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## MOTOR FUEL AND METHOD OF PREPARING SAME

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This invention relates to novel motor fuels especially having high octane number and to methods of preparing same.

Broadly, the invention comprises adding to a light hydrocarbon liquid, serving as a motor fuel base stock, a substantial proportion of a chemical compound belonging to the class of ketones, together with a small amount of metallo-organic anti-knock agent. The invention may be typified by the following composition:

| | Per cent |
|---|---|
| Petroleum naphtha | 75 |
| Methyl propyl ketone | 25 |
| Lead tetraethyl ___cc. per gallon of mixture | 1 |

The primary object of the invention is to prepare motor fuels of high octane number, particularly to prepare those having an especially high octane number such as motor fuels suitable for superior performance in aviation engines. For example, this invention makes possible the preparation of motor fuels meeting the United States Army's aviation requirements for motor fuels having an octane number of 100 or better and makes it possible to do this economically from a commercial point of view.

The motor fuel base stock which may be used in carrying out the invention may be a petroleum naphtha derived from either a single or a mixed crude and may be a straight run naphtha or a cracked naphtha or a blend. This base stock should, of course, meet whatever specifications for stability, gum, corrosion, etc. which are to be met by the finished blended motor fuel. Other types of hydrocarbon liquids may also be used, such as hydrogenated naphtha prepared by destructive hydrogenation of hydrocarbon liquids boiling in the range from gasoline, kerosene and lubricating oil, or a reformed naphtha, or a light liquid fraction prepared by polymerization of lower boiling or gaseous olefines.

The ketones intended to be used according to the invention may be considered as compounds having the general formula: R.CO.R', in which R and R' represent the same or different alkyl or aryl or mixed hydrocarbon radicals although substitutes and derivatives thereof may also be used, providing they have the same general properties of the ketones described. Cyclic, unsaturated, branched and polycarbonyl ketones may be used. The simplest member of the ketone group is dimethyl ketone, commonly known as acetone, and this material comes within the scope of the invention although its relatively great water-solubility is objectionable to a certain extent because it is readily removed from blends by water. Generally the ketones of a higher molecular weight are to be preferred, such as methyl ethyl ketone, methyl propyl ketone, methyl isopropyl ketone, methyl tertiary butyl ketone, methyl phenyl ketone, methyl benzyl ketone and a large number of other similar ketones in which the methyl group has been replaced by other higher molecular weight groups. Other ketones which may be used include diketones such as diacetyl $CH_3COCOCH_3$, diacetone alcohol $CH_3COCH_2C(CH_3)_2OH$, benzalacetone $C_6H_5CH:CHCOCH_3$ (made by reacting acetone with benzaldehyde), methyl vinyl ketone, butyrone, phorone, and pinacolin. Generally, the boiling point of the ketone should be within the boiling range of gasoline or, in other words, between the approximate limits of 100° F. to 400° F. or roughly between 40° C. and 200 or 210° C.; generally, ketones having from 4 to 10 carbon atoms fill this requirement most effectively. Also, the ketones having a very branched structure are preferred. For example, diisopropyl ketone, isopropyl tertiary butyl ketone, di-tertiary butyl ketone and the like are very good. Aryl or mixed alkyl-aryl or cyclic ketones may also be used, e. g. acetophenone, cyclohexanone.

By the term metallo-organic anti-knock agent, it is intended to include primarily compounds having a structure similar to lead tetraethyl, i. e. metallo-alkyl compounds such as lead tetraethyl, lead tetramethyl, tin tetraethyl, bismuth triethyl, bismuth triphenyl, etc., although carbonyl compounds, such as iron or nickel carbonyl, may also be used.

It is recognized that certain ketones, particularly acetone, have been previously suggested for addition to motor fuels for reducing the knocking of engines. However, the improvement obtained by the use of these ketones themselves in a motor fuel hardly is sufficient to justify their cost and furthermore, as will appear from the data below, even with relatively large amounts of the ketones themselves it is not possible to obtain blends having extreme high octane numbers. Furthermore, it is also recognized that lead tetraethyl has been added to motor fuels, but as will appear from the following data, although a small amount of lead tetraethyl effects a substantial increase in octane number of the naphtha to which it is added, yet successive further additions of lead tetraethyl effect successively smaller improvements in octane number, so that by the use of lead tetraethyl as an addition to petroleum naphtha motor fuels it is practically impossible to obtain exceedingly high octane numbers such as, for example, 95 or 100 or more, without the use of exceedingly large, expensive and consequently impractical amounts of lead tetraethyl.

