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MOTOR FUEL

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9 Claims. (Cl. 44—70)

This application is a division of my copending application Serial No. 276,623, filed May 31, 1939, now United States Patent No. 2,228,662.

This invention relates to the addition of certain esters to motor fuels consisting essentially of branched chain paraffin hydrocarbons and having a relatively high antiknock value to increase the antiknock quality thereof.

One object of this invention is to make motor fuels for internal combustion engines, especially for aviation engines, which fuels have antiknock values hitherto unobtainable without the use of relatively high concentrations of such metallo-organic antiknock agents as lead tetraethyl and iron carbonyl.

Another object is to increase the antiknock value of motor fuels consisting essentially of branched chain paraffin hydrocarbons and having initially a relatively high antiknock value and simultaneously to improve the volatility or distillation characteristics of such motor fuels.

Another object is to provide motor fuels consisting essentially of branched chain paraffin hydrocarbons having antiknock values higher than any heretofore known for such fuels.

Still another object is to provide motor fuels particularly adapted for use in aviation engines of the liquid-cooled or air-cooled type.

Other objects will be apparent to those skilled in the art from the disclosure of my invention which follows.

The unusually high antiknock quality of the branched chain paraffin hydrocarbons, such as 2,2,4-trimethyl pentane for example, has been recognized for years, but until very recently pure branched chain paraffin hydrocarbon compounds having such relatively high antiknock values were little more than laboratory curiosities. However, within the past two or three years polymerization processes have been developed which convert gaseous olefins such as propylene, 1-butene, and isobutene into branched chain liquid olefins, which in turn may be converted to the relatively high antiknock paraffins of corresponding structure by direct hydrogenation. Also, more recently, these relatively high antiknock branched chain paraffin hydrocarbons have been produced by alkylation. Since the development of these processes of polymerization followed by hydrogenation and of alkylation, the

high antiknock relatively pure branched chain liquid paraffins have become commercially available and are sold as iso-octane or "hydroctane." This iso-octane or "hydroctane" of commerce, however, even though having a relatively high antiknock value, usually is not alone a satisfactory motor fuel, for it is usually necessary that more volatile constituents, such as natural gasoline for example, be blended with it to make a finished fuel having the desired volatility or distillation curve, so that the fuel will have the desired characteristics relating to starting, acceleration, etc. This blending is objectionable because the available, more volatile blending stocks themselves, such as natural gasoline, usually have relatively low antiknock values, and have the effect of lowering the antiknock value of the blend. Even relatively pure isopentane, which is probably the best available volatile blending agent with regard to antiknock value, fails to improve the antiknock value of such base fuels to any appreciable extent, if at all. Thus, in view of the difficulty of increasing the antiknock value of such fuels while at the same time obtaining the desired volatility, it has been necessary to make up the deficiencies in octane number by the use of such organo-metallic antiknock agents as lead tetraethyl. This problem has been especially difficult in the cases in which, from such commercial iso-octanes, motor fuels have been made which are required to meet the volatility and octane number specifications in the field of aviation and racing, where, for example, octane numbers in the range of 90 to 100 and higher are demanded.

Although the use of small concentrations of such metallo-organic antiknock agents as lead tetraethyl and iron carbonyl may not be objectionable, the use of high concentrations has certain recognized disadvantages, such as valve corrosion and spark plug fouling, for example. Moreover, because of such disadvantages, many consumers limit the concentration of such antiknock agents to certain maximum figures, for example, 3 cc. of lead tetraethyl per gallon. Even if the concentration of such antiknock agent were not limited by specifications, the maximum octane number which can be obtained therewith in the final fuel is limited largely by the octane number of the fuel without the antiknock agent

present, since it is well known that the first increment of such antiknock agent added gives the major octane number increase and further increments result in progressively smaller increases in octane number. Upon the continued addition of increments of such antiknock agent, eventually a point is reached, around 15 to 20 octane numbers higher than that of the base fuel, at which further addition thereof is either without appreciable effect or is at least entirely uneconomical.

