody>
<tr>
<td>Benzene</td>
<td>80 C</td>
<td>94.8 mmHg(25)</td>
<td>1.8g/l (25)</td>
<td>2.13</td>
<td>82</td>
<td>4700 mg/kg (mouse, oral)</td>
</tr>
<tr>
<td>MMT</td>
<td>238 C</td>
<td>0.047 mmHg(20)</td>
<td>29 mg/l(25)</td>
<td>3.7</td>
<td>ND</td>
<td>50 mg/kg (rat, oral)</td>
</tr>
<tr>
<td>MTBE</td>
<td>56 C</td>
<td>250 mmHg(25)</td>
<td>51g/l(25)</td>
<td>0.94</td>
<td>6</td>
<td>2560 mg/kg (rat, oral)</td>
</tr>
<tr>
<td>Ethanol</td>
<td>75 C</td>
<td>59.3 mmHg(25)</td>
<td>miscible</td>
<td>-0.31</td>
<td>ND</td>
<td>12387 mg/kg (rat, oral)</td>
</tr>
<tr>
<td>Isooctane</td>
<td>96 C</td>
<td>40.6 mm Hg(21)</td>
<td>0</td>
<td></td>
<td>ND</td>
<td>same as gasoline</td>
</tr>
<tr>
<td>N-ethyl aniline</td>
<td>205 C</td>
<td>0.24 mmHg(26)</td>
<td>~0</td>
<td>2.18</td>
<td>120</td>
<td>334 mg/kg (rat, oral)</td>
</tr>
</tbody>
</table>
aniline in combination between N-methylaniline, N-ethylaniline or a combination of both. Ethanol is added to control environmental emissions by providing oxygen for improved combustion of the gasoline. Minimum levels are specified, as below those minimum levels the desired beneficial effect is not achieved. Maximum levels are specified, as above those maximum levels room is being taken up in the formulation which is necessary for the other ingredients. Where vapour pressure is of concern, not less than 5% and not more than 30% by volume of iso-octane is added.

Preferred Working Range:
not less than 30% and not more than 65% by volume of at least one of N-methylaniline or N-ethylaniline;

not less than 20% and not more than 60% by volume of aniline; and

not less than 5% and not more than 45% by volume of ethanol.

The preferred range sets forth a narrower working range, which it is recommended that one skilled in the art operate within in order to achieve the best results.

Sample Formulation I:
60% N-methylaniline or N-ethylaniline
30% Aniline
10% ethanol

Sample Formulation II:
15% N-methylaniline
15% N-ethylaniline
20% aniline
10% iso-octane
5% ethanol

Variations:

Sample formulation I is prepared to obtain a maximum octane boost, without regard to other factors. 60% of that formulation includes N-methylaniline, N-ethylaniline or a combination of both. This is combined with a further 30% aniline. Whether sample formulation I set forth above is used will depend upon a number of factors. One factor is oxygen content of the gasoline and the emissions produced by the gasoline. Another factor is the composition of the gasoline. A practical consideration will, at times, be the cost and availability of the constituent chemicals. The cost per litre of gasoline must be kept as low as possible. If the price of N-methylaniline were to rise significantly, substitution would have to be made for increased quantities of the other ingredients. Sample formulation II demonstrates an adjusted formulation, that still falls within the preferred ranges. Such a formulation might be used if N-methylaniline and N-ethylaniline were to increase in price or become difficult to obtain in desired quantities. It also might be used if adjustments were required to increase oxygen content and reduce environmental emissions. Iso-octane would be added to reduce vapour pressure, in order to reduce gasoline evaporative emissions.

The Charts which follow demonstrate performance obtained in preliminary tests.
### OCTANE ENHANCERS

<table>
<thead>
<tr>
<th>% methylaniline added</th>
<th>RON</th>
<th>MON</th>
<th>Octane #</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>90.4</td>
<td>81.8</td>
<td>86.1</td>
</tr>
<tr>
<td>1</td>
<td>93.8</td>
<td>84.6</td>
<td>89.2</td>
</tr>
<tr>
<td>2</td>
<td>96.8</td>
<td>85.6</td>
<td>91.3</td>
</tr>
<tr>
<td>3</td>
<td>98.6</td>
<td>86.9</td>
<td>92.8</td>
</tr>
</tbody>
</table>