It has now been found that the combination of both ketones and lead tetraethyl effect a result which is superior to that which is possible with equivalent amounts of either (on a cost basis) when used separately. Thus, in many cases, according to the present invention, the products containing both ketones and lead tetraethyl have an octane number which is at least equal or superior to the sum of the improvements in octane number which might normally be expected from the individual constituents present, whereas ordinarily octane number improvements of various addition agents in motor fuel are not additive, i. e they generally give results which are less than the sum of the separate constituents.

The proportions to be used in preparing motor fuels according to the present invention may vary over a fairly large range depending, of course, on the severity of the specifications or demands which must be met from the point of view of operation and performance as well as upon the cost figures which must be met and the raw materials available. However, generally the ketones (i. e. either single compounds or mixtures) should be used in amounts between the approximate limits of 5% and 50% or more, about 10, 20 or 30% being preferable for most purposes. The metallo-organic anti-knock agent, on the other hand, is used in much smaller amounts, for example, between the limits of 0.5 and 5 cc. per gallon of motor fuel, although for racing fuels and other fuels demanding exceptional performance considerably larger amounts, for example, 10, 15 or even more cc. per gallon, may be used.

The following table sets forth the results of a number of experiments which have been made to compare the relative effect of the combination of ketones with lead tetraethyl in contradistinction to these materials when used separately.

TABLE 1

*Octane number data on blends with aviation gasoline made from Pecos Crude*

| Test No. | Per-cent | Blending agent | A. S. T. M. Octane No. (at 212° F.) $PbEt_4$ added | | |
|---|---|---|---|---|---|
| | | | None | 1 cc. | 3 cc. |
| 1 | | None | 74.0 | 82.5 | 88.5 |
| 2 | 10 | Dimethyl ketone | 75.0 | | 89.5 |
| 3 | 25 | do | 78.1 | | 94.0 |
| 4 | 50 | do | 85.9 | | 100+ |
| 5 | 25 | Methyl ethyl ketone | 80.5 | 88.8 | 93.0 |
| 6 | 25 | Methyl n-propyl ketone | 80.5 | 89.5 | 95.0 |
| 7 | 25 | Methyl n-butyl ketone | 78.0 | 88.0 | 93.5 |

This table shows that additions of lead tetraethyl and ketones together to the gasoline base stock resulted in much higher octane numbers, measured on the C. F. R. engine at 212° F., than were obtainable with either addition agent alone, for it is apparent that since, in the gasoline not containing any ketones, 1 cc. of lead tetraethyl produced an increase of 8.5 in octane number and the next 2 ccs. only obtained a further increase of 6.0 in octane number, it would require an extremely large amount of lead tetraethyl to raise the octane number of the base stock up to 95 or 100. On the other hand, even 50% of the ketone when used without any lead tetraethyl only raised the octane number of the base stock up to 85.9, whereas with combinations of 25 and 50% of the dimethyl ketone with 3 cc. of lead tetraethyl, the octane number was raised to 94 and 100+, respectively. The table also shows similarly good results with other ketones including methyl ethyl-, methyl propyl-, and methyl butyl ketones.

Based upon the data for dimethyl ketone (acetone) in the above Table 1 some cost calculations have been made which illustrate the particular value of the invention and show that it is most useful when applied to the obtaining of large octane number increases in a motor fuel base stock. These calculations are, of course, subject to variations depending upon the actual cost of the materials and may be considered relative only.

TABLE 1A

*Estimated cost (¢/gal.) of obtaining various O. N. improvements by adding lead tetraethyl, acetone or mixtures thereof to a motor fuel* *

| Addition agent | O. N. increase desired | | | |
|---|---|---|---|---|
| | 10 | 20 | 30 | 40 |
| Lead tetraethyl alone | 2.8 | 11.2 | (30) | (60) |
| Acetone | 18.0 | 32 | Impossible | Impossible |
| 10% acetone+q. s. $PbEt_4$** | 6.4 | 13.6 | 26 | (42) |
| 25% acetone+q. s. $PbEt_4$** | 11.6 | 16 | 24 | (36) |
| 50% acetone + q. s. $PbEt_4$** | | 22.4 | 28 | (38) |

*Based on: acetone at 40¢/gal. and $PbEt_4$ at 2¢/cc. (or 1¢/cc. for ethyl fluid).
**q. s. means quantity sufficient to produce the desired octane number increase.
The figures in parentheses are based on curves extrapolated from the data in Table 1.