Thus, from the foregoing considerations it may be readily seen that the problem of increasing the antiknock value of such base fuels as those consisting essentially of branched chain paraffin hydrocarbons, such as hydrogenated polymers obtained by polymerization and hydrogenation and alkylmers obtained by alkylation, which themselves initially have an unusually high antiknock value, and at the same time obtaining a motor fuel having the desired distillation characteristics, is an exceedingly difficult one. This problem is especially acute in the field of aviation gasolines where antiknock values of 100 octane number and well above are now being demanded. As a result of the limitations described above, the fuel manufacturer is forced to maintain high octane number values not only on his commercial iso-octane but also on his more volatile blending stock. However, even with the most careful expensive controls to obtain high antiknock standards both on the base fuel and on the volatile blending stock, the result, especially with regard to the simultaneous attainment of the required antiknock value and distillation curve, is not as satisfactory as is desired.

I have now discovered that certain low-boiling esters are especially suited for blending with high octane motor fuels consisting essentially of branched chain paraffin hydrocarbons to increase the antiknock quality of such fuels. Not only do these esters give an unexpectedly high increase in antiknock value to these motor fuels, which initially have an unusually high antiknock value, but also at the same time many of them aid in producing a motor fuel having the desired volatility or distillation characteristics and reduce, and in some cases even eliminate, the proportion of volatile constituents which have an adverse effect on or fail to improve the antiknock value, such as natural gasoline or isopentane, which proportion is otherwise required to be blended with the base fuel to produce a fuel having the desired volatility or distillation characteristics.

The esters which may be used according to this invention are the saturated aliphatic esters of monocarboxylic acids, the esters containing from three to seven carbon atoms per molecule and boiling over the range from 130 to 300° F. Examples are methyl acetate, methyl propionate, methyl normal butyrate, methyl isobutyrate, methyl valerate, methyl caproate, ethyl formate, ethyl acetate, ethyl valerate, normal propyl formate, isopropyl acetate, isopropyl normal butyrate, normal butyl formate, normal butyl acetate, tertiary butyl propionate, normal amyl acetate, and isohexyl formate.

From the point of view of the number of carbon atoms per molecule the esters containing four and five carbon atoms per molecule, such as ethyl acetate, and isopropyl acetate, are preferred since they have a relatively low water solubility and at the same time a relatively high volatility and high heat of combustion. Although the esters containing four and five carbon atoms per mole-

cule are preferred, the esters containing three carbon atoms per molecule may be used where higher volatility is desired and relatively high water solubility and low heat of combustion are not undesirable, and esters containing six to seven carbon atoms per molecule may be used where relatively low water solubility and a high heat of combustion are desirable and relatively low volatility offers no problem.

The branched chain paraffin stocks used as base fuels, according to this invention, comprise those branched chain paraffins containing from five to twelve carbon atoms per molecule. Specific examples are 3-methyl pentane, 2,3-dimethyl pentane, 2,4-dimethyl pentane, 2,2,3-trimethyl butane, 2,2-dimethyl hexane, 2,5-dimethyl hexane, 2,2,4-trimethyl pentane, 2,2,3-trimethyl pentane, 2,3,4-trimethyl hexane, 2,2,4-trimethyl hexane, 2,3,5-trimethyl heptane, neohexane, and 2,2-dimethyl butane. These compounds are at present made by hydrogenation of the polymers usually obtained by the polymerization of normally gaseous olefinic hydrocarbons or made by the alkylation of isoparaffins with normally gaseous olefinic hydrocarbons. However, the invention embraces the branched chain paraffin hydrocarbon compounds themselves and is not restricted to any specific method of their manufacture. Thus, although these stocks are frequently referred to as hydrogenated stocks for convenience, the base fuels may be made by reactions involving no hydrogenation step. For example, as suggested above, the products obtained by alkylation of isobutane and isopentane with propylene, normal butenes, and isobutene in the presence of sulfuric acid or aluminum chloride catalysts, are included within the scope of this invention. Furthermore, this invention embraces the addition of the esters to any one, or a mixture of any two or more, of these branched chain paraffin hydrocarbon compounds containing from five to twelve carbon atoms per molecule. It is especially significant that the best results are obtained when the branched chain base fuel has an octane number of at least about 85 and may have an octane number much higher, as high as 100 in the case of 2,2,4-trimethyl pentane, for example, or above 100 in the case of some of the other pure branched chain paraffin hydrocarbons.

