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MOTOR FUEL

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This invention relates to motor fuels and methods of preparing same and more particularly to motor fuels containing blending agents which tend to reduce the knocking of the motor.

Broadly, the invention comprises the addition of both a tertiary alcohol and a metallo-organic anti-knock agent to a light liquid hydrocarbon fuel base to produce a three-component fuel having exceptionally good anti-knock properties.

It has been discovered that the tertiary alcohols, which are alcohols in which the hydroxyl group is attached directly to the carbon atom at which the branching occurs, are superior to the other alcohols used heretofore in motor fuels, because they show both high anti-knock characteristics and particularly high lead susceptibility, and at the same time cause a lower loss in heating value compared to the hydrocarbon fuel with which they are blended.

In comparing the anti-knock characteristics of various fuels, the octane number (O. N.) may be used as a satisfactory test standard. The "octane number" is defined as the percentage by volume of iso-octane (2,2,4 trimethyl pentane) in a mixture of iso-octane and normal heptane required to match the anti-knock value of a given fuel under certain specified conditions in a standard test engine. The term "lead susceptibility" is intended to mean the increase in octane number obtained by the addition of 1 cc. of lead tetraethyl or equivalent amount of other metallo-organic anti-knock agent per gallon of motor fuel. For instance, of two fuels having the same anti-knock characteristics in themselves the one having the higher lead susceptibility, i. e., the one which will show the greatest increase in octane number with the addition of 1 cc. of lead tetraethyl, will ordinarily be superior to the other as it produces the highest anti-knock blend when lead is added. This is very important because, as will be apparent in the table below, a greater improvement is obtained by lead tetraethyl with some blends than with others.

In preparing improved motor fuels according to the present invention, a tertiary alcohol such as tertiary butyl or tertiary amyl alcohol and lead tetraethyl or other metallo-organic anti-knock agent such as tin tetraethyl, iron or nickel carbonyl, lead tetraphenyl, diethyl selenide, etc. are added to a hydrocarbon fuel base such as straight run gasoline, a hydrogenated gasoline as claimed by F. A. Howard in co-pending application Serial No. 465,450 filed July 2, 1930, or a gasoline obtained at least in part by cracking heavier hydrocarbons. Generally from 1 to 50% of the alcohol is used, whereas the amount of metallo-organic anti-knock agent usually ranges from about 0.01% to 2.0% or more.

Some of the advantages of the present invention are apparent from the following table which shows the effect of branching of the carbon chain on the anti-knock properties and lead susceptibility of the alcohols:

Test No.	Fuel	Structure of alcohol	Octane No. at 375° F.*	Increase in O. N. due to the alcohol	O. N. at 375° F. after adding 1 cc. Pb (Et)$_4$	Lead susceptibility	Percent difference between increase with blend (of Pb and alc.) compared to sum of separate increases
1	Aviation gasoline		68.2		77.7	9.5	
	30% blend in aviation gasoline						
2	Ethyl alcohol	C—C—OH	77.5	9.3	82.1	4.6	−26
3	Butyl alcohol	C—C—C—C—OH	69.9	1.7	71.0	1.1	−75
4	Sec-butyl alcohol	C—C—C—C | OH	76.0	7.8	79.8	3.8	−33
5	Isobutyl alcohol	C—C—C—OH | C	75.2	7.0	77.1	1.9	−46
6	Tert. butyl alcohol	C | C—C—OH | C	77.5	9.3	87.2	9.7	+1
7	N-amyl alcohol	C—C—C—C—C—OH	66.0	−2.2	68.8	2.8	−92
8	Tert. amyl alcohol	C | C—C—C—C | OH	75.2	7.0	86.6	11.4	+11

* 375° F. jacket temperature, 900 R. P. M., on Series 30 engine.