![Graph showing the relationship between N-Methylaniline % and response for Series 1, Series 2, and Series 3.](chart.png)
MA - N-methylaniline
A - aniline
MI - methyl iodide
EA - N-ethylaniline
DMA - N-dimethylaniline
Isoct - iso-octane
<table>
<thead>
<tr>
<th>Chemical</th>
<th>BP</th>
<th>VP</th>
<th>LD50</th>
<th>Water Sol</th>
<th>log Kow</th>
<th>Koc</th>
</tr>
</thead>
<tbody>
<tr>
<td>benzene</td>
<td>80°C</td>
<td>94.8 mmHg @25°C</td>
<td>4700 mg/kg Mouse oral</td>
<td>1.8 g/l @25°C</td>
<td>2.13</td>
<td>82</td>
</tr>
<tr>
<td>MMT</td>
<td>233°C</td>
<td>0.047 mmHg @20°C</td>
<td>50 mg/kg rat oral</td>
<td>29 mg/l @25°C</td>
<td>3.7</td>
<td>ND</td>
</tr>
<tr>
<td>MTBE</td>
<td>55°C</td>
<td>250 mmHg @25°C</td>
<td>2960 mg/kg Rat oral</td>
<td>51 g/l @25°C</td>
<td>0.94</td>
<td>6</td>
</tr>
<tr>
<td>Aniline</td>
<td>184°C</td>
<td>0.49 mmHg @25°C</td>
<td>250 mg/kg Rat oral</td>
<td>35 g/l @25°C</td>
<td>0.9</td>
<td>63</td>
</tr>
<tr>
<td>Me-Aniline</td>
<td>186°C</td>
<td>0.453 mm Hg @25°C</td>
<td>similar to aniline</td>
<td>5.6 g/l @25°C</td>
<td>1.66</td>
<td>65</td>
</tr>
<tr>
<td>Ethanol</td>
<td>78.5°C</td>
<td>59.3 mmHg @25°C</td>
<td>12387 mg/kg Rat oral</td>
<td>Miscible</td>
<td>-0.31</td>
<td>ND</td>
</tr>
<tr>
<td>Isooctane</td>
<td>99°C</td>
<td>40.6 mmHg @21°C</td>
<td>same as gasoline</td>
<td></td>
<td>0</td>
<td></td>
</tr>
</tbody>
</table>

In this patent document, the word "comprising" is used in its non-limiting sense to mean that items following the word are included, but items not specifically mentioned are not excluded. A reference to an element by the indefinite article "a" does not exclude the possibility that more than one of the element is present, unless the context clearly requires that there be one and only one of the elements.

It will be apparent to one skilled in the art that modifications may be made to the illustrated embodiment without departing from the spirit and scope of the invention as hereinafter defined in the Claims.
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An octane increasing additive for gasoline, comprising:
   not less than 5% and not more than 70% by volume of at least one of N-methylaniline or N-ethylaniline;
   not less than 10% and not more than 50% by volume of aniline; and
   not less than 5% and not more than 60% by volume of ethanol.

2. The octane increasing additive for gasoline as defined in Claim 1, further including not less than 5% and not more than 30% by volume of iso-octane.

3. The octane increasing additive for gasoline as defined in Claim 1, including N-Methylaniline, but not N-ethylaniline.

4. The octane increasing additive for gasoline as defined in Claim 1, including N-ethylaniline, but not N-Methylaniline.

5. The octane increasing additive for gasoline as defined in Claim 1, including both N-Methylaniline and N-ethylaniline.

6. The octane increasing additive for gasoline as defined in Claim 1, comprising:
   not less than 30% and not more than 65% by volume of at least one of N-methylaniline or N-ethylaniline;
   not less than 20% and not more than 60% by volume of
aniline; and

not less than 5% and not more than 45% by volume of ethanol.

7. The octane increasing additive for gasoline as defined in Claim 6, further including not less than 5% and not more than 30% by volume of iso-octane.
8. An octane increasing additive for gasoline, comprising:

not less than 30% and not more than 65% by volume of a mixture of N-methylaniline and N-ethylaniline;

not less than 20% and not more than 60% by volume of aniline;

not less than 5% and not more than 45% by volume of ethanol; and

not less than 5% and not more than 10% by volume of iso-octane.