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FUEL COMPOSITION

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This invention relates to an improved motor fuel composition for use in high output aircraft engines. More specifically, this invention relates to an aviation fuel conforming to rigid specifications of antiknock rating, vapor pressure, and distillation characteristics, and having, in addition, combustion characteristics which provide superior power output over a broad range of fuel-air ratios, and particularly over the range classified as rich mixtures.

High octane number aviation fuels are manufactured and blended according to specifications so strict that the selection of suitable components is limited in many cases to high purity synthetic blending agents and naturally occurring base stocks which are segregated with such precision as to approximate the purity of the synthetic hydrocarbons. Such fuels must have high octane number ratings and this in turn means that the components must have high octane number ratings and/or excellent response to the addition of antidetonants. Further, the unsaturation of the components must be exceedingly low in order that the fuels be substantially free of gum and of susceptibility to gum formation. These qualifications together with rigid requirements for vapor pressure, end point, and distillation characteristics sharply limit the choice of fuel components to the relatively low-boiling predominantly paraffinic hydrocarbons, say of 5 to 9 carbon atoms, and preferably to the higher octane number branched-chain or isoparaffins.

In the manufacture of aviation fuels of 90 to 100 octane number or those fuels having antiknock ratings beyond the conventional octane number scale, the procedure usually includes the manufacture of synthetic isoparaffins as one blending component. For example, processes, such as selective polymerization, thermal or catalytic alkylation, or the like, may be utilized to prepare concentrates of iso-octanes together with usually much smaller amounts of higher and lower homologues. Thermal alkylation may produce such stocks as neohexane which are highly desirable blending agents. As a second component, base stocks comprising isohexanes, isoheptanes, iso-octanes, etc., may in many instances be prepared by precise fractionation schemes from crude oil and/or natural gasolines.

A third component which is ordinarily considered separately is iso-pentane which can be prepared in substantially pure form by fractionation of hydrocarbon mixtures containing it. This last-named material is ordinarily the lowest boiling stock included in aviation fuels, and it functions as a source of volatility to adjust the vapor

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pressure of the blend and to produce desirable distillation characteristics, especially in the initial portion of the distillation curve.

Since the synthetic iso-paraffin blending agents are often available in somewhat smaller volume than base stocks prepared from naturally occurring distillates, blending formulas which require minimum volumes of such synthetic stocks may be preferred. Assuming that isopentane is plentiful and used to the maximum extent possible within vapor pressure and front-end volatility limits, it then remains to select and prepare other components, commonly termed base stocks, of both high octane number and low vapor pressure. These characteristics are most conveniently obtained by segregation of iso-paraffins, such as the iso-hexanes, etc., as being more valuable than a full boiling range naphtha, unless the naphtha is deficient in normal (low octane) paraffins or has an unusually high octane number.

The net result of the above-described blending procedure is the production of fuels of suitable distillation characteristics, vapor pressure, gum stability and octane number rating, comprising largely isoparaffins of 5 to about 8 or 9 carbon atoms, substantially free of C₄ hydrocarbons, and preferably containing only minor amounts of C₅ to C₉ normal paraffins. The content of naphthenes may vary and is often small, since these compounds are usually present in only small quantities, or in many cases, are removed more or less completely by the precise fractionation which separates the normal C₅, C₆, and C₇ paraffins from the iso-paraffins in naphtha base stocks.

The complex and strenuous requirements of military aviation under present war conditions have emphasized some deficiencies of aviation fuels under certain conditions. Such conditions, for example, are those which require increased or emergency power for improved and rapid take-off, particularly with heavy loads, rapid acceleration and climb during combat. The production of maximum power output under these conditions is of primary importance and the development of fuels which will meet these severe requirements under all conditions is an essential military requirement. It is also obvious that fuels which meet rigid military requirements will be of great value in the development of commercial aviation.

The term "rich mixture performance" as now used by the art, and as referred to herein, describes the power output of aviation engines under rich mixture conditions, such, for example, as would be obtained by substantially increasing the fuel concentration in an air-fuel mixture at

the intake of an aviation engine. This performance is usually defined in terms related to a standard 100 octane reference fuel, the relative improvement being stated in ml. of tetraethyl lead.

While laboratory test and octane number ratings by the conventional methods employed for aviation fuels indicate satisfactory performance, more recent test procedures involving fuel performance in supercharged test engines (for example Method AN-VV-F-748) have indicated a deficiency in the power output of said predominantly isoparaffinic fuels. This deficiency has been shown to occur most markedly in rich mixture ratings of the fuel corresponding to take-off or emergency power requirements in aircraft at fuel-air ratios very much higher than the lean mixture ratios ordinarily employed for efficient cruising operation. This discrepancy in the incremental power output with greatly increased fuel-air ratio and fuel consumption has introduced a new consideration into the previous blending formulas to deal with the rich mixture rating of the finished fuels.