This table shows that although a number of the alcohols effect an appreciable increase in octane number (7.0 to 9.3) yet the lead susceptibility of these alcohols varies over a wide range, the tertiary butyl alcohol and tertiary amyl alcohol being the only ones in the table which have a lead susceptibility over 5.0. A striking contrast is presented by Tests Nos. 5 and 8, representing isobutyl alcohol and tertiary amyl alcohol respectively. The fuel containing the alcohol alone, in each case, showed an increase in octane number of 7.0, whereas the isobutyl alcohol had a lead susceptibility of only 1.9 compared to the 11.4 for the tertiary amyl alcohol. The tertiary butyl alcohol did not show quite as high lead susceptibility (9.7) as the tertiary amyl alcohol but the increase in octane number in a fuel containing the alcohol alone without any lead compound was 9.3 which is slightly higher than the corresponding figure for the tertiary amyl alcohol so that the octane number of the three-component blend (gasoline+alcohol+lead tetraethyl) was even greater for the tertiary butyl alcohol (87.2) than for the tertiary amyl alcohol (86.6). The contrast of the three-component blends is even greater when comparing, for example, normal amyl alcohol with tertiary amyl alcohol, the octane numbers of which were respectively 68.8 and 86.6, which means that the use of 30% of normal amyl alcohol in addition to 1 cc. of lead tetraethyl only raised the octane number of the reference gasoline to the extent of 0.6 (i. e. from 68.2 to 68.8), whereas 30% of tertiary amyl alcohol with 1 cc. of lead tetraethyl effected a total increase of 18.4 (68.2 to 86.6) or in other words, the tertiary amyl alcohol effected an increase in octane number about 30 times as great in the leaded fuel as did the normal amyl alcohol. Another interesting fact apparent in the table is that the tertiary butyl and amyl alcohol blends containing lead tetraethyl were the only ones which had an octane number greater than 85. The nearest approach in the other alcohols is 82, obtained with a blend of ethyl alcohol and lead tetraethyl.

The figures in the last column of the table express the relationship of the anti-knock properties of the various alcohols in a slightly different manner. This is explained as follows: When 1 cc. of lead tetraethyl is added to the reference gasoline, as shown in Test No. 1, the octane number is raised from 68.2 to 77.7 giving an increase (referred to in the table as lead susceptibility) of 9.5 due to the addition of the lead tetraethyl. Also, when a blend containing 30% of ethyl alcohol in that same reference gasoline is used, the octane number is raised, as shown in Test No. 2, from 68.2 to 77.5 giving an increase of 9.3. Now, if the effects of several different anti-knock compounds were additive, one might expect a blend containing both 1 cc. of lead tetraethyl and 30% of ethyl alcohol to show a total increase in octane number equal to the summation of the separate increases due to the two individual anti-knock addition agents. In other words, one might expect a total increase in octane number of 18.8 (9.5+9.3). However, the three-component blend (as shown in Test No. 2) had an octane number of only 82.1 which amounted to an increase of only 13.9 over the octane number of the reference gasoline. In other words, the three-component blend showed a difference of −4.9 or 26% less than the sum of the separate increases (18.8). This proves that the effects of different anti-knock compounds are not additive; in fact it is already well known to those skilled in the art that the octane numbers of such blends are generally less than the sum of the separate values. A glance at the rest of the figures in the last column shows that, of all of those tested, the tertiary butyl and tertiary amyl alcohols are the only ones which produced an increase in octane number in the three-component blend which was at least equal to the sum of the separate increases due to the individual alcohol and lead tetraethyl. In this respect, a comparison of Tests Nos. 7 and 8, (i. e., normal and tertiary amyl alcohols) is very striking inasmuch as the three-component blend containing the normal amyl alcohol showed an increase in octane number over the reference gasoline of 92% less than the sum of the separate increases obtained by the alcohol and lead tetraethyl, whereas the three-component blend containing the tertiary amyl alcohol showed an increase in octane number 11% greater than would be expected from the mere summation of the separate increases due to the alcohol and the lead tetraethyl. Thus it is apparent that tertiary alcohols in which the hydroxyl group is attached to the tertiary carbon atom are anti-knock blending agents of the highest order inasmuch as they not only effect a high increase in octane number when used alone but also possess high lead susceptibility.

As there is relatively little falling off of the increase in octane number between the tertiary butyl and tertiary amyl alcohols in fuels containing a metallo-organic anti-knock agent, even higher alcohols having this tertiary structure may be used and are considered within the scope of the invention.

These tertiary alcohols may be prepared by any of the known methods, such as reacting on ketones by a suitable Grignard compound. Commercially they are generally manufactured by absorbing cracked petroleum gases (which contain some isobutylene and other iso-olefines) in H_2SO_4 (about 76% conc.), diluting with water to hydrolyze, and finally steam distilling.