Furthermore, although I have found that branched chain paraffin hydrocarbons as a class give good results when in admixture with esters in accordance with this invention, the best results are found to be obtained when the base fuel contains substantial proportions of branched chain paraffin hydrocarbons obtained as the result of the processes of polymerization followed by hydrogenation or the processes of alkylation mentioned above, the distinguishing characteristics of which branched chain paraffin hydrocarbons are that the degree of branching is high, as indicated by the relatively high antiknock value of the base fuel. Such hydrocarbons as 2,4-dimethyl pentane, 2,2,3-trimethyl butane, 2,2,4-trimethyl pentane, 2,2-dimethyl hexane, 2,2,4-trimethyl hexane, and 2,3,5-trimethyl heptane illustrate what is meant by hydrocarbons having a relatively high degree of branching. Such branched chain paraffins have at least two or three or more side branches, and the greater the number of carbon atoms in general the greater the number of side chains from the main straight chain. Such branched chain paraffins having a high degree of branching in the mole-

cule as indicated by the high initial antiknock value can be used alone as single compounds, or in mixtures thereof if desired, to obtain a compound having a high antiknock value when blended with esters in accordance with this invention.

The proportion of esters added to the base fuel consisting essentially of branched chain paraffin hydrocarbons will depend on the octane number and volatility or distillation characteristics desired and should be such that the ester comprises 10 to 50 per cent by volume of the finished fuel. Proportions lower than 10 per cent may, of course, be used but I find that the blending octane numbers increase, in general, with increasing concentration, and the preferred improvement is not reached until about 10 per cent of the ester has been added. Blends containing proportions higher than 50 per cent may be used to obtain a high antiknock value, but are undesirable for some purposes because of the resulting relatively low heats of combustion of such final blends.

The hydrocarbon component comprising 50 to 90 per cent of the finished fuel may be made up entirely of branched chain paraffin hydrocarbon stocks as described above, or entirely of one or more of the branched chain paraffin hydrocarbons also described above, or it may also contain substantial proportions, for example 10 to 50 per cent, of volatile blending stocks such as natural gasoline. A particularly suitable volatile blending stock for this purpose is isopentane. Moreover, the high antiknock fuel of my invention may, of course, be blended with other motor fuels in the usual manner.

In order to illustrate the invention, examples of motor fuels made up in accordance therewith and data obtained from tests made thereon are given in Table I below:

TABLE I
Base fuel-commercial iso-octane

Ester	Oct. No. of base fuel	Oct. No. of blend	Vol. % ester in blend	Blending oct. No. of ester
Methyl acetate.....	90.0	93.8	25	105.2
Do.....	90.0	99.7	50	109.4
Ethyl formate.....	90.0	92.9	25	101.0
Ethyl acetate.....	90.0	94.9	25	109.6
Do.....	90.0	100+	50	110+
Isopropyl formate.....	90.0	93.9	25	105.6
Do.....	90.0	100	50	110.0
Isopropyl acetate.....	90.0	94.8	25	109.2
Do.....	90.0	100+	50	110+
Ethyl propionate.....	90.0	94.8	25	109.2
Do.....	90.0	100+	50	110+
Secondary butyl acetate.....	90.0	93.6	25	104.4
Do.....	90.0	97.9	50	105.8
Tertiary butyl acetate.....	90.0	93.2	25	102.8
Do.....	90.0	97.8	50	105.8