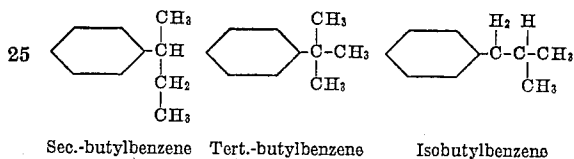
Since the predominantly isoparaffinic fuel compositions are very satisfactory from the standpoint of most specifications not involving rich mixture requirements, and permit the production of larger volumes of finished fuel per volume of synthetic blending stocks than are possible with other blending formulas, it is ordinarily most advantageous to retain the isoparaffin blending formulas insofar as possible. This procedure requires that such special performance characteristics as lean and rich mixture ratings be obtained through the inclusion minor proportions of substantially pure hydrocarbon additives. These additive compounds must be carefully selected so that the desired improvements are obtained with such small quantities that other fuel characteristics are not impaired and blend specifications are not infringed.

It is an object of the present invention to provide an improved fuel composition for use in aircraft engines whereby the power output of the engines is improved. It is a further object of this invention to provide an improvement in the blending formulas for preparing predominantly isoparaffinic aviation fuels whereby rich mixture deficiencies which may characterize said isoparaffin blends are effectively eliminated. Another object is to provide a method for improving the power output of aviation fuels under rich mixture conditions. A further object is to provide an isoparaffinic aviation fuel of 100 octane number rating or better containing a relatively minor proportion of an added compound provided greatly improved rich mixture characteristics without undesirably affecting the other characteristics of the fuel. A still further object is to provide a hydrocarbon fuel composition which will meet all desired specifications for volatility, vapor pressure, distillation characteristics, and octane number together with a method for its preparation.

We have now found that aviation fuels of the type described and comprising isoparaffin hydrocarbons have greatly improved octane number ratings at high fuel-air ratios when minor proportions of mono-butylbenzenes are added. These mono-butylbenzenes are employed as the substantially pure compounds since their efficacy is highly specific and definitely superior to other aromatic homologues which might be present in varying quantities in crude or impure alkylated benzenes. A further purpose served by the use of the pure compounds is the elimination of associated im-

purities which may have a deteriorative effect on the fuels and/or on the aircraft fuel systems in which said fuels are used.

In our co-pending application, Serial No. 436,714, filed March 28, 1942, we have disclosed the specific benefits obtained from the addition of isopropylbenzene to aviation fuels, and have further disclosed that isopropylbenzene is generally superior to benzene, toluene, and ethylbenzene for the purposes described although the latter may be used in some instances. In accordance with the present disclosure, we have further discovered that the butylbenzenes in which the alkyl group exhibits a branched chain structure, namely, the isomeric butyl benzene compounds which include secondary and tertiary butylbenzenes as well as isobutyl benzene, are superior to the normal (straight chain) derivative. Furthermore, as shown hereinafter, the tertiary derivative is superior to the secondary derivative. The formulas of these preferred compounds are as follows:



30 Isobutylbenzene is not ordinarily encountered because the conditions and reagents necessary for its formation produce the tertiary derivative almost exclusively. The properties of the isobutylbenzene for the purposes of this invention are intermediate those of the secondary and tertiary derivatives. In view of the related properties of isopropyl benzene and the mono-butylbenzenes described herein, for the improvement of rich mixture rating, mixtures of these additive components may be utilized in any desired relative proportion, such mixtures being utilized as minor proportions of the final fuel composition and being compounded to produce fuels having desired vapor pressure and distillation characteristics.

In the investigation and testing of isoparaffinic aviation fuel blends containing aromatic hydrocarbon additives, the wide variations in the properties and uses of said aromatic hydrocarbons have been emphasized. For example, whereas aromatics, as a class, have been regarded heretofore as improving the octane number of ordinary fuels, it is necessary in the present instance to limit the quantity of aromatic additive to avoid degradation of the octane number and response to lead alkyl antidetonants. Further, while aromatic hydrocarbons have been regarded heretofore as substantially equivalents within the limits of their physical properties, such equivalency is lacking in the present application as will be illustrated hereinafter.

While the present invention may be employed in a great variety of blending operations involving all suitable blending agents and base stocks, one satisfactory procedure may be outlined in the following operations. A fuel may be prepared according to a blending formula which requires definite proportions of iso-octane, isopentane, and a naphtha comprising C₆ and C₇ isoparaffins in order to produce a composition rating 100 octane number with a given concentration of tetraethyl lead. Said blending formula is altered according to the present invention to include the mono-butylbenzene by use of an isopentane-butylbenzene mixture having a vapor pressure substan-

tially equal to that of the finished fuel, usually 7-pound Reid vapor pressure. The volume of the mixture used replaces a substantially corresponding volume of base stock and blending agent with the blending proportions of the latter usually being readjusted to produce the same octane rating as before. The butylbenzene may be added alone to fuel blends, but it is often more convenient to employ the isopentane mixture. The

or rubber-like materials with which the compounds or fuels containing them are in contact. Comparative data are given below for an isoparaffinic aviation fuel (blend A) and for said fuel after addition of 5 and 15 volume per cent of benzene, secondary butylbenzene, and tertiary butylbenzene, in contact with a moderately oil-resistant type of synthetic rubber as represented by Hycar OR.