By the use of the tertiary alcohols described above there is less loss in heating value of the hydrocarbon fuel than there is when a low molecular weight alcohol is used as the blending agent in gasoline. Compared to gasoline as 100%, the fuel values of methyl and ethyl alcohol are only 47% and 63% respectively, whereas those of tertiary butyl and amyl alcohols are about 76% and 79% respectively, and the higher alcohols have still higher fuel values. The heats of combustion of the normal butyl and amyl alcohols are 77 and 80% respectively, nearly the same as those of the corresponding tertiary ones. Thus the tertiary alcohols or alcohols containing at least four carbon atoms have a fuel value at least 75% of that of an average gasoline.

Since the latent heat of the alcohols is higher than that of the hydrocarbons, they have a greater cooling effect, thereby giving rise to a higher thermal efficiency in the alcohols than in the hydrocarbon fuel.

In addition to the tertiary alcohol blending agents and metallo-organic anti-knock agents, other materials may also be added to the motor fuel, such as mutual solvents of any type, materials having lubricating or gum-fluxing properties especially the hydrocarbons having a kauri butanol solvency above 15 claimed in co-pending application of Sloane and Wasson, Serial No. 658,153 filed February 23, 1933, and the high-boiling esters described and claimed in the co-pending application of Jones I. Wasson, Serial No. 667,039 filed April 20, 1933, benzol, alkylated aromatics, or other aromatic hydrocarbons or olefines having particularly good anti-knock properties or other compounds such as the branched ethers described in the co-pending application of H. E. Buc, Serial No. 648,211 filed December 21, 1932, thickening agents, dyes and inhibitors.

Also, instead of using the tertiary alcohols alone, primary and/or secondary alcohols may be used in conjunction with the tertiary alcohols such as a low molecular weight alcohol (methyl or ethyl alcohol) or a medium molecular weight alcohol such as isopropyl alcohol along with the tertiary alcohol.

It is not intended that the invention be limited to any of the specific examples given nor to any theories as to the operation of the invention but it is desired to claim all novelty inherent in the invention as broadly as the prior art permits.

I claim:

1. A motor fuel for internal combustion engines comprising a light petroleum distillate, a substantial amount, sufficient to materially improve the lead susceptibility of the fuel, of a tertiary alcohol having a boiling point substantially within the range of said distillate and a relatively small amount of a lead alkyl anti-knock compound sufficient to materially improve the anti-knock properties of said motor fuel.

2. A motor fuel for internal combustion motors comprising a light petroleum distillate, a substantial amount, sufficient to materially improve the lead susceptibility of the fuel, of a tertiary alcohol having a boiling point substantially within the range of said distillate and a relatively small amount of lead tetraethyl sufficient to materially improve the anti-knock properties of said motor fuel.

3. A motor fuel for internal combustion motors comprising a major portion of light petroleum distillate, a substantial portion, sufficient to materially improve the lead susceptibility of the fuel, of a tertiary alcohol containing not more than 5 carbon atoms and a relatively small amount of a lead alkyl anti-knock agent sufficient to materially improve the anti-knock properties of said motor fuel.

4. A motor fuel for internal combustion motors comprising a light petroleum distillate, a substantial portion, sufficient to materially improve the lead susceptibility of the fuel, of a tertiary alcohol containing not more than 5 carbon atoms and a relatively small amount of lead tetraethyl sufficient to materially improve the anti-knock properties of the motor fuel.

5. A motor fuel for internal combustion motors comprising a major portion of light petroleum distillate of gasoline boiling range, a minor portion, sufficient to materially improve the lead susceptibility of the fuel of a tertiary alcohol taken from the class consisting of tertiary butyl and tertiary amyl alcohols in an amount sufficient to substantially improve the lead susceptibility of the petroleum distillate and a relatively small amount of a lead alkyl anti-knock agent sufficient to materially improve the anti-knock properties of the motor fuel.

6. A motor fuel for internal combustion motors comprising a major portion of light petroleum distillate within the gasoline boiling range, a minor portion, sufficient to materially improve the lead susceptibility of the fuel of a tertiary alcohol taken from the class consisting of tertiary butyl and tertiary amyl alcohols in an amount sufficient to materially improve the anti-knock properties of the distillate and a relatively small amount of lead tetraethyl sufficient to materially improve the anti-knock properties of the motor fuel.

7. A motor fuel comprising about 70% gasoline, about 30% tertiary butyl alcohol and about 1 cc. of lead tetraethyl per gallon of fuel.

8. A motor fuel comprising about 70% gasoline, about 30% tertiary amyl alcohol and about 1 cc. of lead tetraethyl per gallon of fuel.

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