In Table I are given the octane number of the base fuel, the octane number of the blend, the volume per cent of ester in the blend, and the "blending octane number of the ester." The "blending octane number of the ester" is obtained by multiplying the difference between the octane number of the blend and the octane number of the base fuel by the factor of 100 divided by the volume per cent of the ester in the blend and adding this quantity to the octane number of the base fuel. The blending value is therefore a measure of the effectiveness of the particular ester in the particular stock with which such ester is blended. The octane numbers given in Table I were obtained by the A. S. T. M.-C. F. R. D357-37T method, commonly referred to as the "motor method." This test is recom-

mended by the Cooperative Fuel Research Committee of the American Society for Testing Materials.

It is apparent from the results set forth in Table I that by means of a mixture of branched chain paraffin hydrocarbons and saturated aliphatic esters of monocarboxylic acids as disclosed herein, motor fuels may be obtained having antiknock values higher than any heretofore known for such base fuels. In each case in Table I the blending value is above 100 for 25 volume per cent of the ester and, in each case where a test was made with 50 per cent, the blending value for 50 per cent was greater than for 25 per cent, showing that the susceptibility of the branched chain paraffin hydrocarbons to increase in anti-knock value by the ester added increases with the proportion of ester added. In other words, the blending octane numbers of these esters increase with increasing concentration. Thus, from the data here given it is seen that such a fuel containing a large proportion of such ester has a very high anti-knock value, and its anti-knock value is higher than any known for such a base motor fuel. This is especially true of ethyl acetate and ethyl propionate. Moreover, blending such esters with branched chain paraffin hydrocarbons having anti-knock value well above 90.0 octane number, as high as 100 as for 2,2,4-trimethyl pentane, for example, or even above 100, will give still higher antiknock value. No figures can be given to indicate the octane number of these fuels having an anti-knock value above 100 octane number, because no test has been devised for compounds having such a high octane number; however, as indication of what the anti-knock value is can be obtained from the blending value shown in Table I above. Moreover, the anti-knock value of these blends can be still further increased by the addition of a small concentration of such a metallo-organic anti-knock agent as lead tetraethyl.

The examples in Table I are cited to illustrate the effect of the esters on anti-knock value. Although the compounds blended as indicated in Table I may be used as motor fuels, usually the addition of some isopentane, natural gasoline, or the equivalent, is required in order to meet the usual gasoline boiling point specifications, the amount of isopentane or natural gasoline required, however, usually being substantially less than if no ester had been added. Moreover, although each of the specific examples given in Table I above indicates the use of a single ester, two or more esters may be added to the base fuel, and such compositions are included in this invention. Furthermore, as indicated above, one branched chain paraffin hydrocarbon component of the base fuel may be used alone or a mixture of these components thereof may be used.

Results obtained from tests on representative esters indicate that, although an increase in octane number is obtained when such organic compounds are added to base fuels other than those consisting essentially of branched chain paraffin hydrocarbons described above, an unexpectedly and unpredictably high increase in anti-knock value is obtained with the branched chain paraffin hydrocarbons, as indicated by the relatively high blending values obtained therefor, which are shown in the following table, Table II, as compared with the corresponding blending values obtained for the other gasoline tested.

TABLE II

Ester	Base fuel	Oct. No. of base fuel	Oct. No. of blend	Vol. % ester in blend	Blending oct. No. of ester
Ethyl acetate.....	Commercial iso-octane.....	90.0	94.9	25	100.6
Do.....	Stanavo base.....	76.3	80.8	25	94.3
Do.....	Commercial iso-octane.....	90.0	1100+	50	1110+
Do.....	Unhydrogenated polymers.....	80.3	89.5	50	98.7
Do.....	Stanavo base.....	76.8	91.7	50	106.6
Secondary butyl acetate.....	Commercial iso-octane.....	90.0	93.6	25	104.4
Do.....	Stanavo base.....	76.3	82.4	25	100.7

¹ These values are indefinitely higher than the values given because of the impossibility of measuring octane number of the blend where the value is above 100.