	Blend A	Aromatic additive					
		Benzene		Sec-butybenzene		Tert-butylbenzene	
Aromatic concentration (volume per cent).....	None.....	5	15	5	15	5	15
Per cent swelling (24 hours).....	Zero.....	2.2	3.48	0.37	1.38	0.5	1.99
Diffusion (grams/hour).....	0.014.....	0.035	0.122	0.017	0.019	0.022	0.027
Increased solvency due to aromatic (mgm./gm. rubber/24 hours).....	(Reference).....	10.7	18.7	4.0	5.8	2.7	5.4

advantages lie in the maximum utilization of isopentane and less difficulty in blending to meet vapor pressure and distillation specifications.

The butylbenzene employed in the fuel compositions may be obtained from any suitable source, provided a substantially pure product is obtained. In many cases, it is difficult to separate butylbenzenes, and particularly, one specific butylbenzene from complex mixtures of aromatic and other types of hydrocarbons such as may result from the non-selective alkylation of gasoline stocks or the like. For this reason, the preferred source of the butylbenzenes is the selective alkylation of benzene with butylenes and/or isobutylene or their equivalent alkylating agents in the presence of suitable catalysts such as hydrogen fluoride or boron fluoride which produce the corresponding branched-chain derivatives, exclusively. The butylbenzene which is produced by such methods is substantially free of undesirable impurities and is readily separated from unreacted benzene and/or polyalkylated derivatives.

The amount of the butylbenzene added to specific fuels will obviously be dependent to a large extent on the nature and quality of the other components and on the rich mixture rating which is desired in the final blend. In most cases, the butylbenzene will vary between about 1 and about 10 volume per cent of the blend, with a somewhat narrower range of about 2 to about 7 volume per cent usually preferred. The compound in substantially pure form is relatively expensive and hence is not ordinarily used to replace the conventional blending ingredients. Also, excessive amounts may tend to decrease the lead response of the blend and/or impart sufficient aromaticity to the fuel to increase the solvent and swelling action on rubber-lined fuel tanks.

In this connection, it has been found that the butylbenzenes described herein, particularly those having the branched chain alkyl substituent exhibit quite different properties from those of the commoner aromatics, such as benzene. One way in which the more desirable properties of these butylbenzenes are evidenced is in reduced swelling of and diffusion through rubber

These results indicate that the swelling, diffusion, and solvency effects with these butylbenzenes are appreciably less than with benzene itself. This effect is apparently due to decreased aromaticity resulting from the alkyl substituent, and particularly due to the size and configuration of the side chain. This means that better service characteristics result from the use of these butylbenzenes and/or that larger concentrations of the butylbenzenes may be employed without encountering difficulties in service.

Test method AN-VV-F-746 as referred to herein is the method identified as Army-Navy Aeronautical Specification Fuel; Aircraft-Engine, General Specifications (Method for Knock-Test) AN-VV-F-746, dated October 5, 1940. This method is utilized for determining ordinary octane number ratings of 100 octane aviation fuels. Test method AN-VV-F-748, as referred to herein is identified as Army-Navy Aeronautical Specification Fuel; Aircraft-Engine, General Specification (Method for Supercharged Knock Test) AN-VV-F-748 dated September 22, 1941. The test method described therein is used for determining lean and rich mixture ratings of 100 octane number aviation fuels. In this latter specification (AN-VV-F-748) a lean mixture is shown to be about .06 pound of fuel per pound of air and a rich mixture at least about .09 pound of fuel per pound of air.

As illustrations of the improved performance characteristics obtained by the addition of butylbenzene to aviation fuels, the following typical data are cited:

Example

A 100 octane number aviation fuel was prepared according to blending formula A given below, with 4 ml. TEL per gallon. This formula was then modified to permit the inclusion of 5 volume per cent of each of the following aromatic additives: (1) benzene, (2) sec-butylbenzene, and (3) tert-butylbenzene. These three modified blends noted below as B, C, and D conformed to fuel specifications and rated approximately 100 octane number with 4 ml. TEL per gallon.