These estimated costs, as shown in Table 1A, indicate that under the circumstances of this particular case, although blends containing both acetone and lead tetraethyl having an octane number increase of only 10 or 20 over the base stock could not be produced cheaper than with lead tetraethyl alone, yet when an octane number increase of 30 or 40 is desired it could be obtained most economically, if at all, only with a blend containing both acetone and lead tetraethyl. It is also apparent from Table 1A that the higher the increase in octane number desired, the more acetone must be used in blends containing lead tetraethyl in order to obtain the most economical product.

In Table 2 are given the results of a similar although not quite as complete series of tests made on a Series 30 engine with a jacket temperature of 375° F.

TABLE 2

| Test No. | Per-cent | Blending agent | Series 30 engine at 375° F., $PbEt_4$ | | |
|---|---|---|---|---|---|
| | | | None | 1 cc. | 3 cc. |
| 8 | | None | 69.1 | 82.0 | 88.5 |
| 9 | 25 | Dimethyl ketone | 75.4 | | 93.0 |
| 10 | 30 | do | 76.8 | 88.8 | 96.9 |

This table shows that the same unexpected high octane numbers resulting from the combined use of lead tetraethyl with ketones in a gasoline base stock are obtained under these conditions as were obtained under the conditions of Table 1.

TABLE 3

*Octane number data on blends of methyl propyl ketone with aviation gasoline made from Pecos Crude*

| Test No. | Per-cent | Blending agent | A. S. T. M. Octane No. $PbEt_4$ added | |
|---|---|---|---|---|
| | | | None | 3 cc./gal. |
| 11 | 0 | None | 75.3 | 89.3 |
| 12 | 10 | Methyl n-propyl ketone | 78.8 | 89.9 |
| 13 | 35 | do | 83.3 | 100 |
| 14 | 50 | do | 88.9 | 100+ |

Table 3 shows that even higher increases in octane number and lead susceptibility are obtained with methyl propyl ketone than were obtained with dimethyl ketone (as shown in Table 1).

If desired, other materials such as anti-oxidants or gum inhibitors, dyes, upper cylinder lubricants, gum fluxes, thickeners (soaps, polymers), odorants, aromatics (e. g., benzol), solvent extracts (e. g., $SO_2$ extract), iso-octane, diisobutylene, isopropyl ether, alcohols, etc., may be added to the motor fuels prepared as described above.

It is not intended that this invention be limited to any specific examples which are given herein only for the sake of illustration, nor to any theories to the operation of the invention, but it is to be limited only by the appended claims in which it is intended to claim all novelty inherent in the invention as broadly as the prior art permits.

We claim:

1. A motor fuel comprising a light hydrocarbon liquid base stock, at least 25% of a ketone having not more than 10 carbon atoms and a small amount of a lead-organic anti-knock agent.

2. A motor fuel comprising a major portion of light hydrocarbon liquid and a minor portion, amounting to at least 25% of a ketone having not more than 10 carbon atoms and a small amount of a lead organic anti-knock agent of the general formula $PbR_4$, in which R is a lower alkyl or aryl group.

3. Composition according to claim 2, in which the anti-knock agent is lead tetraethyl.

4. Composition according to claim 2, in which the ketone has from 4 to 10 carbon atoms.

5. A motor fuel containing a major proportion of light hydrocarbon liquid and also containing from 25 to 50% of a ketone having from 4 to 10 carbon atoms and from 0.5 to 5 cc. of lead tetraethyl.

6. A motor fuel comprising a light hydrocarbon liquid base stock and containing lead tetraethyl and at least 25% of acetone.

7. A motor fuel according to claim 2, in which the ketone used has the general formula $R \cdot CO \cdot R'$, in which the R and R' represent hydrocarbon radicals at least one of which has a branched structure.

8. A motor fuel according to claim 2, in which the ketone used has the general formula $R \cdot CO \cdot R'$, in which the R and R' represent hydrocarbon radicals at least one of which has a tertiary structure.

9. A motor fuel comprising a major portion of light hydrocarbon liquid; a small amount of a lead organic anti-knock agent and a sufficient amount being at least 25% of ketone having not more than ten carbon atoms to improve the octane number of the light hydrocarbon liquid substantially more than 15 points on the A. S. T. M. scale.

10. Motor fuel according to claim 2 in which the metallo-organic anti-knock agent is of the type $PbR_4$ where R represents alkyl groups not having substantially more than 2 carbon atoms.

11. Motor fuel according to claim 2 in which the ketone is methyl propyl ketone.

12. A motor fuel comprising a major portion of light hydrocarbon liquid; 3 cc. of a lead anti-knock agent per gallon of light hydrocarbon liquid and ketone having not more than ten carbon atoms in a quantity of at least 25% sufficient to improve the octane number of the light hydrocarbon liquid 30 points on the A. S. T. M. scale.

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