In Table II above the gasoline designated "Commercial iso-octane" is a motor fuel consisting essentially of branched chain paraffin hydrocarbons, the degree of branching of which is high, obtained as the result of polymerization and hydrogenation as mentioned above. The gasoline designated "unhydrogenated polymers" consists essentially of olefin hydrocarbons and the gasoline designated "Stanavo base" is a straight run gasoline. It will be clear from Table II when the esters of this invention are added to gasolines having an anti-knock value above about 85 and consisting essentially of branched chain paraffin hydrocarbons, the anti-knock value increase is surprisingly high as compared with the increase found for other gasolines having a relatively high anti-knock value of 75 to about 85 and not consisting essentially of branched chain paraffin hydrocarbons.

Table II above also indicates that the esters as disclosed are effective in base fuels other than those in which they give such unusual results, and this invention therefore comprehends the novel blends of such esters with other base fuels to increase the anti-knock value thereof.

Although one of the objects of the invention is to provide high octane fuels containing little or no metallo-organic anti-knock agent, I have found that the blends herein described are readily susceptible to further improvement in octane number by addition of such an agent as lead tetraethyl. Thus, with the addition of a relatively small quantity of such metallo-organic anti-knock agents as lead tetraethyl extremely high anti-knock values can be obtained. It will therefore be understood that motor fuels with or without such metallo-organic anti-knock agents are embraced by this invention.

The term "metallo-organic anti-knock agent" is used herein with the intention that it include those organic compounds of metals, especially the metallo-alkyl compounds such as the well known lead tetraethyl, and the carbonyl compounds, like iron and nickel carbonyl, which are effective to increase the anti-knock value of motor fuel.

It is to be understood that, although specific branched chain paraffin hydrocarbons, specific esters, and certain proportions of the constituents of my new motor fuel have been disclosed for the purpose of illustration, my invention is not to be limited thereby but includes all modifications thereof within the scope of the appended claims.

I claim:

1. A high antiknock motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and a sufficient proportion of isopropyl formate effective to increase substantially the antiknock value of said base fuel.

2. A high antiknock motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and from about 10 to about 50% by volume of isopropyl formate to increase substantially the antiknock value of said base fuel.

3. A high antiknock motor fuel as defined in claim 1 in which said base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons has an antiknock value of at least about 85 octane number without said isopropyl formate.

4. A high antiknock motor fuel having an anti-knock value above 100 octane number comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and a sufficient proportion of isopropyl formate effective to increase the anti-knock value of said base fuel to above 100.

5. A high antiknock motor fuel as defined in claim 1 containing a minor proportion of a metallo-organic antiknock agent.

6. A high antiknock motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and a sufficient proportion of methyl acetate effective to increase substantially the anti-knock value of said base fuel.

7. A high antiknock motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and a sufficient proportion of secondary butyl acetate effective to increase substantially the antiknock value of said base fuel.

8. A high antiknock motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and a sufficient proportion of an ester selected from the group consisting of saturated aliphatic esters of formic acid and acetic acid containing three to seven carbon atoms and boiling within the range of 130° to 300° F. effective to increase substantially the antiknock value of said base fuel.

9. A high antiknock aviation motor fuel comprising a base fuel consisting essentially of isoparaffinic motor fuel hydrocarbons of the type produced by the alkylation of isoparaffins with normally gaseous olefins and having an anti-knock value above about 85 and a sufficient proportion of an ester selected from the group consisting of saturated aliphatic esters of formic acid and acetic acid containing three to seven carbon atoms and boiling within the range of 130° to 300° F. effective to increase substantially the antiknock value of said base fuel.

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