Formula	Isoparaffin components, vol. per cent				Aromatic additive (5 vol. per cent)
	Iso-octane	Isoheptane	Isohexane	Isopentane	
A.....	33.0	18.0	36.0	13.0	None.
B.....	30.9	16.9	33.8	13.5	Benzene.
C.....	30.9	16.5	33.7	13.9	Sec-butylbenzene.
D.....	30.9	16.5	33.7	13.9	Tert-butylbenzene.

These blends were rated according to test method AN-VV-F-746 and also according to the super-charged engine method AN-VV-F-748. Octane numbers above 100 are recorded as ml. of tetraethyl lead in 100 octane number iso-octane in the following table:

Formula	Antiknock rating		
	AN-VV-F-746	AN-VV-F-748	
		Lean mixture	Rich mixture
A.....	MI. TEL 0.03	MI. TEL 0.20	MI. TEL 0.65
B.....	100	0.30	0.80
C.....	0.02	0.20	1.00
D.....	0.03	0.22	1.45

These results indicate the substantially improved rich mixture rating provided by the butylbenzenes as compared to fuel A alone and to formula B containing benzene, while the effect on lean mixture rating and on the conventional (F-746) rating is slight.

While the foregoing specific examples provide illustrations of the improvement obtained through the practice of the present invention, it will be apparent that the variations which can be produced through changing the volume ratio, quality and hydrocarbon type of the blending components are numerous. Therefore, no limitation of the scope of the invention is intended. Also, while the invention has been described and exemplified in applications to predominantly isoparaffinic fuel blends, it is broadly applicable to fuel compositions suitable for the purposes outlined and within the limits prescribed.

We claim:

1. An improved method of operating an aviation gasoline engine requiring a fuel having an octane number of at least about 100, which consists of supplying to said engine as the fuel during an operating period a gasoline comprising essentially a mixture of isoparaffin hydrocarbons having five, six, seven, eight and nine carbon atoms per molecule and between about 2 and about 7% by volume of a mono-butylbenzene other than normal butylbenzene and at least about 3 ml. of tetraethyl lead fluid per gallon, said hydrocarbons being so proportioned that said mixture has gasoline characteristics of distillation range and contains isopentane in an amount not more than is sufficient to result in a Reid vapor pressure not greater than seven pounds, and maintaining during said operating period for said aviation engine rich-mixture operating conditions such that the fuel-air ratio is at least about .09.

2. An improved method of operating an aviation gasoline engine requiring a fuel having an octane number of at least about 100, which consists of supplying to said engine as the fuel during an operating period a gasoline comprising essentially a mixture of isoparaffin hydrocarbons having not less than 5 and not more than 9 carbon atoms per molecule and between about 2 and

about 7% by volume of a mono-butylbenzene other than normal butylbenzene and at least about 3 ml. of tetraethyl lead fluid per gallon, said hydrocarbons being so proportioned that said mixture has gasoline characteristics of distillation range and contains isopentane in an amount not more than is sufficient to result in a Reid vapor pressure not greater than seven pounds, and maintaining during said operating period for said aviation engine rich-mixture operating conditions such that the fuel-air ratio is at least about .09.

3. An improved method of operating an aviation gasoline engine requiring a fuel having an octane number of at least about 100, which comprises supplying to said engine as the fuel during an operating period a gasoline which consists of a mixture of isoparaffin hydrocarbons having not less than five nor more than nine carbon atoms per molecule and a mono-butylbenzene other than normal butylbenzene in an amount between about 1 and about 10% by volume of the total and at least about 3 ml. of tetraethyl lead fluid per gallon, said hydrocarbons being so proportioned that said mixture has gasoline characteristics of distillation range and contains isopentane in an amount not more than is sufficient to result in a Reid vapor pressure not greater than about seven pounds, and maintaining during said operating period for said aviation engine rich-mixture operating conditions such that the fuel-air ratio is at least about .09.

4. An improved method of operating an aviation gasoline engine requiring a fuel having an octane number of at least about 100, which comprises supplying to said engine as the fuel during an operating period a gasoline comprising essentially a mixture of isoparaffin hydrocarbons having not less than five nor more than nine carbon atoms per molecule and a mono-butylbenzene other than normal butylbenzene in an amount between about 2 and about 7% by volume of the total and at least about 3 ml. of tetraethyl lead fluid per gallon, said hydrocarbons being so proportioned that said mixture has gasoline characteristics of distillation range and contains isopentane in an amount not more than is sufficient to result in a Reid vapor pressure not greater than about seven pounds, and maintaining during said operating period for said aviation engine rich-mixing operating conditions such that the fuel-air ratio is at least about .09.

5. The method of claim 1 in which the mono-butylbenzene in the fuel supplied is tertiary butylbenzene.

6. The method of claim 3 in which the mono-butylbenzene in the fuel supplied is tertiary butylbenzene.

7. The method of claim 4 in which the mono-butylbenzene in the fuel supplied is tertiary butylbenzene.

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